Feedstock Recycling and Pyrolysis of Waste Plastics:

Converting Waste Plastics into Diesel and Other Fuels

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Feedstock Recycling and Pyrolysis of Waste Plastics:

Converting Waste Plastics into Diesel and Other Fuels

Edited by

JOHN SCHEIRS
ExcelPlas Australia

and

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Series Preface

The Wiley Series in Polymer Science aims to cover topics in polymer science where significant advances have been made over the past decade. Key features of the series will be developing areas and new frontiers in polymer science and technology. Emerging fields with strong growth potential for the twenty-first century such as nanotechnology, photopolymers, electro-optic polymers will be covered. Additionally, those polymer classes in which important new members have appeared in recent years will be revisited to provide a comprehensive update.

Written by foremost experts in the field from industry and academia, these books have particular emphasis on structure–property relationships of polymers and manufacturing technologies as well as their practical and novel applications. The aim of each book in the series is to provide readers with an in-depth treatment of the state-of-the-art in that field of polymer technology. Collectively, the series will provide a definitive library of the latest advances in the major polymer families as well as significant new fields of development in polymer science.

This approach will lead to a better understanding and improve the cross-fertilization of ideas between scientists and engineers of many disciplines. The series will be of interest to all polymer scientists and engineers, providing excellent up-to-date coverage of diverse topics in polymer science, and thus will serve as an invaluable ongoing reference collection for any technical library.

John Scheirs
June 1997

Preface

This book covers thermal and catalytic pyrolysis processes that produce liquid fuels (or other useful chemicals) from waste plastics. The book provides a comprehensive overview of the main commercial plastics pyrolysis processes, the types of plastics that can be processed, the properties of the respective fuels produced and the key variables influencing the pyrolysis of plastics such as temperature, residence time, pressure and catalyst types.

Only some 15–20% of all waste plastics can be effectively recycled by conventional mechanical recycling technologies (i.e. sort/grind/wash/extrusion). Beyond this level the plastics become increasingly commingled and contaminated with extraneous materials such as soil, dirt, aluminium foils, paper labels and food remnants.

Pyrolysis is a tertiary or feedstock recycling technique capable of converting plastic waste into fuels, monomers, or other valuable materials by thermal and catalytic cracking processes. This method can be applied to transform both thermoplastics and thermosets in high-quality fuels and chemicals. Moreover it allows the treatment of mixed, unwashed plastic wastes.

In its simplest definition pyrolysis is the degradation of polymers at high temperatures under nonoxidative conditions to yield valuable products (e.g. fuels and oils). Pyrolysis is also referred to as polymer cracking and its main advantages are that it can deal with plastic waste which is otherwise difficult to recycle and it creates reusable products with unlimited market acceptance.

As feedstock recycling and pyrolysis is not incineration there are no toxic or environmentally harmful emissions. Pyrolysis recycling of mixed plastics thus has great potential for heterogenous plastic waste that cannot be economically separated.

This book provides an overview of the science and technology of pyrolysis of waste plastics. The book will describe the types of plastics that are suitable for pyrolysis recycling, the mechanism of pyrolytic degradation of various plastics, characterization of the pyrolysis products and details of commercially mature pyrolysis technologies.

The major advantage of the pyrolysis technology is its ability to handle unsorted, unwashed plastic. This means that heavily contaminated plastics such as mulch film (which sometimes contains as much as 20% adherent dirt/soil) can be processed without difficulty. Other normally hard to recycle plastics such as laminates of incompatible polymers, multilayer films or polymer mixtures can also be processed with ease, unlike in conventional plastic recycling techniques. In fact, most plastics can be processed directly, even if contaminated with dirt, aluminium laminates, printing inks, oil residues, etc.

The production of gasoline, kerosene and diesel from waste plastics is an emerging technological solution to the vast amount of plastics that cannot be economically recovered by conventional mechanical recycling.

Pyrolysis recycling of mixed waste plastics into generator and transportation fuels is seen by many as the answer for recovering value from unwashed, commingled plastics and achieving their desired diversion from landfill. Pyrolytic recycling of plastic wastes has already been achieved on commercial scale albeit to a limited extent. Nevertheless, the development and improvement of the pyrolysis plastics recycling technologies in recent years has great commercial potential. The development of bench-scale experiments carried out in laboratories to full-scale pyrolysis processes have now resulted in a number of technically mature processes.

Through the use of low-temperature vacuum pyrolysis and cracking catalysts, liquid fuels yield of up to 80% are possible with the resultant product resembling diesel fuel, kerosene, gasoline or other useful hydrocarbon liquids. There are now emerging a number of processes which will take post-consumer plastics and catalytically convert them into gasoline and low-sulfur diesel fuel. The diesel fuel meets or exceeds both European and Federal EPA standards for emissions and is designed specifically for the solid waste disposal industry that has significant investment in diesel-powered equipment. The types of plastic targeted as feedstock for this project have no commercial value and would otherwise be sent to landfill.

High-temperature pyrolysis and cracking of waste thermoplastic polymers, such as polyethylene, polypropylene and polystyrene is an environmentally acceptable method of recycling. These type of processes embrace both thermal pyrolysis and cracking, catalytic cracking and hydrocracking in the presence of hydrogen. Mainly polyethylene, polypropylene and polystyrene are used as the feedstock for pyrolysis since they have no heteroatom content and the liquid products are theoretically free of sulfur.

The principal output products are gaseous and liquid hydrocarbon fractions that are remarkably similar to the refinery cracking products. Their chemical composition and properties strongly depend on the input feed composition, (i.e. proportion of polyethylene, polypropylene and polystyrene in the feedstock) and they can also be unstable due to their high reactive olefins content (especially from polyethylene and polystyrene cracking).

The book also explores the application of various acidic catalysts, such as silica–alumina, zeolites (HY, HZSM-5, mordenite) or alkaline compounds such as zinc oxide. However, the main problem with catalytic cracking is that in the course of the cracking process all catalysts deactivate very quickly. Expensive zeolite catalysts increase the cost of waste plastics cracking process to the point where it becomes economically unacceptable since the catalyst becomes contained in coke residue and therefore cannot be recovered and regenerated.

Effective engineering design of the cracking reactor for waste plastic processing is very important since the carbonaceous solid residue is one of the cracking products (levels up to 10% or more) and its continuous removal from the reactor is necessary to ensure profitable running. Stirred vessel reactors which have augers in the bases to facilitate continuous char removal are presented.

This book is truely international in scope with contributing authors from Spain, Saudi Arabia, Italy, New Zealand, Japan, Turkey, Hungary, Poland, Belgium, France, Germany, Korea, UK, USA, India, China and Australia.

John Scheirs
Walter Kaminsky
8 August, 2005

About the Editors

Dr John Scheirs is a polymer research specialist with an emphasis on plastic recycling and pyrolysis of waste plastics into fuels. He serves as a consultant for Ozmotech Australia and has worked on the development of their Thermofuel process which can convert unwashed mixed plastics into low-sulfur diesel transportation fuel. He has studied the pyrolysis of HDPE, PP, PET and engineering plastics.

John Scheirs is the author of the leading book on plastics recycling entitled *Polymer Recycling: Science, Technology and Applications* published by John Wiley & Sons Ltd, Chichester in 1998. He is also a member of the editorial board of the international journal *Polymer Degradation and Stabilization*, Elsevier Scientific, Netherlands.

John Scheirs is now the principal consultant with ExcelPlas Polymer Technology where he specializes in polymer recycling, polymer degradation, polymer processing and testing.

Professor Walter Kaminsky was born 1941 in Hamburg and studied chemistry at the University of Hamburg. His thesis was in the field of metallocene chemistry and his habilitation in the field of recycling of polymers by pyrolysis. Since 1979, he has occupied the role of Full Professor of Technical and Macromolecular Chemistry at the University of Hamburg.

He is currently supervising a group of 15 students and scientists in the field of pyrolysis of plastic waste in a fluidized bed process and a group in the field of metallocene/methylaluminoxane chemistry. His past experience includes the development of pilot plants for the feedstock recycling of plastic wastes and scrap tires, and discovering highly active metallocene catalysts for the polymerization of olefins. He has published more than 300 papers and books and holds 20 patents. He has organized several international symposia in the field of pyrolysis and olefin polymerization.

In 1987 he received, together with Hansjörg Sinn, the European Research Prize for the development of the Hamburg process for pyrolysis of polymers. In 1997 he received the Carothers Award of the American Chemical Society (Delaware Section), and in the same year the Walter Ahlström Prize in Helsinki, Finland. Since 1998 he has been an Honorary Member of the Royal Society of Chemistry in London, and Honorary Professor of the Zhejiang University in China. In 1999 he received the Benjamin Franklin Medal for Chemistry, Philadelphia and in 2003 the Hermann Staudinger Prize of the German Chemical Society (GDCh).

PART I

Introduction

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1

Introduction to Feedstock Recycling of Plastics

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ABBREVIATIONS

ABS	acrylonitrile–butadiene–styrene
APP	atactic polypropylene
ASR	automobile shredder residue
EVA	ethylene vinyl acetata
HDPE	high-density polyethylene
HIPS	high impact polystyrene
LDPE	low-density polyethylene
Low (LD)PE	low-molecular-weight polyethylene
MSW	municipal solid waste
MW	molecular weight
PA	polyamides, Trade Name Nylons
PC	polycarbonate
PE	polyethylene
PET	polyethylene terephthalate
PIB	polyisobutylene
PP	polypropylene
PS	polystyrene
PTFE	polytetrafluorethylene, Trade Name Teflon
PU or PUR	polyurethane
PVC	polyvinyl chloride
WEEE	waste electric and electronic equipment

1 INTRODUCTION

This review focuses on some technical and practical aspects of the *pyrolysis* or *thermal cracking* of waste plastics, to yield liquid fuels and monomers as a main product. It

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briefly enumerates some alternative products, such as synthesis gas, carbon, hydrogen chloride, or bromine, or techniques, such as combustion, partial oxidation or gasification, or feedstock recycling by chemical rather than thermal methods.

Some of the *practical aspects* to be considered are:

- the adequate availability and ensured supply of waste plastics,
- their collection, transportation, handling, storage, pre-treatment, and conditioning for feedstock recycling;
- their general management, as well as the typical cost of such operations.

2 NOMENCLATURE

Plastics are a generic group of synthetic or natural materials, composed of high-molecular chains whose sole or major element is carbon. In common usage the terms plastics, *polymers* and *resins* are roughly equivalent. A plastic material is (Society of Plastics Industry, cited in Brady and Clauser, [1]) 'any one of a large group of materials consisting wholly or in part of combinations of carbon with oxygen, hydrogen, nitrogen, and other organic or inorganic elements which, while solid in the finished state, at some stage in its manufacture is made liquid, and thus capable of being formed into various shapes, most usually through the application, either singly or together, of heat and pressure.'

Plastics are manufactured from *monomers*, i.e. a repeatable molecular unit and building block, by means of various chemical processes, such as:

- a catalytic or peroxide-initiated polymerization of monomer(s), e.g. ethylene, propylene, or butadiene + styrene (copolymers);
- a polycondensation of dissimilar monomers (e.g. bifunctional organic acids and alcohols or amines);
- polyaddition of reactive monomer molecules.

Especially the first group forms an attractive feedstock for pyrolysis processes.

Important monomers are polymerization grade (i.e. very high purity) ethylene, propylene, butadiene, three products obtained by thermal cracking or pyrolysis of e.g. naphtha, light gas-oil, or liquefied petroleum gases (LPG = propane or butane) and purified by low-temperature, high-pressure distillation, up to polymerization grade chemicals. Adding hetero-atoms to the monomer, such as chlorine in vinyl chloride monomer, creates additional difficulties in pyrolysis processes and methods for separating waste plastics at the source or by mechanical means, e.g. sink/float, froth flotation, separation after identification on the basis of absorption or reflection spectra, or electrostatic sorting after tribo-electric charging, is an important practical consideration.

Before its conversion into plastic products the resulting resin is almost always compounded with various *additives* of different nature and constitution, meant to improve processing, stability, or mechanical specifications as a function of a given application (outdoors, i.e. UV-light exposed, oxidation, high-temperature processing). Such additives are regularly used as:

- antioxidants (1%),
- heat and light stabilizers (5%),
- plasticizers (40%),

- impact resistance enhancers (10%),
- pigments, colorants and dyestuffs (5%),
- flame retardants (15%),
- mould-release agents,
- foaming agents (2%),
- fillers (40%)

(maximum amount encountered, in weight percent). Other additives are used as anti-blocker, anti-fogging and anti-static agents, bio-stabilizers, chemical blowing agents, cross-linking agents, high polymeric impact strength additives and processing aids, lubricants, metal deactivators, optical brighteners, property modifiers, reinforcements, smoke and afterglow suppressants, wetting agents, etc. Their presence, as well as chemicals used in initiating or terminating polymerization, is a complicating factor in *feedstock recycling*, also termed *chemical recycling* or, in a more restricted sense, *pyrolysis* or *thermal cracking* of waste plastics, since their nature, amount, and behaviour during pyrolysis (thermal volatilization or breakdown) and eventual influence upon reaction products and mechanism are somewhat unpredictable, especially for waste plastics of unknown origin and formulation. PVC absorbs more additive volume than any other resin.

Plastics can be classified on the basis of numerous criteria, e.g.:

- *chemical composition*, directly connected with the nature of the monomer(s) and the method of polymerization. Plastics are thus subdivided into classes, e.g. polyolefins, vinyl polymers, styrenics, polyamides, polyesters, epoxy resins, polycarbonates, polyurethanes, etc.;
- chemical *structure*, e.g. linear (high-density polyethylene), branched (low-density polyethylene), cross-linked and three-dimensionally networked (*thermosets, rubbers*);
- *stiffness*: elastic, flexible, or rigid;
- type of *application*: commodity vs engineering, general purpose vs specialty plastics;
- *processing method* used (injecting moulding, extrusion, film blowing, blow moulding, thermoforming, casting, calendaring, and many other techniques);

Thermoplastics still soften when heated and harden again when cooled, because there is little or no bonding between individual molecular chains. *Thermosets* show three-dimensional structures and rather than softening, thermally decompose while heating. All commodity plastics are thermoplastic.

Rubber has a structure intermediate between thermosets and thermoplastics, with molecular chains linked by sulphur bridges during vulcanization. In pyrolysis, the main material is tyre rubber, a compound of styrene- butadiene- and isoprene-based rubber (SBR), of carbon black, sulphur, vulcanization aids, and zinc oxide.

The history, statistics, classification, barrier properties, main resins of bulk plastics, etc. can be read from websites [2], with typical applications [3]. Plastics also show some other characteristic properties:

- an amorphous, i.e. noncrystalline structure, related to disorder among polymer chains;
- low thermal conductivity;
- high electrical resistance;
- low softening temperatures;
- viscous–elastic behaviour.

The *world production* of plastics keeps rising, and so does waste generation, albeit with a time lag, dictated by lifetime. This lifetime spans from weeks (packaging), over months (agricultural film) and years (cars, household appliances, furniture), even to the order of a century (in some building applications). In numerous building applications (water distribution ducts, flooring, roofing, window frames) such lifetimes are not known with certainty. Still, *take-back schemes* more and more affect important markets, such as packaging, automobile, or electrical and electronic equipment. Such schemes are still developing, confronted with the immense variety in applications, resins, additives, and with the difficulty in identification and light weight of plastics.

Plastics waste arises at the levels of *production, conversion*, and *consumption*. In the first two categories source separation, identification, and recycling, is straightforward. Such simple source separation concepts no longer hold for post-consumer recycling, where entropy is immense: plastic products both geographically and functionally are widely spread, more often than not compounded with unknown additives, or mixed, soiled, composite, and difficult to collect at a reasonable cost.

Mechanical recycling, i.e. reusing as a plastic material in similar applications (closed-loop recycling, e.g. film-to-film) provides the highest value to waste plastics. Loss in mechanical properties restricts recycling to simpler applications and geomembranes, sometimes simply replacing low-grade wood, as in urban furniture, such as park benches. *Feedstock recycling* converts plastics into monomer, mixes of chemicals, or into synthesis gas or reducing gas. *Thermal recycling* (combustion) merely recovers the heat of combustion.

3 PYROLYSIS OF PLASTICS AND RUBBER

Pyrolysis, also termed thermolysis (Greek: pur = fire; $thermos$ = warm; luo = loosen), is a process of chemical and thermal decomposition, generally leading to smaller molecules. Semantically, the term thermolysis is more appropriate than pyrolysis, since fire implies the presence of oxygen and hence of reactive and oxygen-bearing intermediates. In most pyrolysis processes, however, air is excluded, for reasons of safety, product quality, and yield.

Pyrolysis can be conducted at various temperature levels, reaction times, pressures, and in the presence or absence of reactive gases or liquids, and of catalysts. Plastics pyrolysis proceeds at low ($<400°C$), medium ($400–600°C$) or high temperature ($>600°C$). The pressure is generally atmospheric. Subatmospheric operation, whether using vacuum or diluents, e.g. steam, may be selected if the most desirable products are thermally unstable, e.g. easily repolymerizing, as in the pyrolysis of rubber or styrenics.

The thermal decomposition of polymers yields gases, distillates and char, albeit in widely variable relative amounts. These can be applied as fuels, petrochemicals, and monomers. Depending on the polymers or polymer mixtures fed and the operating conditions used, yields can vary widely. As a rule both gaseous and liquid products are mixtures of numerous different compounds. The problem of fractionating these effluents and upgrading to commercial specifications, while separating undesirable impurities, must be investigated on a case-by-case basis. The char incorporates fillers, pigments, and ash.

Pyrolysis processes involve breaking bonds and are often endothermic, so that ensuring a supply of heat to the reacting material is essential and generally rate-determining. Partial oxidation supplies such heat internally, but the pyrolysis products are diluted by oxidation or combustion products.

Polyolefin resins contain only carbon and hydrogen, and additives, such as some antioxidants and UV stabilizers. Moreover, the presence of hetero-elements, such as chlorine and bromine is undesirable, as these elements distribute over the three product phases-gas, liquid, and solids, reducing the market potential and value of each of these. Studying their elimination is a major consideration in developing processes for mixed plastics.

3.1 SURVEY OF PREVIOUS WORK

Most work on plastics pyrolysis has been *academic* and directed at the analysis of polymers, their molecular structures and thermal stability, at the study of pyrolysis products, e.g. fire research, or at feedstock recycling at a laboratory or pilot scale. An early survey was given by Madorsky [4]. Given the large number of possible purposes, or different resins, additives, and operating conditions, the field is as wide as the sky!

Since the introduction of modern instruments (*ca* 1962) the thermal analysis of polymers as a research field has expanded very rapidly, encompassing specific techniques such as:

- differential scanning calorimetry (DSC), for measurements of specific heat and enthalpies of phase transition;
- differential thermal analysis (DTA), measuring the temperature difference between the sample and a reference and indicating the occurrence of any heat effect and of abrupt changes in heat capacity;
- thermogravimetric analysis (TGA), for assessing thermal stability and decomposition temperatures;
- thermomechanical analysis (TMA), for establishing the mechanical response of polymer systems to temperature changes. It includes dilatometry, penetration, torsion modulus, and stress/strain behaviour, as well as establishing the softening temperature, as determined by the Vicat penetration test, the deflection temperature or heat distortion test, the zero strength temperature test, the polymer melt or stick temperature test;
- flammability testing. Plastics used in furniture, mattresses, cars, electronics, etc. must satisfy specifications regarding fire behaviour and flame retardancy.

These techniques are often coupled with evolved gas analysis. TGA is a basic technique in studies on thermal decomposition. An excellent introduction is given in [5]. A systematic study of both physical and chemical aspects in plastics pyrolysis was launched in the E.U. Cycleplast project [6], aiming at a systematic scientific evaluation of various steps. The (German) Society for Thermal Testing listed methods relating to thermal testing [7]. Since 1965, prestigious, at present biannual meetings on Analytical and Applied Pyrolysis have been chaired by authoritative scientists such as G. Guiochon (1965), C.E.R. Jones (1972), J. Kistemaker (1976), T. Szekely (1979), K.J. Voorhees (1982), I. Lüderwald & H.-R. Schulten (1984), C. Gutteridge (1986), I. Ericsson (1988), J.J. Boon (1990), W. Kaminsky (1992), S. Tsuge (1994), G. Audisio (1996), A. Kettrup (1998), F.J. Gonzalez-Vila (2000), J. Fink (2002), R. Font & A. Marcilla (2004), and M. Blaszo (2006). Themes such as *instrumentation and analytical methods, elucidation of chemical structure, thermo-oxidation* and *photo-oxidation, mechanisms and kinetics* are much more central in such work than is feedstock recycling.

On the *industrial side*, there has been a lively interest in plastics pyrolysis, since the breakthrough of mass production of plastics in the 1960s. A major tribute is to be paid to a first wave of Japanese enterprise, actively promoting plastics pyrolysis as a technical solution. New initiatives in Japan were launched in the 1980s and 1990s, such as the double fluid bed systems operated by Ebara Co. (Stardust Project, Yokohama), and, with less success, Tsukishima Kikai. At present these steady efforts are culminating in nationwide pyrolysis systems for converting waste plastics, separately collected from households, to yield liquid fuels and monomers, or used as a reducing agent in blast furnaces or as a coal substitute in coking plants. Plastics are converted in liquid phase, stirred tank reactors in plants at Niigata and Sapporo, PVC in rotary kiln units to coke and HCl by the former Nihon Kokan (at present JFE Holdings). Ube Industries jointly with Ebara Co. have developed an elevated pressure gasification process; the synthesis gas is cleaned and piped to a synthesis plant at the same site.

Japanese ventures were confronted with their counterparts in Europe and the USA during the International Symposia on Feedstock Recycling from Plastics, or ISFR, held at Sendai (1999), Ostend (2002) [8, 9] or at Karlsruhe (2005).

3.2 PRODUCTS FROM POLYMERS

3.2.1 Major Operating Conditions

The major factors of influence determining the product distribution resulting from plastics pyrolysis are summarized in Table 1.1.

Chemical composition plays a dual role:

1. Mass conservation dictates that the pyrolysis products, distributed over the three phases, gas, liquid, and solid, consist of the same elements as the raw materials and that their relative amounts are conserved. There is a redistribution of relevant elements during pyrolysis, with hydrogen and chlorine enriching the gas phase, carbon in the coke.
2. There is a direct link between polymer structure and its primary pyrolysis products, the latter primarily resulting from the breakage of bonds followed by some molecular or free radical rearrangement. Of course, secondary reactions do occur and gradually convert the primary products into more stable, less reactive alternatives. The product distribution hence depends on time, and relative rates of bond breakage and subsequent processes, but can be found only by experiment. As a rule, bond breakage becomes easier at high temperature.

Temperature is the most important operating variable, since it determines both the rate of thermal decomposition and the stability of feedstock and reaction products. High temperature (>600°C) and both vacuum and product dilution favour the production of simple small gaseous molecules, low temperature (<400°C) and increased pressure lead to more viscous liquid products, higher rates of pyrolysis, a higher coking tendency, more secondary products and dehydrogenation.

Pyrolysis, for most plastics, begins at ~300°C and for some thermosensitive resins even earlier, e.g. for vinyl-based polymers. The onset of the pyrolysis reaction is strongly influenced by the presence of additives, such as stabilizers, plasticizers and pigments. In most processes a medium temperature (400–500°C) is selected and the plastics are in

Table 1.1 Factors affecting product distribution

Factor of influence	Effect
Chemical composition of the resins	The primary pyrolysis products relate directly to the chemical structure and composition of the resin, and also to the mechanism of its decomposition (purely thermal or catalytic)
Pyrolysis temperature and heating rate	Higher operating temperatures and high heating rates both enhance bond breaking and favour the production of small molecules
Pyrolysis time	Longer residence times favour a secondary conversion of primary products, yielding more coke, tar, as well as thermally stable products, thus gradually obscuring the effect of original polymer structure
Reactor type	Determines mainly the quality of heat transfer, mixing, gas and liquid phase residence times, and the escape of primary products
Operating pressure	Low pressure reduces the condensation of reactive fragments forming coke and heavies
Presence of reactive gases, such as (air) oxygen or hydrogen	Such presence internally generates heat, dilutes the products and influences upon equilibriums, kinetics, and mechanisms
Use of catalysts	Their use influences upon kinetics and mechanisms, and hence, the product distribution
Additives incorporated	The additives generally either evaporate or decompose. Some may influence kinetics and mechanism
Liquid or ‘gas’ phase	Liquid phase pyrolysis retards the escape of evolving products, thus enhancing interactions

a molten state. ‘Gas phase’ processes feature liquid polymer films, distributed over the grains of fluidized bed pyrolysis reactors.

The required *reaction time* is determined principally by reaction temperature. The formation of primary products, e.g. monomers, is favoured by short residence times, the formation of more thermodynamically stable products (H_2, CH_4, aromatics, carbon) by long ones. Low pressure (under vacuum, or in the presence of inert diluent) favours the production of primary products, including monomer, high pressure that of complex, liquid fractions.

The *reactor type* is selected mainly on the basis of technical considerations, mainly its heat transfer and feed and residue handling characteristics. In many processes proposed the polymer is first dissolved in a bath of molten polymer or wax, or dispersed in a salt bath, to reduce the viscosity of the melt. Other processes suggest the use of the excellent heat transfer and mixing properties of fluidized bed thermal or catalytic reactors. Increasing temperatures has an influence upon thermodynamics, i.e. the relative stability of various products, as well as upon kinetics and physical conditions of the reacting mixture. High temperatures and heating rates, low pressures and residence times favour the formation of primary products. Conversely, long residence times lead to a preponderance of stable products. In the Hamburg pyrolysis process developed by Professor Kaminsky and Professor Sinn, conditions were so selected that the main output was aromatics, whatever the feedstock.

In the presence of oxygen, part of the feedstock is oxidized (partial oxidation) and carbon monoxide and dioxide are inevitable products, while oxygenated organics are also arising as by-products. The process is termed *gasification* when the production of combustible gas or synthesis gas is emphasized. Gasification is a high temperature process that completely destroys the original chemical structures. However, the resulting gas is tailor-made to requirements using well-known and large-scale techniques.

Pyrolysis or gasification, as processes, are both much easier to control than direct firing of plastics. The latter is impossible on mechanical grates, equipping conventional incinerators for municipal solid waste (MSW). On the other hand, thermal conversion is feasible by means of fluidized bed technology. The few percent of plastics, as in traditional MSW is unproblematic and the calorific content is converted into heat and often into power, albeit at a disappointing level of conversion efficiency, of the order of 15–25%.

Theoretically, waste plastics have excellent fuel value, quite comparable to that of gas oil, when only polyolefins are considered. Introducing hetero-atoms, such as oxygen, nitrogen, or chlorine, reduces the heating value. Moreover, chlorine acts as an inhibitor and generates strongly acid gas. In practice, however, plastics are difficult to burn, because of an almost uncontrollable combustion rate, locally leading to oxygen deficiency and products of incomplete combustion.

Hydrogenating conditions lead to the elimination of hetero-atoms and yield more saturated products as well, an important consideration regarding the marketing of pyrolysis products.

Catalysts are a class of compounds specially selected, designed and optimized for influencing the reaction mechanism. The main purpose of catalysts is to convert vapour-phase products into a higher-octane petrol (gasoline). Another purpose may be in accelerating decomposition, using acids and bases for promoting the decomposition of polyamides and polyesters. Throw-away catalysts may be used for scavenging impurities. Catalyst activity, selectivity, and stability are major considerations. Some research directions can be derived from the themes of 2nd ISFR papers [9]:

- catalytic cracking of polyolefins, possibly containing EVA, by J. Aguado *et al.*;
- the presence of polycyclic aromatic hydrocarbons in the product fractions, by P.T. Williams and R. Bagri;
- co-catcracking with residues from light Arabian crude, by M. F. Ali;
- comparison of fresh, steam deactivated, and used FCC catalyst, by S. Ali and A. Garforth;
- PP and PET cracking over TiO_2/SiO_2 catalysts, by K. Nakano *et al.*;
- using red mud as a low-grade hydrocracking catalyst by J. Yanik *et al.*;
- hydro-cracking of MSW-plastics with vacuum gas oil by T. Karayildrim *et al.*;

Catalytic cracking is potentially an important route to produce high-value products from plastic feedstock. The catalyst converts naphtha to higher-value petrol (gasoline). Little is known on the effect of fillers or coke precursors (styrene, butadiene) on catalytic activity and catalyst fouling, coking, or clogging. Another area of interest is the effect of catalyst addition on the thermal decomposition in the liquid phase. It seems unlikely that the macromolecules can contact the internal catalyst surface in a productive fashion. Some additives may also influence the product distribution by modifying the cracking mechanism and hence, product distribution. Generally, their effect is unknown but also often much smaller than that expected from catalysts.

3.2.2 Decomposition Modes

As a rule, the pyrolysis of plastics follows complex routes that cannot be described by one or more chemical reactions, but only and still rather imperfectly by either empirical formulas featuring fractional stoichiometric coefficients or comprehensive systems of elementary reactions, i.e. reactions that really proceed as written. Moreover, the composition and structure of these reaction systems may vary with details of molecular structure, such as chain irregularities, incorporation of initiators or catalysts, etc. As a consequence, precise mechanisms are of only scientific interest, an industrial approach being limited to overall considerations, such as the heat effect and the product distribution resulting under particular reaction conditions.

Decomposition modes are often subdivided according to the prevailing reaction patterns, which are mainly dictated by molecular structure and the presence of catalysts:

1. Decomposition into monomer units (PMMA, PA 6) mainly, often termed *unzipping*. This decomposition mode is of very large practical interest, since monomer is a high-value product, typically commanding a price several times the equivalent of fuel value. The pyrolysis of PMMA is in general use and economically warranted, with typical scrap prices of the order of 300–400 €/tonne, monomer yields well in excess of 90%, and monomer values of the order of up to 1500 €/tonne. Hence, PMMA waste is highly valued! The MMA generated is not necessarily fit as polymerization grade, and often used as a viscosity index improver of lubricating oil, in acrylic varnishes, rather than as a monomer.
2. *Random fragmentation* of the principle polymer chain (PE, PP) into fragments of variable, intermediate length. The size distribution over the resulting fragments is largely Gaussian, with the average M.W. continuously descending with rising pyrolysis temperature and time. Thus, polyolefins are converted into PE waxes and oils, often high in α-olefins and a sulphur-free, premium diesel oil. Conversely, PP products yield a much more branched product mix.
3. Decomposition according to both previous schemes combined (PS, PIB). In a polystyrene production plant, PS could conveniently be converted into monomer, since facilities for separating the various pyrolysis products (styrene and its oligomers, ethylbenzene, toluene, benzene, etc.) are available already on site. However, huge PS production plants generally generate insufficient off-spec. scrap to feed a pyrolysis unit of even a small industrial size!
4. *Elimination of simple, stable molecules* from adjacent atoms (PVC yields HCl, PVAc yields acetic acid, PVOH yields water). Such thermal cleavage leaves unsaturated, charring, residual chain residues.
5. *Elimination of side-chains*, followed by cross-linking and creating a porous charred residue, including the non-volatile additives. This scheme is followed by most thermosets and other cross-linked polymers.

Polymer resins and their major possible products are collected in Table 1.2. A high purity of the feedstock is the best guarantee of clean and possibly marketable products. Generally, the value of the products obtained is insufficient to warrant the process. However, recently the concept of feedstock recycling created a political current that is more favourable to pyrolysis than the corresponding economic context.

Table 1.2 Polymer resins and major possible products of thermal decomposition

Resin	Mode of thermal decomposition	Low-temperature products	High-temperature products
PE	Random chain rupture	Waxes, paraffin oils, α-olefins	Gases and light oils
PP	Random chain rupture	Vaseline, olefins	Gases and light oils
PVC	Elimination of HCl from the chain, chain dehydrogenation and cyclization	HCl (<300°C), benzene	Toluene (>300°C)
PS	Combination of unzipping, and chain rupture, forming oligomers	Styrene and its oligomers	Styrene and its oligomers
PMMA	Unzipping	MMA	Less MMA, more decomposition
PTFE	Unzipping	Monomer	TFE
PET	β-Hydrogen transfer, rearrangement and de-carboxylation	Benzoic acid and vinyl terephthalate	
PA-6	Unzipping	Caprolactam	

3.2.3 Resins and Products

A systematic study of both physical and chemical aspects in plastics pyrolysis was launched in the Cycleplast project [6]. Thermal degradation of commodity polymers, including kinetic factors and mechanism, were systematically investigated by Professor Bockhorn and collaborators, using thermogravimetry, linked with mass spectrometry, as well as closed loop laboratory-scale pyrolysis reactors. The resulting kinetic parameters are discussed further.

Polyolefins, mainly PE and PP, the main commodity plastics, decompose into a range of paraffins and olefins, according to route 2. The molecular weight distribution and the paraffin-to-olefin ratio decrease with rising reaction temperature and time.

Polystyrene PS mainly yields styrene, as well as its oligomers, mainly dimers and trimers. Mixtures of PS + PE decompose as usual in the case of PS, with the pyrolysis products somewhat more saturated, the PE providing the required hydrogen. The decomposition of PE is somewhat accelerated by the presence of PS.

Polyvinylchloride (PVC) decomposes into two distinct steps, the first yielding hydrogen chloride and benzene, the second a mix of aromatics. The kinetic results vary with the amount of sample and the experimental modes (programmed heating or isothermal) are different for hydrogen chloride evolution, with activation energy 136 vs 120 kJ/mol, and reaction order 1.54 and 1.98.

PET decomposes via β-hydrogen transfer, rearrangement and decarboxylation, with major products benzoic acid and vinyl terephthalate.

Polyamide 6 depolymerizes into caprolactam with high yields. The decomposition is catalysed by both strong acids and bases.

Kinetic study may describe decomposition, generally using first-order models and a reaction rate parameter linked to temperature by the Arrhenius law. Closer scrutiny reveals a more complex behaviour, with kinetic parameters that continuously evolve with experimental conditions. These studies yield values for activation energy ranging from ~140 kJ/mol (PVC-dechlorination) to 290 kJ/mol (second step in PVC-pyrolysis, and dynamic cracking of PS). Also the reaction orders observed vary widely, from 0.3 (dynamic cracking of PP) to 2 (dynamic cracking of PVC, second step). However, such kinetic parameters vary with the experimental conditions, in line with the complexity of the reaction system, composed of innumerable elementary chemical reactions.

In actual industrial practice, these figures are relatively meaningless, since actual pyrolysis kinetics are normally determined by the rate of heat transfer [10]. A number of interesting simulations of the effect of heat transfer upon apparent rates were performed by both Hornung *et al.* and by Vergneaud in the framework of the E.U. Cycleplast project [6].

Other studies focused on a mix of MSW plastics, whether resulting from selective collection or mechanical separation. Six thermoplastics, which represent more than two-thirds of all polymer production in western Europe, were pyrolysed in a static batch reactor in a nitrogen atmosphere. These were high-density polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET) and polyvinylchloride (PVC). The heating rate used was 25°C min^{-1} to a final temperature of 700°C. These six plastics were then mixed together to simulate the plastic fraction of municipal solid waste found in Europe. The effect of mixing on the product yield and composition was examined. The results showed that the polymers studied did not react independently, but some interaction between samples was observed. The product yield for the mixture of plastics at 700°C was 9.63% gas, 75.11% oil, 2.87% char and 2.31% HCl. The gases identified were H_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8, C_4H_{10}, CO_2 and CO. The composition of oils were determined using Fourier transform infrared spectrometry and size exclusion chromatography. Analysis showed the presence mainly of aliphatic compounds with small amounts of aromatic compounds [11].

The results of an interesting study on copyrolysis of naphtha and added polyolefins or their kinetics and degradation products were presented at the Analytical and Applied Pyrolysis meeting at Alicante [12] (Table 1.3). The product yields from cracking (450°C) of LDPE and PP are quite different, with more liquid fraction from PP:

The relative and absolute amount of paraffin thus decreases with temperature, that of olefins and di-olefins tends to increase; simultaneously, the ratio of light products ($C_{<15}$)

Table 1.3a Product distribution in the cracking of polyolefins at 450°C

Feedstock	Gas	Oil/wax	Residue
LDPE	20.0	75.0	5.0
PP	11.0	87.8	1.2

Table 1.3b Product distribution in the polyolefins cracking: distribution of C_{15} and Ratio $C_{<15}/C_{>15}$

Temperature	*n*-Pentadecane, wt	1-Pentadecene, wt	1,14-Pentadecadiene, wt	Ratio $C_{<15}/C_{>15}$
450°C	2.80	3.58	0.64	1.27
550°C	0.97	2.16	0.59	2.22
650°C	0.46	1.23	0.42	2.67

to heavies ($C_{>15}$) rises continuously with temperature. The authors also determined the overall kinetic parameters and product distribution for naphtha cracking proper, or after adding LDPE or PP. The kinetics and product distribution were little affected but the rate of coking somewhat increased in the sequence:

$$\text{Naphtha} < \text{naphtha} + \text{LDPE} \ll \text{naphtha} + \text{PP}$$

These authors studied the possibility of blending LDPE and PP into the feedstock of a naphtha cracker. Such units have huge yearly capacity, of the order of 400 000 tonne ethylene or about 1 Mton of feedstock (naphtha). Most plastics pyrolysis units have only a modest scale, ranging from an annual 2000 to 20 000 tonne. This difference in scale obviously reflects in differences in cost, since labour is almost identical for small, medium, or large plant, whereas investment cost I of petrochemical plant typically varies with capacity C as (R = reference basis):

$$I/I_R = (C/C_R)^{2/3}$$

This means that plant cost varies as shown in Table 1.4.

3.2.4 By-products

The major product of pyrolysis is either a monomer (PMMA, PS), or a series of fuel fractions. By-products of plastics pyrolysis are related to the presence of:

Heteroatoms:

- oxygen in the resin or the pyrolysis atmosphere leads to the formation of water and oxygenated products;
- chlorine leaves pyrolysis units mainly as (an irritating and corrosive) hydrogen chloride gas. Normally, no chlorine gas is formed, due to the strongly reducing conditions. Bromine, under similar conditions, is somewhat easier to form;
- nitrogen yields various substances of concern, such as ammonia, hydrogen cyanide, and possibly organic compounds, such as nitriles and amines.

Additives:

- mineral additives generally report to the coke fraction;
- organic additives either volatilize, or decompose. A major additive, in relative amounts, are PVC plasticizers. Some PVC products (flooring) may contain more additives than PVC resin.

Table 1.4 Plant investment cost, relative values, or per unit capacity

	Plant investment cost	
Capacity (tonne/year)	(relative values)	Relative values per unit capacity
1	0.215	2.15
3	0.448	1.49
10	1.000	1.00
30	2.080	0.69

Secondary reactions: Under pyrolysis conditions, most pyrolysis products have only a precarious stability, as well as a marked residual reactivity towards more stable products and ultimately its elements carbon, hydrogen, as well as simple, stable molecules, such as water, ammonia, hydrogen chloride, etc. In some cases conversion along the pyrolytic route will be halted at some point, in order to preserve high-value primary products and reduce the difficulty of separating more complex mixtures.

Coke formation:

- generally, coke formed by pyrolysis is a by-product only. It is a main result of pyrolysing thermosets and PVC. Moreover, resins can be ordered on the basis of coking tendency, but the reaction conditions as well as external surfaces, such as reactor walls or fillers, play a major role;
- coke could be upgraded, by activating it to activated carbon, or leaching out fillers There is no evidence, however, that this has ever been contemplated seriously;
- depending on pyrolysis conditions, polyolefins can be converted almost quantitatively into volatiles. Polystyrene has stronger their coking tendency, and polyvinylchloride always leaves some coke. Thermosets and rubbers leave coke as a major product;
- coking tendency, however, depends on operating conditions and polymer structure, as analysed by Van Krevelen [13]. Moreover, some coke may derive from secondary reactions, involving readily polymerizable products, such as dienes and olefins, or coke precursors, such as aromatics. Metal surfaces and coke may actively catalyse coking.

3.3 HETERO-ATOMS AND SIDE PRODUCTS

A major problem in pyrolysis is in the rather unpredictable specifications of both feedstock, if it is a mix of plastics, and products. Especially the presence of halogens has been considered problematic, both because of product quality and operating problems, such as:

- corrosion by HCl, especially in the presence of water vapour;
- clogging by $CaCl_2$, a problem that once plagued the plant at Ebenhausen, based on the Hamburg University pyrolysis process.

3.3.1 Reactor Types and Processes (Table 1.5)

Professor Fontana and Dr Jung classified all major gasification routes and pyrolysis processes, studying their mass and energy balances as well as operating conditions (refer 2nd ISFR Ostend) [9], predicting the behaviour of mixed plastics during pyrolysis and gasification, in order to assess the production of valuable substitution fuels. Their model was validated by laboratory-scale experiments and the quality of the resulting substitution fuels evaluated, to choose the best thermal process for industrial plants according to the properties of available waste streams.

Extruders are available with capacity of more than 1 tonne/h, to mix and melt plastics and provide profiles, tubes, sheet, etc. They are mostly heated electrically, or else using circulating thermal oil, and can be used in pyrolytic systems for feeding plastics, straining the molten feed, eliminating HCl from PVC at temperatures up to some 400°C. Professor

Table 1.5 Reactor types and their characteristics

Reactor type	Particular characteristics	Applications
Extruder	Operating temperature is limited. Degassing of premature decomposition products is essential	Production of waxes from PE
Tubular reactor	Simplicity	Molten polyolefins
Stirred tank reactor, possibly with external heating loop and/or reflux cooler	Conventional liquid phase reactor. Stirring improves heat transfer. Clogging of downstream ducting has to be avoided	Mixed plastics: BASF, Ludwigshafen Chiyoda Engineering, Niigata
Vertical or shaft reactor	Gravity flow	Rubber pyrolysis Foster Wheeler
Fixed bed reactor	Mainly for catalytic reactions, converting vapours from a first reactor	
Salt or lead bath reactor	The bath acts as a heat transfer agent. Residues accumulate on top of the layer, requiring a periodic shutdown for cleaning	PMMA pyrolysis
Fluidized bed reactor	The fluidized bed acts as a heat transfer agent, dispersing the melting plastic in thin layers. Residues are carried out with the products, requiring a delicate filtration of fines (pigments, fillers)	
Rotary kiln	Simple units, featuring tumbling action and gravity flow. Sealing is delicate.	NKK PVC-pyrolysis process
Autoclave	Reactor for operating under pressure, generally in a batch mode	Hydrogenation

Menges and his successor Professor Michaelis conducted pyrolysis at RWTH-Aachen in an externally heated extruder, up to 430°C, a temperature maximum dictated by materials selection considerations. Early extruder pyrolysis systems were developed by Union Carbide and Japan Steel Works [14].

Tubular, or fixed-bed thermal or catalytic reactors, are a conventional technology in chemical engineering, and provide plug flow, but lack the positive displacement, mixing and plasticizing effect of single or double screw extruders. They were used to a limited extent, e.g. by Japanese Gasoline and Sanyo Electric Co., the latter featuring dielectric heating. *Shaft reactors* have been proposed for rubber pyrolysis, e.g. the cross-flow units in the Warren Spring Laboratories developed process, proposed by Foster Wheeler. *Rotary kiln* reactors have provided an alternative in rubber pyrolysis and were used by Sumitomo Cement and Kobe Steel, at present by Nippon Kokan for PVC [14].

The stirred tank reactor, possibly with external heating loop and/or reflux cooler, is widely proposed as a plastics liquid phase pyrolysis reactor. Both BASF [15] and Professor Bockhorn [6] have used a cascade of well-mixed reactors to produce a step-by-step pyrolysis of resin mixtures.

The required *heat of reaction* is supplied by external heating of the reaction vessel, or, for laboratory-scale or pilot units, by electrical heating. Full-scale plant is either directly fired, or heated by circulating reacting liquids through an external pipe still. Some processes propose a circulating heat carrier, e.g. superheated steam, molten salts, sands or pebbles, to heat the charge. One process (Sanyo Co.) used dielectric losses, arising from the high-frequency oscillation of electrically polarized molecules. The problem of heat transfer can be eliminated altogether by partial oxidation of the reactor contents. In this case, the product stream is diluted, by combustion products that dilute and oxidize the pyrolysis products. This makes the recovery of useful products more difficult and reduces the calorific value of the pyrolysis gas produced.

Numerous liquid phase processes make use of a tank reactor, containing a bath of molten plastics, or a dedicated heat transfer agent, such as molten lead, tin, or salts. The bath is indirectly heated, generally by being mounted into a furnace. The bath contents are stirred, to obtain homogeneous operating conditions, improve heat transfer and avoid charred residues forming upon overheated heat transfer surfaces. A possible alternative to stirring is to circulate the molten plastics using pumps, by transferring the reactor contents through an external furnace or heat exchanger.

Early developments were made by Mitsui Shipbuilding and Engineering, Ruhrchemie (molten salts), Kawasaki Heavy Industries and Mitsubishi Heavy Industries [14]. Mitsui processed low-M.W. PE and atactic PP to form:

- 4–5% gas, mainly C_1–C_4 hydrocarbons;
- 90% oil, consisting mainly of *n*-paraffins, 1-olefins and their isomers;
- 5–6% of residue – fillers, stabilizer residues, pigments, etc.

Mitsubishi Heavy Industries pioneered a two-step pyrolysis of mixed plastics. A primary vessel is used for decomposing PVC at 300°C. Then, HCl is scrubbed out from the effluent. Molten material is fed into a second vessel operating at 400–500°C. The same concept was much later applied by BASF at Ludwigshafen, and extended to achieve a selective pyrolysis, making use of differences in thermal stability of the different resins.

Potential operating problems may occur, due to:

- clogging of effluent lines by entrained droplets or waxy materials. At the Niigata plant such an obstruction led to an uncontrolled pressure rise in the reactor, pushing out part of the reactor contents through the feeder system, and eventually causing a fire;
- charring and fouling of heat transfer surfaces;
- deficient level control.

A fluidized bed is a second frequently used type of reactor. Early developments include Japan Gasoline Co. (PS-waste), Sumitomo Shipbuilding and Machinery Co. and the University of Hamburg. The latter developments led to the construction of a demonstration plant at Ebenhausen that was halted after being confronted to a number of technical operating problems.

3.3.2 Product Specifications

Distinction should be made between monomers, specific petrochemicals, and more or less typical oil fractions, produced by mixed plastics pyrolysis. Potential pyrolysis products from polyolefins are naphtha, kerosene, or gas-oil. These are blends of numerous different

Table 1.6 Typical naphtha specifications and testing methods [18]

Property	Units	Test method	Value
Density (15.6°C)	g/cm^3	ASTM D-4052	0.735 max.
Reid vapour pressure	psig	ASTM D-323	12 max.
Color Saybolt		ASTM D-156	18 min.
Lead content	wt ppb	ASTM D-3559	50 max.
Total sulfur	wt ppm	ASTM D-3120	100 max.
Initial boiling point	°C	ASTM D-86	50 min.
Final boiling point	°C	ASTM D-86	165 max.
Paraffins	wt%	G.C	80 min.
Olefins	wt%	G.C	1 max
Naphthenes + aromatics	wt%	G.C	Balance
Total chlorides	wt ppm	IP-AK/81	10 max.

hydrocarbons, but they still need to satisfy some common commercial specifications. Off-specification products have no market, even if they can be blended in small amounts into other streams that are less critical with respect to the specification compliances. The latter are measured according to established standards, e.g. those of the American Society for Testing Materials (ASTM), the American Petroleum Institute. Most monomers (polymerization grade) are high-purity products: 99.99% or more. The latter is difficult to attain in plastics pyrolysis!

The terminology used in oil refining is found at numerous websites, [16, 17]. As an example, naphtha specifications (Table 1.6) typically involve:

Specifications of other oil fractions obtained may involve (diesel oil) a cetane index, measures of unsaturation, or handling or safety data, such as cloud point or flash point.

3.4 FUNDAMENTALS

3.4.1 Aspect of Fluids Mechanics

As their name implies, plastics are easily deformable and once molten they may be heated not only externally, but also internally, by dissipating friction or dielectric heat. Once the pyrolysis temperature is attained, the melt viscosity starts decreasing rapidly and rising pyrolysis vapour bubbles agitate the mix. Many properties of plastics can be derived using methods used and developed by Van Krevelen [13]. The pyrolyzing plastic's rheology is poorly-documented, however, since the evolution of molecular size and structure with time and the effects of extraneous matter are difficult to predict.

In a number of processes the plastics prior to pyrolysis are dissolved into product oil for example, so that the viscosity is quite controllable. Other options, though today somewhat obsolete, are the use of a molten lead, tin or salt bath. Unfortunately, residues accumulate on top of this bath, and periodic shut-down for cleaning is inevitable. The process has been used commercially for PMMA.

In fluidized bed units the plastics are dispersed over the surface of innumerable sand or catalyst particles, greatly facilitating heat and mass transfer.

3.4.2 Liquid vs Gas Phase Operation

It is somewhat difficult to visualize plastics as a liquid. The viscosity of a plastic melt markedly decreases as the temperature is raised to levels at which pyrolysis becomes rapid for all resins, i.e. 450°C. Several means may be used to bridge the gap between feed temperature, generally room temperature, and reactor temperatures, namely:

- melting, plasticizing and possibly pyrolysing the feed in an extruder–feeder;
- dissolving the cold feed into hot liquid, serving as thermal flywheel and dissolver. Part of the bath must periodically be discharged, to prevent the accumulation of residues and coke. Coking is often a self-catalytic process!

Some processes feature a stepwise heating and decomposition. The idea has been applied for analytical purposes (polymer blends), but seems also attractive for industrial purposes, since it allows initially eliminating hydrogen chloride from mixtures containing polyvinylchloride at low temperature (250–400°C), then passing to a second step of pyrolysis conducted at a more conventional, higher temperature (~450°C), thus ensuring a low residual chlorine content of the products eventually produced. It is essential, however, to ensure a high-quality disengagement of HCl from the melt; otherwise, some HCl reacts, leaving organochlorine compounds in the melt.

Liquid phase pyrolysis often yields liquid fractions of an intermediate boiling point. When applied to polyolefins it leads to synthetic oil fractions, the boiling range of which decreases with rising pyrolysis temperature. Since lighter fractions have higher value than high-boiling ones, there is interest in combining pyrolysis with a simple type of distillation, i.e. refluxing the heavier fractions into the pyrolysis vessel. Another reason for separating heavies at an early stage is the hazard created by having downstream lines clogged by high-molecular-weight paraffin products.

Obviously, it is unfeasible to process polymers directly in the vapour phase. Most gas phase operations feature a fluidized bed, either constituted of inert sand particles, or of a cracking or reforming catalyst. The plastics fed into the bed are almost immediately melted, coating the individual bed particles and pyrolyzing as a multitude of thin layers.

3.4.3 Mass Balances – Processing Margins

It is essential to determine the yield of each major product rather precisely and at different values of the various operating parameters, mainly temperature, residence time, and pressure. Many studies are incompletely documented, considering only gas or liquid phase products, without mention of residues or mass balances. Moreover, in practice the product yield of pyrolysis is reduced by losses inherent to consecutive purification. Inevitable losses occur further during storage, transfer, and separation. Moreover, each raw material as a rule contains nonproductive constituents, such as some moisture, metal inserts, coatings, reinforcement agents, or fillers. These loss factors explain why laboratory data may lead to overly optimistic views regarding possible industrial yields!

Establishing mass balances after pyrolysis tests is also important for economic reasons. Economic figures are related directly with the operating margins, being the difference between the value of the products and the cost of raw materials.

$$
\begin{aligned}
[\text{Operating margin}] = {} & [(\text{Unit value of product})_i(\text{Yield of product})_i] \\
& - (\text{Unit cost of raw material})
\end{aligned}
$$

This operating margin must cover all charges, such as equipment depreciation, and the cost of manpower, and utilities (power, steam, cooling water, compressed air, etc.). Raw materials of good purity and quality command a reasonable price in the marketplace.

3.5 VALUE OF THE RESULTING PRODUCTS

Some pyrolysis products have high value. These are mainly monomers, such as methylmethacrylate, caprolactam (the monomer of PA 6), tetrafluorethylene, or styrene. Others are comparable to standard products with specifications of naphtha, kerosene, or gas-oil. Such fractions have a well-known market, as follows from Table 1.7.

However, it is still questionable as to how far plastics pyrolysis can yield product fractions, according to current specifications without extensive post-pyrolysis purification. At Sapporo University, good olefin yields were obtained in the thermal cracking of oil, derived from the local plastics-to-oil plant. The Niigata oil is locally used in a diesel engine and not for sale!

Today important flows of plastics originate in mandatory recycling schemes, such as those imposed by take-back obligations on packaging, End-of life vehicles, or waste electric and electronic equipment (WEEE). For such materials, the drive for collection and recycling is not normally economic, but mandatory. In such cases, there is often a *dump fee*, to be paid for further processing a stream of waste plastics into recycled products. The value of such fees varies from some 50 €/tonne for injection into blast furnaces in the European Community to as much as 50–100 kYen (∼370–750 €/tonne)

3.5.1 Heat Balances

The major terms in the heat balance of a pyrolysis reactor are:

- evaporating any moisture contained;
- supplying sensible heat and latent melting heat to the plastics;
- supplying heat of reaction to the plastics.

Process heat requirements tend to be lower if the feed is stepwise heated, as in certain multistep or selective decomposition schemes of plastics mixtures, or in case the

Table 1.7 Some commodity prices (*Financial Times*, 3 August 2004)

Oil-Brent Blend (Sep)	39.95	\$/bbl
Unleaded gas (95R)	441–443	\$/metric tonne
Gas Oil (German Htg)	376–378	\$/metric tonne
Heavy Fuel Oil	163–165	\$/metric tonne
Naphtha	403–405	\$/metric tonne
Jet Fuel	422–424	\$/metric tonne
Diesel (French)	399–401	\$/metric tonne
NBP Gas (Aug)	20.65–20.70	£/MWh
Euro Gas (Zeebrugge)	22.43–22.63	£/MWh
UKPX Spot Index	22.84	£/MWh
Conti Power Index	28.9373	£/MWh
Global COAL RB Index™	62.45	\$/metric tonne

bbl = barrel

heat of condensation of product vapours can be used to preheat the feed. On the other hand, such provisions also complicate plant construction and operation, and add to the investment cost.

Another important factor is the rather poor thermal conductivity of plastics. Bockhorn *et al.* [6] cite values for the heat conductivity of PS and PP as low as 0.17 $\mathrm{W\,m^{-1}\,K^{-1}}$, for PET as 0.21 $\mathrm{W\,m^{-1}\,K^{-1}}$, and for HDPE 0.41 $\mathrm{W\,m^{-1}\,K^{-1}}$. The viscosity at 250°C attains 2–3 Pa s (20 $\mathrm{s^{-1}}$).

Heat transfer at a wall is related to the Reynolds number, generally to the power ~0.7. Thus, there is great interest in securing a low viscosity when the heat of pyrolysis is to be supplied. Dissolving the feed in oil is a possible procedure.

3.5.2 Thermodynamics

The relative stability of molecules can be read directly from some literature data tables. The composition corresponding to thermodynamic equilibrium and the corresponding heat of reaction can be derived relatively easily, as long as the required thermodynamic data is available, e.g. in the Janaf Tables [19].

3.5.3 Kinetics and Mechanism of Pyrolysis

The study of kinetics and mechanism of pyrolysis is of considerable scientific interest, with regard to the thermal behaviour of organic molecules, the precise constitution of molecules or copolymers, including irregularities, such as structural defects and incorporation of initiator molecules and radical scavengers, used to control the MW.

Some important results from the team of Professor Bockhorn (Cycleplast project) [6] are shown in Table 1.8.

The kinetic parameters given are derived from the thermogravimetric experiments. The mechanisms of pyrolysis, as discussed by this team, are too complex and varied to be treated here in more detail.

E. Hakejova *et al.* [12], studied the pyrolysis of individual hydrocarbons, and of naphtha, kerosene, gas oil, and hydro-cracking fractions, as well as their copyrolysis with hexadecane, heptane, iso-octane, cyclohexane, and also with heavier feedstocks, i.e. dewaxing

Table 1.8 Some kinetic data (By courtesy of Professor Bockhorn, University of Karlsruhe)

Type of resin	Melting point, (°C)	Density	Temperature range (°C)	Maximum rate of decomposition at (°C)	*E* (kJ/mol)	Apparent reaction order, *n*
PA 6	218–224	1.12	310–450	415	211	~1
PS	110	1.05	320–415	355	172	1.04
PVC	>140	1.4	210–350 (I)	250–280 (I)	140	1.5
			350–500 (II)	425 (II)	290	1.8
HDPE	134	0.954	340–500	475	262	0.83
PP	163	0.91	340–460	425	190	0.3
PET	260	1.41	360–410	400		

cakes, high-boiling hydro-cracking fractions, and waste polymers. Heavier feedstock could not be separately treated, because of coke formation in steam cracking.

The purpose was to evaluate the effects on processing and the product distribution obtained by thermal cracking at 450°C when adding oil and wax products as an additional feedstock, blended with naphtha, the regular feedstock. The thermal cracking mechanism proposed is a Rice–Herzfeld type of free radical mechanism. Using the notations β and μ, respectively for a reactive radical, mainly engaged in H-abstraction and for a larger, mainly decomposing radical, a simple scheme can be written as:

Initiation: $\mu\text{-H} \rightarrow \beta + \beta'$
H-transfer: $\mu\text{-H} + \beta \rightarrow \mu + \beta\text{-H}$
Decomposition: $\mu \rightarrow \beta + \text{Olefin}$
Isomerization: $\mu \leftrightarrow \mu'$
$\mu + \mu\text{-H} \leftrightarrow \mu' + \mu\text{-H}$
Addition: $\beta + \text{Olefin} \rightarrow \mu'$
$\mu + \text{Olefin} \rightarrow \mu''$
H-transfer: $\mu\text{-H} + \mu' \rightarrow \mu + \mu'\text{-H}$
Termination: $2\mu \rightarrow \text{Products}$
$\beta + \mu \rightarrow \text{Products}$
$2\beta \rightarrow \text{Products}$

for describing the kinetics and mechanism of high temperature pyrolysis. Some studies use standard software for this purpose, e.g. Thergas, Kingas [20, 21].

Obviously, depending on the type of catalyst and the operating conditions used, different mechanisms and modes prevail in catalytic cracking.

4 FEEDSTOCK RECYCLING

4.1 SURVEY

Feedstock recycling encompasses processes that convert polyolefins and mixed plastics into oil products, or PVC into HCl and coke. Such plastics pyrolysis, as yet, either in Western Europe or the USA, is not an industrially relevant process, since only the reverse process, the polymerization of monomers to high-molecular entities, creates value. Plastics pyrolysis is technically and economically feasible only for selected polymers that yield high-value, readily marketable monomer products, e.g. PMMA or PA 6. For bulk polymers, such as polyolefins, polystyrene, polyesters, and PVC the scale of production is too small and the margins too low to make plastics pyrolysis an economically viable process. The presence of additives, soil, or other resins, incorporating hetero-atoms, leads to both operating and product specification problems, rendering pyrolysis generally economically unviable. Another important factor is securing an adequate dump fee, to sustain the operation financially, as well as the availability of raw materials, a problem of finding sources, optimizing logistic factors (plastics are light and bulky), sorting, cleaning and handling, and ensuring steady specifications.

The *raison d'être* of feedstock recycling, i.e. thermal or chemical conversion of plastics that cannot be recycled by mechanical routes, is thus not to create economic value, but rather a purely political decision, with limited economic value at current cost and capacity factors.

Polyesters, polyamides and other poly-condensation polymers can be chemically recycled simply by reversing their synthesis process by raising the process temperature, using traditional processes such as *hydrolysis, ammonolysis, acidolysis, transesterification*, etc. Bayer and other interested suppliers pioneered such processes that are beyond the scope of this book. Such processes can also be used for adjusting the MW required in one application (e.g. PET-bottles) to that needed in a different market (e.g. polyester fibres).

Gasification is another route potentially important in feedstock recycling. Basically, plastics are fired with a sub-stoichiometric amount of oxygen + steam or of air, generating a synthesis gas that can eventually be converted into ammonia, methanol, OXO-alcohols, or hydrogen. The processes required for treating and purifying such gases are well known, as well as their fundamentals. On a pilot scale, Texaco Inc. and Shell developed proprietary processes, in which the more usual liquid or pulverized coal fuels are replaced by molten plastics. A few years ago, Texaco intended testing its technology in Rotterdam, The Netherlands at a plant capacity of 50 000 tons of waste plastics a year. The only operating plant at present is that of Ube Industries in Japan, in which plastics arising from households are collected and baled, then gasified in a pressurized fluid bed reactor, developed jointly by Ube and Ebara Co. An alternative is converting mixed, but chlorine-lean plastics into the reducing gas, required in a blast furnace to reduce iron ore and produce pig iron. The process is used in Japan by Nihon Kokan NKK (at present merged into JFE-Holdings). In Europe, the process was also pioneered by Bremen Stahl (Arcelor Group).

Hydrogenation has been pursued at the industrial level at the test plant by Veba Oel in Bottrop, Germany [15].

Some of the techniques used may also apply to other organic compounds with medium-high or high molecular weight, such as rubber, adhesives and glues, varnishes, paints or coatings. Pyrolysis has also been used for cleaning purposes, e.g. separating paints, plastics or rubber from metals. Since such operations are conducted on a small scale and in view of metal recovery, it is uneconomic to recover organics. Rather, these are destroyed by thermal or catalytic post-combustion.

4.2 PROBLEMS WITH HETERO-ATOMS

The major hetero-atoms appearing in polymers are: oxygen, nitrogen, chlorine, bromine, fluorine. After plastics pyrolysis, these elements either appear as intermediate organic compounds still incorporating the hetero-element, or as stable inorganic compounds, i.e. water, ammonia and hydrogen cyanide, hydrogen chloride, hydrogen bromide and bromine, hydrogen fluoride. Most of these are hazardous and corrosive and require a careful selection of construction materials, as well as methods to neutralize or inhibit their effect.

The presence of halogenated polymers and fire retardants, of heavy metals, and the potential formation of dioxins are some of the problems addressed in various studies presented at the successive Symposia on Feedstock Recycling (ISFR). Dehalogenation is a major topic. Some important commercial polymers (PVC, PVDC, chlorinated PE) introduce the element chlorine in almost any mixed feedstock, including those that are derived from MSW plastics, WEEE, or ASR materials. Moreover, the latter two streams also contain brominated fire retardants that may pose problems during recycling. The following important topics were addressed at the 2nd ISFR Symposium:

- elimination of chlorine from mixed plastic fractions, to produce oil, coke and gas fractions, free from chlorine;
- scavenging of halogens from a reaction mixture;
- scrubbing of HCl and HBr from an off-gas flow;
- closing the Br loop, to create a sustainable solution to the problem of fire retardants;
- interactions between the flame retardants based on Br and on Sb in feedstock recycling.

Dehalogenation has been studied at several levels, namely that of (Contributions presented at the 2nd ISFR Symposium [9]):

1. *Dehalogenation* prior to or *during* the *pyrolysis* process. Okuwaki and Yoshioka monitored debromination of Printed Circuit Boards (PCBs), at rising temperatures while heating these under helium. These researchers treated various products arising from plastics liquefaction plant in an autoclave using a mixture of NaOH and water, and obtaining deep dechlorination after 3 h at 250°C. H. Ishihara and M. Kayaba (Hitachi Chemical Co. Ltd., Japan, Sony Co., Japan) focused on epoxy resins, used in most PCBs, and developed a technology to depolymerize brominated epoxy resins in a solvent, in the presence of alkali metal compound. Thus PCBs separated into resin solvent, glass cloth, and metals, including mounted devices and solder. M. P. Luda *et al.* studied the thermal degradation of brominated bisphenol A derivatives. Sakata *et al.* used iron oxide and calcium carbonate compounds to produce a halogen-free oil, or treat gaseous effluents. Kamo *et al.* studied liquid phase cracking in H-donor solvents, such as tetralin and decalin.
2. Dehalogenation of *liquid products*, using a catalyst prepared from goethite and phenol resins for the dechlorination of chlorocyclohexane as a test substance (Matsui *et al.*).
3. HCl and HBr removal from *gaseous effluents*. Bhaskar *et al.* examined Ca-, Fe-, Zn- and Mg-based sorbents for this purpose, obtaining good results with Ca-Z. Hakata *et al.* tested an iron oxide-carbon composite catalyst for the selective vapour phase dechlorination of chloroalkanes.
4. *Dehalogenation* in the presence of antimony, studied by Uddin *et al.*
5. Closing the bromine cycle, with initiatives of the European Brominated Flame Retardant Industry Panel (EBFRIP) in cooperation with the Bromine Science and Environmental Forum (BSEF), including a study prepared by ECN (Petten) on a two-stage pyrolysis/high-temperature gasification process.

4.3 COLLECTION SYSTEMS

Under pressure from legislation, in particular the Packaging and Packaging Waste Directive, 94/62/EC, recycling of packaging products has increased dramatically from 1995. In numerous E.U. countries, collection of waste plastics is part of the mandatory recycling, imposed by the Packaging Directive and National Laws deriving from it (Table 1.9).

Eight countries recovered over half the waste plastics from packaging in 2000: the Netherlands, Switzerland, Denmark, Norway, Germany, Sweden, Austria and Belgium.

Table 1.9 Plastics packaging waste management systems in the E.U.

Country	System responsible for collecting packaging waste
Europe	Pro Europe sprl
Austria	ARA Altstoff Recycling Austria AG
Belgium	asbl Fost Plus vzw
Bulgaria	EcoPack Bulgaria
Cyprus	Green Dot Cyprus Public Company Ltd.
Czech Republic	EKO-KOM, a.s.
Finland	PYR Ltd
France	Eco-Emballages SA; Adelphe
Germany	Duales System Deutschland
Greece	HE.R.R.CO Hellenic Recovery and Recycling Co.
Great Britain	Valpack Ltd; BIFFPACK; WASTEPACK
Hungary	ÖKO-Pannon p.b.c.
Ireland	Repak Ltd.
Italy	CONAI (Consorzio Nationale Imballagi)
Latvia	Latvijas Zalais Punkts, NPO, Ltd
Lithuania	Zaliasis Taskas, UAB
Luxemburg	Valorlux asbl
Malta	GreenPak Malta
Norway	Materialretur A/S; RESIRK
Poland	RekoPol-Organizacja Odzysku S.A.
Portugal	Sociedade Ponto Verde, S.A.
Slovak Republic	Envi-pak, a.s.
Slovenia	Slopak d.d.o.
Spain	Ecoembalajes Espana, S.A.
Sweden	REPA-Reparegistret AB; RETURPACK PET
The Netherlands	SVM-PACT
Turkey	CEVKO

Waste electrical electronic equipment (WEEE) is being selectively collected in an increasing number of E.U. countries, so that this stream can be considered available and harnessed. ASR is available at car shredding plants.

4.4 LOGISTICS OF SUPPLY

Plastic resins are bulk commodities. A naphtha cracker producing ethylene has a typical yearly capacity of 500 000 tonnes of ethylene, necessitating about 1.2 Mtonnes of naphtha feedstock! Polymerization to resins is conducted with a somewhat lower capacity, but still at the same order of magnitude, say 150 000 tonnes. Engineering plastics are produced at lower capacity, but this lower rank is still far superior to the capacity of the largest feedstock recycling units conceived to date!

The problem with post-consumer plastics is their immense variety and widespread application. One tonne of plastics can be converted into either 20 000 two-litre drinks bottles or 120 000 carrier bags! Collecting, sorting, baling, and transporting such numbers of lightweight materials is a tremendous task, with typical cost levels as shown in Table 1.10.

From a dispersed source, such as households, curbside collection, followed by sorting, cleaning, baling, is very expensive. The only way to reduce such cost is to introduce take back systems.

Table 1.10 Cost factors in selective collection from household refuse

Activity	Cost, €/tonne
Curbside collection	750–1000
Sorting	200–250
Recycling	50–750
Residue elimination, ∼15% of feed	15
Total	1000–3000

In some cases plastics or rubber are easier to collect. Automobile shredder residue is such a potential source of waste plastics, arising at car shredding plant, as can be seen at the following web site [22]. Solving the collection problem is trivial, since the waste accumulate only at a limited number of plants. However, it is a mix of numerous different resins, with embedded dirt, metal, and glass, and the best way to derive value is to dismantle very large items (bumpers, dashboard, tyres, battery boxes) and mechanically or thermally treat the balance. Automotive shredding residues are at present generally sent to landfill. Ebara developed a fluid bed gasifier with subsequent combustion of the producer gas and melting of entrained dust in a cyclonic combustion chamber. The molten ash is tapped and granulated in a water quench. The demonstration plant at Aomori, Japan, has operated on two lines since March 2000.

Waste from electrical and electronic equipment arises at the sorting plant, where the frame, the printed circuit board PCB, the cathode ray tube, etc. are separated for recycling. The remaining plastics fraction is in part flame-retarded, hence contains brominated and antimony compounds. The number of WEEE recycling plants is growing, so that the logistics are no longer a major problem.

Sources of raw materials, methods of identification and sorting have been reviewed by Buekens [14, 23, 24]. It is remarkable that the general trends have remained largely unchanged over the years, albeit that today there is another attitude regarding waste management priorities and conceivably a much larger choice in automated sorting systems. Still, sorting on the workfloor has remained mainly a manual operation until very recently: the introduction of automated scanning and take-back machines created a market for sorters, based on spectral fingerprints of bulk plastic streams. Advances are periodically presented at Identiplast [25].

4.4.1 Voluntary Commitment of the PVC Industry

In the frame of Vinyl 2010 [26] the PVC Industry in the European Union made a number of voluntary commitments, regarding the control of emissions from VCM-producing plant, the phasing out of cadmium (both already realized) and lead-based stabilizers (to be completed by 2015) and the voluntary recycling of 200 000 tonnes per year by 2010. Some projects allow for mechanical recycling (Solvay's Vinyloop, at Ferrara), but feedstock recycling is also being considered [26].

In Japan, Nihon Kokan (now merged with Kawasaki Steel into JFE Holdings) developed a rotary kiln technology for converting PVC into HCl and coke and operates a pilot plant at Yokohama. The organic vapours are combusted prior to the recovery of HCl by wet scrubbing.

5 SOME FEASIBLE PROCESSES

A brief survey is given of a number of processes that have been used in Europe for plastics pyrolysis. At present, all of these projects have been mothballed. The most relevant initiatives are according to [15] :

1. Hamburg University Pyrolysis Process, high-temperature pyrolysis of mixed plastics, using a fluid bed reactor. Demonstration plant at Ebenhausen has not survived shakedown, due to various operating problems.
2. BASF low-temperature pyrolysis of mixed plastics, using a battery of stirred tank reactors for liquefaction.
3. BP low-temperature pyrolysis of mixed plastics, using a fluid bed reactor.
4. Veba Oil hydrogenation technologies.

5.1 PILOT AND INDUSTRIAL PLANT OPERATION

5.1.1 Hamburg University, Ebenhausen

A plant operating according to the Hamburg University pyrolysis process was built at Ebenhausen, with a capacity of 5000 tonnes per year. The feasibility of converting polyolefins by pyrolysis was successfully demonstrated, with yields from PE/PP mixtures of typically 51% (m/m) gas, 42% (m/m) liquids and the balance unaccounted for. However, the gas to liquids ratio is very sensitive to pyrolysis temperature. Since gas and oil are the major pyrolysis products, economic viability crucially depends on the price of crude oil. Under present conditions, profitability and economic viability are unsatisfactory at this small scale of operation.

5.1.2 BASF, Ludwigshafen

The BASF feedstock recycling process was designed to handle mixed plastic waste, as supplied by the DSD (Duales System Deutschland) green dot packaging collection system. A large pilot plant, with a substantial capacity of 15 000 tonne/yr, was started up in Ludwigshafen in 1994. At that time DSD estimated the total volume of mixed packaging plastics available for feedstock recycling at around 750 000 ton/yr. BASF offered to erect a full-scale industrial plant with a capacity of 300 000 ton/yr, but decided in 1996 to shut down the pilot plant, since no agreement could be reached on a guaranteed long-term waste supply and a gate fee sufficient to cover the costs.

In the BASF process, plastic waste is converted into petrochemical products in a three-stage process. Before feeding, the plastics are shredded, freed from other materials and agglomerated, to improve handling and enhance the density. In the first stage, the plastics are melted and liquefied in an agitated tank. The gaseous hydrochloric acid, evolving from PVC at temperatures up to 300°C, is absorbed in a water washer, and further processed to aqueous hydrochloric acid, to be reused in other BASF production plants.

In a second stage, the plastic oil was fed into a tubular cracker reactor, heated at over 400°C and thus cracked into compounds of different chain lengths, forming petrochemical raw materials. The oils and gases thus obtained are separated in a third stage, resulting in the production of naphtha, aromatic fractions, and high-boiling oils. About 20–30% of gases and 60–70% of oils are produced and subsequently separated in a distillation column.

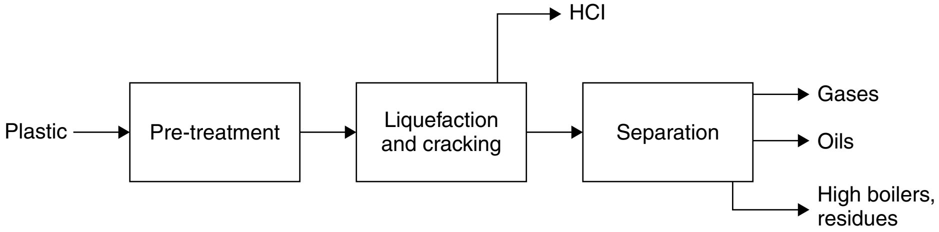

Figure 1.1 Schematic representation of the BASF pyrolysis process. (Reproduced by permission of TNO)

The naphtha produced by the feedstock process is treated in a steam cracker, and the monomers (e.g. ethylene, propylene, butadiene) are recovered. These raw materials are then used for the production of virgin plastic materials. High-boiling oils can be processed into synthesis gas or conversion coke and then be transferred for further use. All these products have outlets in the local BASF production plants.

During two years of trial operation, the pilot plant demonstrated its suitability. Although the process can be considered proven, it is at present neither used by BASF, nor elsewhere in Germany, because the quantities of plastic waste and dump fee needed for the plant to be economically viable are not available in Germany (Figure 1.1).

The process products are:

- HCl, which is either neutralized, or processed in a hydrochloric acid production plant;
- naphtha to be converted into monomers in a steam cracker;
- various monomers, which can be used for the production of virgin plastic materials;
- high-boiling oils, to be processed into synthesis gas or conversion coke;
- process residues, consisting typically of 5% minerals and metals, e.g. pigments or aluminium can lids.

Processing plastic waste by the BASF process would have required a gate fee of 160€/tonne for a plant with a capacity of 300 000 tonne/yr and a fee of 250€/tonne for a plant capacity of 150 000 tonne/yr [15].

5.1.3 BP, Grangemouth

In the early 1990s BP Chemicals first tested technology for feedstock recycling, using a fluid bed cracking process. Research on a laboratory scale was followed (1994) by demonstration at a continuous pilot plant scale (nominal 50 kg/hr) at BP's Grangemouth site, using mixed waste packaging plastics. The technology was further developed with some support from a Consortium of European companies (Elf Atochem, EniChem, DSM, CREED) and from APME. In 1998, BP Chemicals, VALPAK and Shanks & McEwan, set up a joint project (POLSCO), to study the feasibility of a 25 000 tonne/yr plant, including logistics infrastructure for supplying mixed plastics from Scotland. The project was seen as a remedy to the expected UK shortage in recycling capability, required to comply with EU and UK Packaging and Packaging Waste Directive.

Some preparation of the waste plastics feed is required before pyrolysis, including size reduction and removal of most nonplastics. This feed is charged into the heated fluidized bed reactor, operating at 500°C, in the absence of air. The plastics thermally crack to hydrocarbons, which leave the bed together with the fluidizing gas. Solid impurities and some coke either accumulate in the bed or are carried out as fine particles and captured by cyclones.

The decomposition of PVC leads to HCl formation, which is eventually neutralized by contacting the hot gas with solid lime, resulting in a $CaCl_2$ fraction to be landfilled. The process shows very good results concerning the removal of chlorine. With an input of 1% Cl, the products contain ~10 ppm Cl, somewhat higher than the 5 ppm typical of refinery use. Also, metals like Pb, Cd and Sb can be removed to very low levels in the products. Tests have shown that all hydrocarbon products can be used for further treatment in refineries. The purified gas is cooled, condensing to a distillate feedstock, tested against agreed specifications before transfer to the downstream user plant. The light hydrocarbon pyrolysis gases are compressed, reheated and returned to the reactor as fluidizing gas. Part of this stream could be used as fuel gas for heating the cracking reactor, but as it is olefin-rich, recovery options were also considered. The flow scheme is illustrated in Figure 1.2.

The process flow diagram shows hydrocarbon recovery in two stages, since the heavy fraction becomes a wax at about 60°C. Once recovered, the light and heavy fractions (about 85% by weight) could be combined together for shipment to downstream refinery processing if the plastic feed is passed on as hydrocarbon liquid to the downstream plants. The balance is gaseous at ambient temperature and could be used to heat the process. In this way nearly all of the plastic is used with just solids separated as a waste product. The gas has a high content of monomers (ethylene and propylene) with only some 15% being methane.

Conceptually, the process can run in self-sufficient heating mode. In this case, overall gas calorific requirement may need a small net export or import as the product gas quality

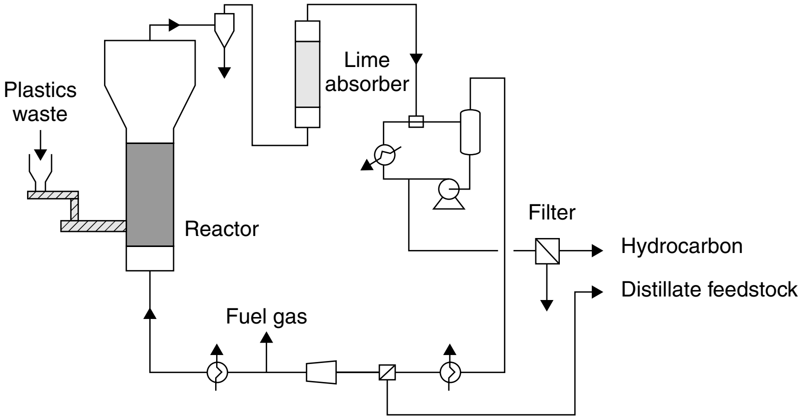

Figure 1.2 Schematic representation of the BP process. (Reproduced by permission of TNO)

varies with plastic feed specification and operating conditions. The other main utilities needed are:

- electrical power ~60 kWh/tonne feed plastic;
- cooling water 40 m^3/tonne feed plastic;
- steam 1.2 tonne/tonne feed.

All emissions are very low and should comply with local regulations.

The cost of treatment depends on many factors such as scale, location, scope, required preparation stages, and economic parameters used. Hence, comparison of the processes is difficult. The investment costs of a plant of 25 000 tpa, located in Western Europe in 1998, were estimated as 15–20 M£. Under these conditions, a gate fee of some 250 €/tonne is necessary. For a 50 000-tpa plant this gate fee could be some 150 €/tonne. These figures exclude the cost of collection and of preparation.

5.1.4 Veba Oil, Bottrop, Germany

From 1981 Veba Oil AG operated a coal-to-oil hydrogenation plant at Kohleöl Anlage Bottrop (KAB) in Germany, using the Bergius Pier coal liquefaction technology to convert coal into naphtha and gas oil. In 1987 the plant was modified, applying Veba Combi Cracking (VCC) technology to convert crude oil vacuum distillation residues into synthetic crude. Since 1988 a share of the petroleum residue feedstock was substituted by chlorine-containing waste (containing, e.g. PCBs). In 1992/1993 a depolymerization unit was added in front, to process exclusively mixed plastics waste from packaging, as collected by DSD. In 1998 some 87 000 tonnes were treated. DSD and Veba both agreed to terminate their contract in 1999, instead of in 2003: hydrogenation was unable to compete economically with treatment in blast furnaces and with the SVZ process at Schwarze Pumpe.

The plant includes first a depolymerization section and then the VCC section (Figure 1.3). In the first section, the agglomerated plastic waste is depolymerized and dechlorinated at 350–400°C. The overhead product is partly condensed. The main part (80%) of the chlorine introduced evolves as gaseous HCl in the light gases and is washed out, yielding technical HCl. The condensate, still containing some 18% of the chlorine input, is fed to a hydrotreater where the chlorine is eliminated together with the water formed. The resulting chlorine-free condensate and gas are again mixed with the depolymerizate for further treatment in the VCC section.

There, the depolymerizate is hydrogenated under high pressure (about 10 MPa) at some 400–450°C, using a liquid phase reactor without internals. Separation yields a synthetic crude oil, which may be processed in any oil refinery. Light cracking products end up in the off-gas and are sent to a treatment section, for removal of ammonia and hydrogen sulphide. A hydrogenated bituminous residue comprises heavy hydrocarbons, still contaminated with ashes, metals and salts. It is blended with coal for coke production (2 wt%).

The input specifications for the plastic waste are:

- particle size <1.0 cm;
- bulk density 300 kg/m^3
- water content <1.0 weight %;
- PVC <4% (2 weight % chlorine);

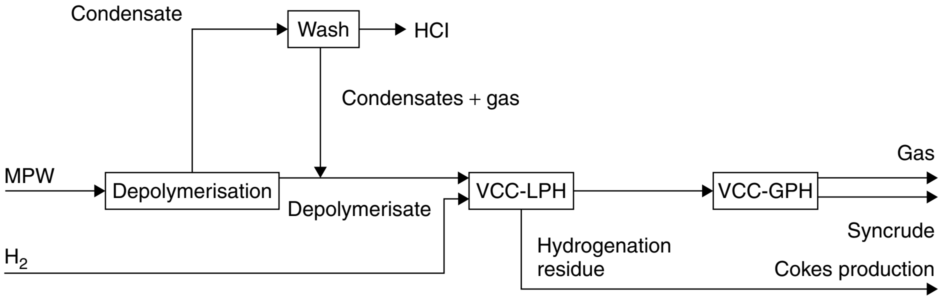

Figure 1.3 Schematic representation of the Veba Oil process. LPH = Liquid phase hydrogenation and GPH = Gas phase hydrogenation. (Reproduced by permission of TNO)

- inerts <4.5 weight % at 650°C;
- metal content <1.0 weight %;
- content of plastic resins >90.0 weight %.

The process outputs are:

- Syncrude, derived from the VCC section. It is free from chlorine and low in oxygen and nitrogen;
- a hydrogenated solid residue, which can be blended with coal for coke production;
- HCl;
- off-gas.

In 1997, successful treatment tests were completed on electric and electronic waste with bromine-containing flame retardants. For this test, 50 tons of WEEE plastics were mixed with some 250 tons of DSD waste.

The liquid products of the coal oil plant in Bottrop were pumped to the Ruhrol refinery, which also processes the plant's let-down gas. The solid residues are coked. A comparison of the yields obtained in pyrolysis and hydrogenation shows that, roughly speaking, 50% of the pyrolysis product is gas and 40% is oil, whereas 10% of the hydrogenation product is gas and 85% is oil. Hetero-atoms contained in the plastics (Cl, O, N, S) are split off and largely absent from product oil. The presence of PVC makes the process more resource-intensive (increased consumption of hydrogen, required neutralization of HCl, disposal of salts) and, hence, the input of Cl should not exceed a certain limit value. Mixed waste plastics also contain physical impurities, such as fillers, pigments and adhering dirt.

Hence, Veba Oil developed a commercial process, operating in a temperature range of 350–450°C and requiring a high hydrogen partial pressure (50–100 bar). The hetero-atoms are hydrogenated to products such as hydrochloric acid or ammonia. A synthetic oil distillate is obtained as the main product. Solid particles are concentrated in the sump of the distillation column. The gate fee for the VCC process was 250 €/tonne. The technology was realized in the coal-to-oil plant at Bottrop, with a capacity of 40 000 tonne annually, doubled at the end of 1995. One tonne of waste plastics yielded:

- 800 kg high-quality liquid products;
- 100 kg methane–butane gas and a further
- 100 kg hydrogenation residues, containing inert and inorganic components.

Schematic representation of the Texaco process, the Shell process, the AKZO steam gasification process, the Linde KCA process, the NCR process and the BSL incineration process are given by TNO [15].

5.2 CONCLUSIONS

Only few polymers can be recycled by pyrolysis under economically favourable conditions. Nevertheless, important amounts are collected with the aim of realizing recycling quota that were introduced under environmental pressure. The logistical problems of plastics waste collection are huge: even collecting astronomical numbers of films or bottles generates only rather modest amounts of materials, sufficient only to feed a pilot plant.

6 WASTE MANAGEMENT

6.1 PRINCIPLES

Waste management was once a down-to-earth technical problem, to be solved under thrifty, yet environmentally ‘acceptable’ and hygienic conditions and preferably performed by unskilled labour. Most waste was disposed of in landfills, except in densely populated regions, where volume reduction by incineration was a practical necessity. The recovery of heat, distributed in district heating systems or converted into electrical power was a means of cooling flue gases prior to their cleaning, but barely contributes to cost reduction, especially since a deep cleaning of flue gases became mandatory.

Today, however, waste management has turned into a fashionable legislation-driven business, a responsibility of top management, as part of the environmental profile of each corporation, and requiring expert knowledge in Law, Ethics, Politics and Sustainable Development. Operators belong to the world’s largest service companies.

The E.U. waste management policy focuses on waste hierarchy, giving great priority to waste prevention or reduction (elimination of technical or economic impediments and distortions that encourage the over-production of wastes) followed by re-use, recycling, recovery and residual management. Such a strategy includes an *integrated approach to waste management* with emphasis on material recycling that is preferred over energy recovery.

Waste prevention (or reduction) involves both (upstream) alterations in product design as well as in consumer habits (downstream). Such strategies assure that the two objectives of (quantity) less waste produced and (quality) less hazardous constituents utilized in production (so that less hazardous wastes is generated) are both met. Waste prevention is a strategy that prevents waste and its associated risks from being produced in the first place.

In this process also the costs have soared, starting from a logic that the more expensive it is to engender waste, the less there will be procreated and the more one will seek to segregate it at the source or after a selective collection, and upgrade it to a secondary raw material.

6.2 PLASTICS WASTE

Pre-consumer plastic wastes are generated during the manufacture of virgin plastics from raw materials (oil, natural gas, salt, etc.) and from the conversion of plastics into plastic products. The nature of waste arising in various processing methods is discussed in [14]. Such waste streams are soiled (floor sweepings, skimmings from wastewater treatment, crusts from polymerization reactors), mixed (laboratory testing), or off-specifications. Both production and conversion waste are easily identified and collected and handled by professional scrap dealers that discover and develop applications and market outlets that allow the use of secondary resins with less stringent and less defined specifications.

The amount of plastic waste generated is still considerably less than that of plastics produced: in numerous applications (building, furniture, appliances) plastics meet long-term requirements before their disposal and therefore do not yet occur in the waste stream in big quantities. The majority of plastic wastes are found in municipal solid waste (MSW), as well as in waste streams arising in distribution, agriculture, construction and demolition, furniture and household ware, automotive, electronic and electrical, or medical applications. For a number of years the APME has ordered studies to be made that compile inventories of on the one hand production figures, on the other waste arising, by resin, country, and application and activity.

In their efforts to educate the public and curtail the expansion of waste arising the authorities have devised a number of legal instruments to make inappropriate disposal more expensive (various levies, such as landfill taxes) and recycling more attractive, if not mandatory. More and more waste streams are forced into this route, by means of take-back obligations and minimum recycling quota. Under pressure from legislation, recycling of packaging products has increased dramatically from 1995. These directives are:

- Packaging and Packaging Waste Directive 94/62/EC;
- End of Life Vehicles Directive 2000/53/EC;
- Electrical and Electronic Waste: WEEE Directive 2000/96/EC;
- ROHS Directive 2000/95/EC.

However, the effect is not identical for all materials. Table 1.11 shows the results of such take-back obligation for different packaging materials in Belgium, the collection and recycling of which is entrusted to Fost Plus.

It follows that in Belgium (10 M inhabitants) Fost Plus pays more than 280 €/ton for ensuring the collection and recycling of used packaging, including:

- 5.77 kg PET/inhabitant per year;
- 1.65 kg HDPE/inhabitant per year.

In Denmark the amount of plastic packaging waste collected for recycling amounted in 2001 to 3.9 kg per inhabitant or 8.6 kg per household, compared with the potential amount, equivalent to 28.1 kg per inhabitant or 62.0 kg per household.

Waste from the automotive industry, particularly from *end-of-life-vehicles (ELV)*, has been identified by the E.U. as another priority waste stream. After dismantling larger parts suitable for mechanical recycling, the vehicle is shredded, the metal fraction (about 75%) is removed, and the remaining residue is known as automotive shredder residue (ASR),

Table 1.11 Packaging materials recycled by Fost Plus, Belgium (2003)

Material recycled	Tonnage (kton)	Contribution (M€)	Contribution (€/ton)
Glass	309.6	7.2	23.3
Paper and board	133.3	2.1	15.7
Steel	80.8	5.1	63.1
Aluminium	9.9	2.2	222
PET	57.7	16.3	282
HDPE	16.5	4.7	285
Beverage cartons	20.5	5	244
Other recyclables	98.2	36.8	375
Other nonrecyclables	0.8	0.3	375
Total	727.3	79.7	110

a mixture of many different materials (Wittstock, BASF, at 2nd ISFR). ASR is a major problem, since car manufacturers in Europe and Japan are forced to respect high recycling quotas, suggesting the following conclusions (Schaeper, Audi AG, at 2nd ISFR):

- weight-related quota for mechanical recycling impede a lightweight design;
- feedstock processes are favourable to recover lightweight cars;
- feedstock processes should count as recycling processes;
- there is a need to increase acceptance of feedstock processes.

Feedstock recovery of ASR is conceivable via conversion into reducing gases after injecting into the blast furnace in integrated iron and steel mills. Other gasification routes were developed by Dow, Shell, Texaco, and Lurgi (Schwarze Pumpe). Ebara Co. developed fluid bed gasifiers for MSW, ASR and plastics from selective collection. The latter are converted into synthesis gas at an operating pressure of 2–3 MPa, a development in collaboration with Ube Industries. Full-scale plants are operating at present on each of these feedstocks, e.g. Sakata (MSW), Aomori (ASR) and Ube (mixed plastics).

At 2nd ISFR, T. Yamamoto presented the gasification/melting system developed by Sumitomo Metal Industries for converting MSW into high-calorific gas using metallurgical techniques and oxygen.

Yasuda *et al.* studied the hydro-gasification of HDPE. Advanced rapid coal hydrogasification (ARCH) in Japan is developed as a route in the conversion of coal into synthetic natural gas.

Worldwide use of plastics in consumer electronics and electrical equipment is growing very rapidly, as is the waste volume related to such products, albeit with a time lag. Similar rules affect the resulting *electronic and electrical scrap (E & E)*, consisting of a broad mix of thermoplastics (e.g. HIPS, ABS, ABS-PC) for the casings and thermosets (epoxy resins) as major printed circuit board (PCB) material. The material is shredded, metal parts separated and sent to metal processing companies. Van Schijndel and Van Kasteren consider reprocessing using reactive agents such as siloxanes. The heavy metal content of casings, e.g. from computer monitors or TV sets, is very low and these streams can be separately shredded. An innovative depolymerization process using supercritical CO_2 can process heavy-metal-containing thermosets. In this way monomer recovery takes place and heavy metals are separated from the materials for reprocessing.

Several case studies in electronic and electrical scrap were presented at 2nd ISFR:

- components of a telephone were pyrolysed by Day *et al.* (National Research Council of America),
- Satoh *et al.* (Sony Co.) reclaimed the magnetic material from tapes using supercritical water to dissolve the resin;
- Noboru Kawai *et al.* (Victor Company of Japan, Ltd; National Institute of Advanced Industrial Science and Technology) tackled the Chemical Recovery of bisphenol-A from waste CDs or other polycarbonate resins.

An interesting alternative solution was developed in Denmark by Watech. However, industrial preference was given to another process, combining hydrolysis as a method for converting chlorine into hydroxyl substituents.

6.3 RUBBER WASTE

Rubber tyres are by far the most visible of rubber products. Identification is trivial and collection is well organized. Recycling and disposal, however, are less evident. A major route for tyres is their use as a supplemental fuel in cement kilns. Major compounds in tyres are: styrene–butadiene rubber (SBR), synthetic and natural polyisoprene rubber, steel cord, carbon black, zinc oxide, sulphur and vulcanization-controlling chemicals. Tyres can be retreaded, which is economic for large sizes (truck tyres), or ground to crumb or powder (cryogenic grinding). Such materials have some limited market potential as an additive in asphalt, and in surfaces for tennis courts or athletics.

The macromolecular structure of (vulcanized) rubber can be degraded using thermal, mechanical, and chemical means [14]. The resulting reclaim was once incorporated in limited amounts in new tyres. Safety and quality considerations dried up this outlet.

Pyrolysis of tyres is a feasible, yet technically difficult operation. The handling of the remnants of the steel carcass, the carbon black, the zinc oxide, as well as the tendency to repolymerize of the major products are serious stumbling blocks. Various rubber pyrolysis technologies have been developed, using, e.g. fluid bed, rotary kiln (Sumitomo Cement), molten salts, or cross-flow shaft systems (WSL/Foster Wheeler).

Microwave pyrolysis results in relatively high-molecular-weight olefins and a high proportion of valuable products such as ethylene, propylene, butene, aromatics, etc. The short process time contributes to a reduction in the processing cost. Whole tyres or larger chips can be processed, which greatly reduces pre-processing cost. The rubber is transformed from a solid to a highly viscous fluid within milliseconds. With additional curative agents the viscous material can be moulded into new products.

Supercritical water can be used to controllably depolymerize the rubber compounds. Tires decompose into high-molecular-weight olefins (MW 1000–10 000), or oils (max. 90%). Roy [9] discussed vacuum pyrolysis at 2nd ISFR.

6.4 PLASTICS PYROLYSIS AS A WASTE MANAGEMENT OPTION

6.4.1 Status in the E.U

Almost since its foundation (1975) the Association of Plastics Manufacturers in Europe (APME, Brussels) has monitored plastics production, consumption and waste generation.

Major sectors are packaging, building and construction, automotive, electrical and electronics (E & E), agriculture, and others (e.g. furniture, houseware, toys, engineering). After a short (e.g. packaging), medium (e.g. toys) or long lifetime (e.g. building) the plastic product reports to one of various waste streams, such as municipal solid waste (MSW), separately collected packaging, other recyclables, shredding waste (cars, white goods, etc.), construction and demolition waste, agricultural waste, E & E-waste-etc.

Such waste streams differ internally with respect to their composition, the feasible methods or modes of collection, and their legal status: producer responsibility has been introduced for a steadily rising number of streams, requiring separate collection, adequate treatment, and often mandatory recycling.

Already in the early 1970s the pyrolysis of plastic wastes to liquid fuels raised considerable interest, first in Japan, later also in Western Europe, with pioneering work of Professor Hansjorg Sinn and Walter Kaminsky, who developed the fluid bed Hamburg pyrolysis process, and of Professor Menges at the RWTH Aachen. However, despite extensive work at laboratory, pilot, or even an industrial scale, such work was jeopardized by both technical problems and disastrous economic figures. Hence, in Western Europe and the USA it is still at best a tentative process, balancing between political pressures and economic reality. Major corporations, such as BASF, BP, Shell, Texaco considered various options in pyrolysis and gasification, yet concluded that their large-scale implementation remains illusory as long as suitable dump fees fail to be guaranteed on the basis of contracts of sufficiently long duration and consequent volumes.

In Japan, however, plastics pyrolysis can now be considered to be state-of-the-art, and making part of the integrated waste plastics recycling system. Still, the process is operating at huge losses at both the levels of (1) collection cost and (2) treatment cost, and very few signs are apparent that one day this situation may reverse. Treatment cost is of the order of 100 000 Yen/tonne of household plastics supplied at the plant. At 2nd ISFR [9] Kusakawa reviewed and explained current Japanese environmental regulations, including the status of polymer recycling and activities in industrial segments, such as packaging, automotive, electrical/electronic industries. He mentions the relevant technological development in Japan and importance of polymer recycling efforts to comply with the regulations. Among these are the Recycling Promotion Law, the Containers and Packaging Recycling Law, the Electrical Appliances Recycling Law, the Building Recycling Law, the Foods Recycling Law, the Automotive Recycling Law.

Thus, the average consumer and industry are paying for realizing political long-term views based on sustainable systems and oil and gas scarcity.

6.4.2 Japanese Initiatives and Processes

Both the Ministry of International Trade and Industry (MITI) and the Plastics Waste Management Institute (PWMI) have been very active in promoting plastics recycling from early in the seventies. In Tokyo, plastics and metals were considered as waste, unfit for incineration and separately collected (1973) and treated in a Nippon Steel shaft furnace. Early Japanese systems, e.g. from Japan Steel Works, Japan Gasoline Co., Kawasaki H. I. Co., Mitsui Shipbuilding & Engineering Co., Mitsubishi H. I. Co., Nichimen, Sanyo Electric Co., Sumitomo Shipbuilding, Toyo Engineering Co have been reviewed [14, 26]. A large variety of pyrolysis systems, featuring extruders, tubular reactor units, as well as larger fluidized bed or stirred tank reactor units was tested, as soon as plastics became a visible component of municipal solid waste. More recently various commercial plants for feedstock recycling of waste plastics are operating at a full scale:

1. 'Liquefaction' units (not to be confused with the hydrogenation processes) using continuous stirred tank reactors, at Niigata and Sapporo.
2. Blast furnace at the NKK (now JFE Holdings) Mikasa works.
3. Coke oven pyrolysis by Nippon Steel Corp.
4. High-pressure gasification by EBARA-UBE.
5. ASR gasification at Aomori (Ebara Co.).
6. Glycolysis of PET bottles by Teijin. Separated PET bottles are now used as raw material for polyester fibres.

These Japanese successes are related to the practical implementation of the Containers and Packaging Recycling Law, carried out in 1997 for PET bottles and in 2000 for the other plastics. This law affords allocating the cost for feedstock recycling of waste plastics separated in homes. It has created attractive markets and thus the separated waste plastics are even in short supply in Japan. Recovery of plastics increased dramatically since 2000, when the law was carried out. On the other hand, the cost for recycling decreased gradually. This trend suggests that active competition improves both techniques and logistic systems.

The Home Appliances Recycling Law came into full force in 2001 and is to be revised within a few years. In such processes, not only the plastic cases, but also printed circuit boards are recycled. the Law for Recycling End-of-Life Vehicles passed through the Parliament, 2002. Clearly this law should promote the recycling of automotive shredder residue.

The environmental policy of the Japanese Government traditionally has promoted the recycling of waste plastics in Japan [27].

6.4.3 Ethical and Political considerations

In principle, it makes no sense to collect waste streams separately, unless suitable outlets are secured for such flows. This seems the case for soiled and mixed plastic packaging wastes, since these cannot be reprocessed to any better materials than those that substitute low-grade wood and since the option of feedstock recycling is operating at a huge economic loss. Moreover, no serious health, toxicity, or safety problems become apparent in case of less strict collection requirements.

However, Green parties contend that the only way to reduce waste generation is to make it prohibitively expensive. As a counter-argument, it may be stated that the funds lost in plastics recycling are better invested in health, education, and social needs. At present, most recycling options have mainly been introduced on an ideological basis, with limited attention to their economic cost and social consequences. These can be tackled using life-cycle analysis methods, i.e. the study of all environmental elements in a product's life-cycle [28]. According to RDC-Environment, Belgium, and Pira International, UK, the selective collection and recycling of plastics has a positive cost–benefit balance for some important applications, but is negative for others. Local parameters (quality of collected material, availability of output market, efficiency of the selective collection) play an important role.

6.4.4 Safety Aspects

Plastics are often considered quite harmless and were specifically excluded from early lists of hazardous waste, e.g. in Belgium (1976) and the Netherlands (1977). An exception was the plastic packaging that served for packing hazardous compounds, such as pesticides.

Still, some harmful compounds can appear in waste plastics, e.g. additives containing antimony, cadmium, lead, zinc, or hexavalent chromium, and plasticizers. Brominated flame retardants spreading into the environment is another reason for concern and a rational argument for dealing with WEEE and ASR-plastics [37].

6.4.5 Environmental Aspects

Little has appeared on the environmental effects of waste plastics pyrolysis. Conceptually, the topic can be subdivided in those environmental aspects related to:

- collection, transportation of feed materials;
- pre-processing;
- heating and pyrolysis;
- pyrolysis products.

Sorting of plastics is often manual and can cause allergic and health problems. Remarkably, plastic waste is not without a smell, and air extracted from storage and handling is thermally deodorized, e.g. at the Ube Industries gasification plant. Part of the pyrolysis products can be regarded as toxic.

6.4.6 Useful Publications

APME (Association of Plastics Manufacturers Europe, today Plastics Europe), with member companies given in [29] has classified plastic waste in a series of categories and monitors their origin and recycling, according to their field of application. Several early publications are still of interest, to compare past and present. A recent book on plastics recycling is Scheirs [38]. A few sites of interest are also:

- *Community Recycling*, a comprehensive guide to setting up, maintaining or expanding a local recycling scheme [30];
- *Waste at Work*, a practical guide to dealing with office waste, reducing and reusing everything from toner cartridges through to toilet rolls, as well as a step-by-step guide to setting up an office recycling scheme [31];
- *The National Recycling Directory*, listing United Kingdom national and regional contacts for recycling of various materials including local authority, industry and community organisations [32];
- *The Recycled Products Guide*, the searchable UK listing of products made from recycled material [33];

- *Plastics in the UK Economy,* a guide to polymer use and the opportunities for recycling in different industry sectors [34, 35].

7 CONCLUSIONS

Plastics pyrolysis has long been topical in academic circles and also continues to inspire industrial R&D and demonstration projects. Still, the pyrolysis of mixed plastics is economically to be proven, because of the small scale of the potential pyrolysis plant and the huge cost expenditure for collecting, cleaning and grading considerable tonnages of plastics. It is hoped that these costs will be covered by the value of the products obtained and, economically speaking, incineration is today a more reasonable option for the larger part of household plastics waste. Indeed, in only very few cases plastics pyrolysis is an economically viable process, e.g. PMMA and PA-6 pyrolysis, because of the high value of the monomers produced. The size of pyrolysis plant there is limited by the availability of scrap.

Still, today industry is obliged by political pressure to consider plastics pyrolysis, or more in general, feedstock recycling attentively: under green pressure there is a legal obligation to collect and recycle certain streams, such as those of packaging, automobile shredder residue ASR, and waste electronic and electrical equipment. Industry has an obligation to take back and recycle such materials, and is forced to consider all options, optimizing or at least testing recycling processes as a function of technical possibilities, feedstock characteristics, and, most of all, legal constraints. The boundary conditions of directives and their translation into national laws is still open for discussion, as follows from the different modes and levels of recycling, applied in the various member states and from the exportation of such flows to low-labour-cost countries.

The concept of feedstock recycling is based on a thermal and sometimes catalytic breakdown of polymer structure, yielding monomers (PMMA, PA-6, PS, PTFE), oil fractions, aromatic fractions, synthetic crude, or synthesis gas. To some extent plastics can be converted in the framework of oil refinery processes, such as viscosity breaking, fluid catalytic cracking, hydro-cracking and delayed coking, or in coal liquefaction [36], but these applications may require a preliminary thermal breakdown or dissolution into or extensive dilution by more conventional feedstock. The desired product and its specification requirements are essential in selecting operating modes and conditions and should be considered on a case by case basis.

The ‘thermal cracking’ of this plastic waste stream is realized via pyrolysis, hydrogenation, or gasification. Since the recovered hydrocarbon products are mostly used in petrochemical processes, their specifications limit the amounts of halogens into the ppm range. Subsequently, the collected mixed waste streams are pre-treated and graded according to their chlorine content. Another possibility is thermal dehalogenation, either in a liquid or in a fluidized bed pyrolysis, before the pre-treated product is further processed. The hydrochloric acid produced is either neutralized or separated for industrial use, e.g. in the pickling of steel, or in chemical industry.

Feedstock recycling is complementary to mechanical recycling since it is less sensitive to unsorted or contaminated plastics waste and enlarges the overall recycling capacities for large waste quantities to be supplied in the future. Examples of such mixed streams are specific composites (laminated films, artificial leather, footwear), but mainly packaging, ASR, WEEE. These materials are connected to each other for performance reasons, but economic separation is impossible.

Technical processes for feedstock recycling have inspired large corporations, universities, and inventors alike and are the origin of numerous patents. As many of the feedstock recycling processes described in this chapter are still in development, their economic viability also remains yet to be established. This will become clearer over the next several years, in tandem with technical progress and the increased volumes of available plastics wastes [38].

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PART II

Catalytic Cracking

Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels Edited by
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2

Acid-Catalyzed Cracking of Polyolefins: Primary Reaction Mechanisms

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1 INTRODUCTION

New plastic waste recycling alternatives that are based on catalytic cracking can potentially lower costs and increase yields of valuable products. Future development of effective plastic waste recycling methods that involve catalytic cracking will require detailed knowledge of the relationship between cracking conditions and product distributions. Operating conditions that maximize the production of valuable hydrocarbon products and minimize catalyst deactivation must be sought. In particular, reaction conditions under which polymers are efficiently converted to small paraffins (C_5–C_{10}) are desired because these substances are used as feedstocks by industry and as fuels and therefore constitute high-value products. During the past 35 years, numerous studies have been reported in which a variety of catalysts and reaction conditions have been employed to convert waste polymers into hydrocarbon mixtures.

Previous catalytic cracking research has focused primarily on polyolefin feedstocks because these polymers are the most abundant in plastic wastes. In one of the first polymer catalytic cracking studies, Uemichi and co-workers reported the use of silica–alumina, activated carbon, Pt/silica–alumina, and Pt/alumina catalysts for poly(ethylene) (PE) cracking [1–4]. Several years later, Takesue and co-workers reported that PE cracking under mild conditions with a silica–alumina catalyst could be used to shorten polymer chains and increase chain branching [5–8]. In 1989, Beltrame and Carniti compared alumina, silica, HY, REY, and silica–alumina catalysts and reported results from PE catalytic cracking in a batch reactor at reduced pressures [9]. Using activation energy calculations, they found that the zeolite catalysts (HY and REY) were the most effective of those

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tested. Ivanova *et al.* described the effects of Lewis acid catalysts on PE cracking in 1991 [10]. They found that volatile product selectivity could be varied by changing the catalyst acidity. For example, when PE was cracked by $AlCl_3$, 41% of the volatile products were C_4 hydrocarbons. C_4 hydrocarbon yield increased to 85% when $MgCl_2 \bullet AlCl_3$ catalyst was employed. During the early 1990s, several groups became interested in using catalysts to reform PE thermal decomposition products [11–15]. In these studies, PE was thermally cracked and the resulting polymer fragments were subjected to catalytic reforming. The number of published reports pertaining to PE cracking increased substantially in the past six years [16–57]. Most of this research has focused on the effects of catalyst structure on cracking products with emphasis on finding conditions that maximize production of hydrocarbon mixtures that could be used as fuels.

Compared with PE, fewer reports of poly(styrene) (PS) catalytic cracking have been published. In 1976, Yamamoto *et al.* reported that heating PS in the presence of a silica–alumina catalyst yielded large amounts of benzene, cumene, and toluene [58]. Five years later, Pukanszky and co-workers reported that addition of Lewis acids to PS melt resulted in chain shortening and formation of double bonds [59]. In 1990, Audisio *et al.* reported the use of silica, alumina, silica–alumina, HY, and REY catalysts for cracking PS under vacuum at temperatures between 200 and 550°C [60]. In 1997, Sedran and co-workers used a fluidized-bed reactor to crack PS [61, 62]. More recently, PS cracking by zeolites, mesoporous MCM-41 and amorphous silica–alumina were compared [63] and metal-supported carbon catalysts were used to crack PS in decalin [64]. Guoxi *et al.* tested the effects of various metal powders on PS thermal decomposition [65]. They found a correlation between activity for styrene production and metal electronegativity.

The use of a wide variety of reactor designs and operating conditions with catalysts having different properties to crack waste polymers have led to reports of cracking product distributions that on the surface appear to vary significantly. In addition to the primary products that result from interactions between polymer and catalyst, secondary reactions can lead to additional substances in the product slate. The amount and identities of these additional substances are dependent on reactor design and operating conditions. In order to compare and contrast polymer cracking reaction processes and to associate reaction pathways with specific polymer–catalyst interactions, it is necessary to design experiments so as to keep reaction conditions as constant as possible and to employ reactors that minimize secondary reactions. This can be achieved by using samples containing low polymer-to-catalyst ratios, employing low cracking temperatures, and designing experiments so that volatile products are efficiently removed from catalyst surfaces.

2 POLYETHYLENE CRACKING

Although a wide variety of catalysts have been employed to crack PE, zeolites have proven particularly effective. For example, Garforth *et al.* reported that activation energies (E_a) measured when PE was catalytically cracked by HZSM-5, HY, and MCM-41 were much lower than when no catalyst was present. [66] They concluded that HZSM-5 and HY have similar activities and that both of these zeolites were more effective than MCM-41. Manos and co-workers found that catalytic cracking of PE by HZSM-5 and HY was effective in producing gasoline size hydrocarbons in a laboratory semi-batch reactor [67, 68]. Mordi and co-workers reported that H-Theta-1 and H-Mordenite zeolites, which have pore diameters that are comparable to those for HZSM-5 and HY, were relatively ineffective in producing gasoline size hydrocarbons from PE cracking [69]. Clearly, catalyst pore size and acidity are important factors in polymer catalytic cracking.

Most PE catalytic cracking studies have been performed by heating reactor vessels containing catalyst and polymer and subsequently collecting and analyzing the products. This batch processing approach provides no information regarding the order in which products form. In addition, if sealed reaction vessels are employed, initial reaction products may react with catalyst to form secondary products. Recently, repetitive injection GC/MS has been used to characterize the volatile products generated by polymer cracking. This evolved gas analyzer facilitates real-time separation, identification, and quantification of volatiles generated by heating solid samples [70]. A diagram of this apparatus is shown in Figure 2.1. Thermal analyzer effluent (TA effluent) is the purge gas exiting from a thermogravimetric analyzer or a tube furnace in which the sample is heated. A thermogravimetric analyzer is employed when weight loss information is desired. Volatile polymer cracking products are separated by a small gas chromatograph which can be heated rapidly (300°C/min) and cooled rapidly (600°C/min) in order to facilitate rapid capillary gas chromatography separations employing column temperature ramps. Repetitive gas chromatographic injections are made by using an eight-port valve to divert effluent trapped in the injection loop onto the gas chromatographic column. The end of

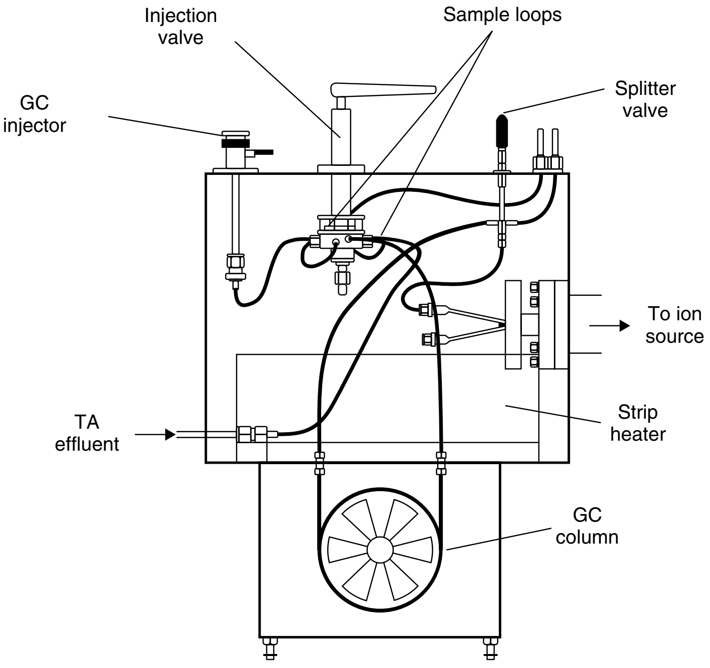


Figure 2.1 Apparatus used for repetitive injection gas chromatography analysis of volatile polymer decomposition products. (Reproduced from the Journal of Chromatographic Science by permission of Preston Publications, a Division of Preston Industries, Inc)

the fused silica capillary gas chromatography column is attached to the ion source of a quadrupole mass spectrometer for detection and analysis of eluting volatile products. By using this apparatus, product trapping is not required. Instead, volatile products are removed from catalysts with an inert purge gas and then analyzed on-line. This approach was used to study the primary reaction processes when PE is cracked by HZSM-5, HY, and MCM-41 aluminosilicate catalysts [71]. Because these three acid catalysts possess different acid strengths and pore structures, information regarding the effects of pore size and acid strength on cracking processes were obtained by comparing volatile product evolution profiles.

Figure 2.2 shows repetitive injection GC/MS chromatograms obtained while heating PE-catalyst samples at 2°C/min in a helium atmosphere. The tick marks on the *x*-axes in Figure 2.2 denote PE-catalyst sample temperatures at which evolved gases were injected into the gas chromatograph. Twenty-five successive gas chromatograms were obtained for each of the PE-catalyst samples. Purge gas effluent was analyzed at 5- min intervals, which corresponded to 10°C sample temperature increments. Figure 2.2 shows that the temperature range over which volatiles were produced depended on the choice of cracking catalyst. The maximum volatile product evolution rate for the PE-HY sample

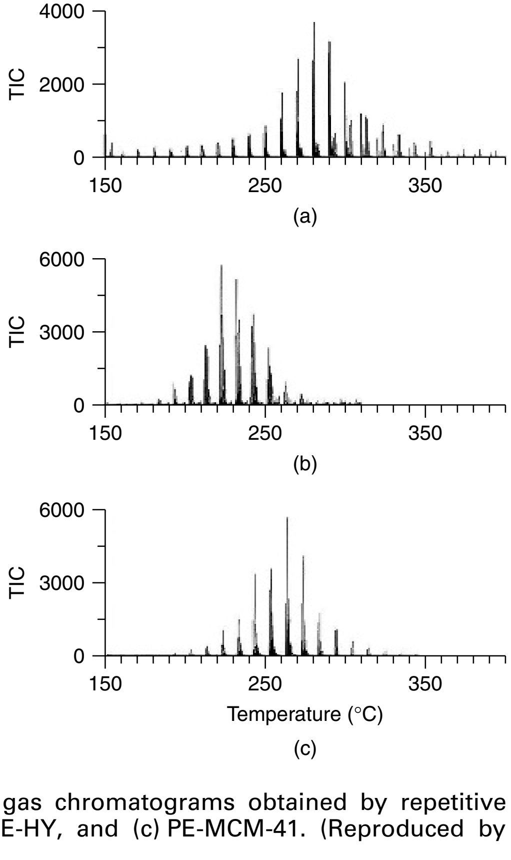


Figure 2.2 Evolved gas chromatograms obtained by repetitive injection GC/MS for (a) PE-HZSM-5, (b) PE-HY, and (c) PE-MCM-41. (Reproduced by permission of John Wiley & Sons Ltd)

occurred at the lowest temperature (220°C), followed by the PE-MCM-41 (260°C), and PE-HZSM-5 (280°C) samples. After comparing the shapes of successive chromatograms in Figure 2.2(a), it is apparent that volatile product distributions changed significantly for the PE-HZSM-5 sample above 290°C. The dominant volatile species detected above 310°C were alkyl aromatics. Similar variations are apparent in the PE-HY chromatograms. Although volatile product slates for the PE-MCM-41 sample also changed with temperature, no alkyl aromatic species were detected in the repetitive injection chromatograms for this sample.

Chromatograms obtained while heating the three PE-catalyst samples show catalyst-dependent differences in volatile product distributions. Figure 2.3 shows the gas chromatograms obtained at the temperatures corresponding to the maximum volatile product evolution rates for each PE-catalyst sample. Figure 2.3 clearly shows that relative hydrocarbon product yields depended on which catalyst was employed. For the PE-HZSM-5 sample, many isomeric hydrocarbons were detected, most of which were low molecular weight substances with short retention times. Volatile product diversity is less evident

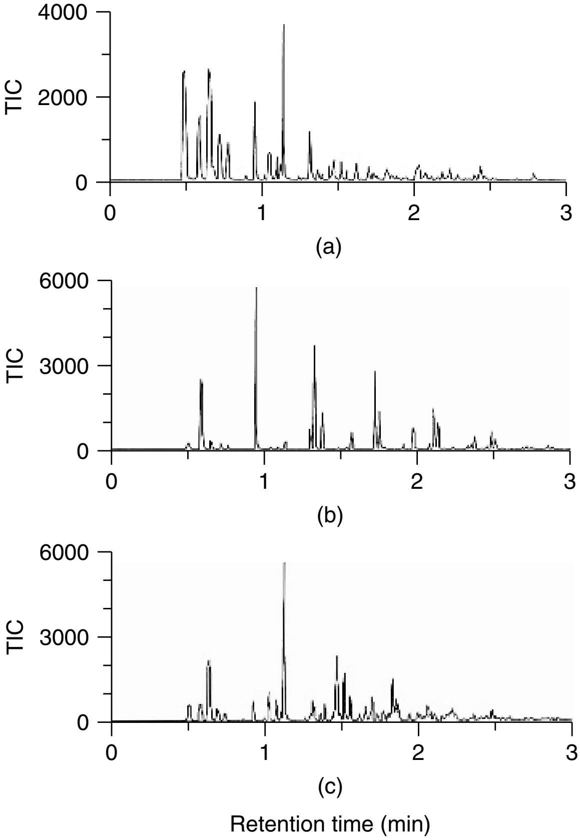


Figure 2.3 GC/MS chromatograms obtained at sample temperatures corresponding to maximum volatile product evolution for: (a) PE-HZSM-5 (280°C), (b) PE-HY (220°C); (c) PE-MCM-41 (260°C). (Reproduced by permission of John Wiley & Sons, Ltd)

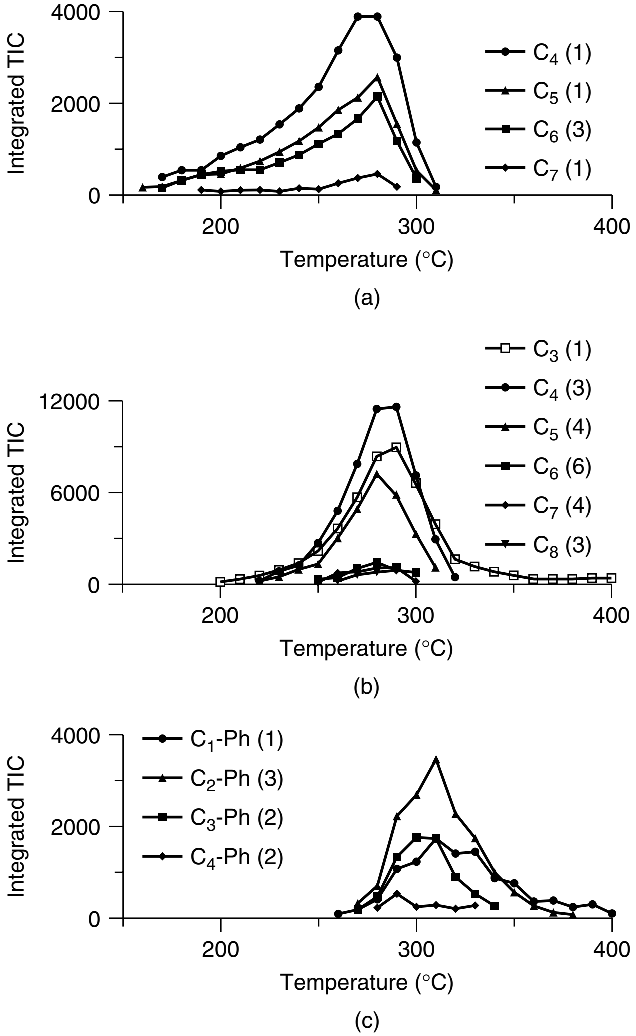


Figure 2.4 Species-specific evolution profiles for: (a) paraffin; (b) olefin; (c) alkyl aromatic products obtained when a PE-HZSM-5 sample was heated. (Reproduced by permission of John Wiley & Sons, Ltd)

in the PE-HY chromatogram. The volatile product slate generated by heating the PE-MCM-41 sample was similar to that obtained for the PE-HZSM-5 sample, except that low-molecular-weight products were not as abundant.

Figure 2.4 shows species-specific evolution profiles for paraffin, olefin, and alkyl aromatic volatile products formed by heating the PE-HZSM-5 sample. The numbers in parentheses denote the number of isomers detected. The volatile product slates for the PE-HZSM-5 sample reflect that C_3–C_5 hydrocarbons were the dominant species formed. The temperature corresponding to the maximum paraffin and olefin evolution rates was 280°C, whereas alkyl aromatic evolution maximized at 310°C. Below 200°C, volatile product mixtures were composed entirely of paraffins. Mass spectra for paraffin products were consistent with branched rather than straight-chain structures. The only C_4 and C_5 paraffins detected were isobutane and isopentane. Above 200°C, many different olefin isomers were detected in volatile mixtures. In addition to paraffin and olefin products, substantial quantities of alkyl aromatics were detected for the PE-HZSM-5 sample. Figure 2.4(c) shows that aromatics with C_1–C_4 alkyl groups were detected and that C_2-substituted aromatics (xylenes and possibly ethyl benzene) were the dominant aromatic products.

Species-specific evolution profiles for the PE-HY sample are shown in Figure 2.5. Unlike the PE-HZSM-5 results, volatile mixtures were primarily composed of C_4–C_8 paraffin rather than olefin products. Evolution profiles for paraffins and olefins had similar shapes with maximum evolution rates occurring at 230–240°C. Like the paraffin evolution profiles for the PE-HZSM-5 sample, isobutane and isopentane were significant paraffin products and no straight-chain isomers were detected. Alkyl aromatic yields for the PE-HY sample were much lower than for the PE-HZSM-5 sample.

Species-specific evolution profiles for the PE-MCM-41 sample are shown in Figure 2.6. Like the PE-HZSM-5 sample, olefin yields were much greater than paraffin yields for the PE-MCM-41 sample. Paraffin evolution profiles in Figure 2.6(a) mostly represent single isomers. In contrast, many olefin isomeric species were detected. C_4–C_6 olefins comprised the largest fraction of volatile mixtures. Unlike the PE-HZSM-5 sample, propene was a minor volatile product. Alkyl aromatic products were not detected for this sample.

Volatile products derived from cracking PE with solid acid catalysts can be rationalized by carbenium ion mechanisms. Under steady-state conditions, hydrocarbon cracking processes that yield volatile products can be represented by initiation, disproportionation, β-scission, and termination reactions [72, 73]. Initiation involves the protolysis of PE with Brönsted acid sites (H^+ S^-) to yield paraffins and surface carbenium ions:

$$C_nH_{2n+2} + H^+S^- \rightarrow C_mH_{2m+2} + C_{n-m}H^+{}_{2(n-m)+1}S^-$$

Propagation reactions involve disproportionation between feed molecules and surface carbenium ions to yield paraffins:

$$C_nH_{2n+2} + C_mH^+{}_{2m+1}S^- \quad \rightarrow C_{m+x}H_{2(m+x)+2} + C_{n-x}H^+{}_{2(n-x)+1}S^-$$

When a surface carbenium ion undergoes β-scission to form olefin products, smaller carbenium ions are left on the catalyst surface:

$$C_nH^+{}_{2n+1}S^- \rightarrow C_xH_{2x} + C_{n-x}H^+{}_{2(n-x)+1}S^-$$

When sufficiently small, olefins may desorb from catalyst surfaces. Surface olefins may also be protonated to form new carbenium ions. Termination reactions involve the destruction of surface carbenium ions. For example, surface carbenium ions may desorb to produce olefins and regenerate Brönsted acid sites:

$$C_nH^+{}_{2n+1}S^- \rightarrow C_nH_{2n} + H^+S^-$$

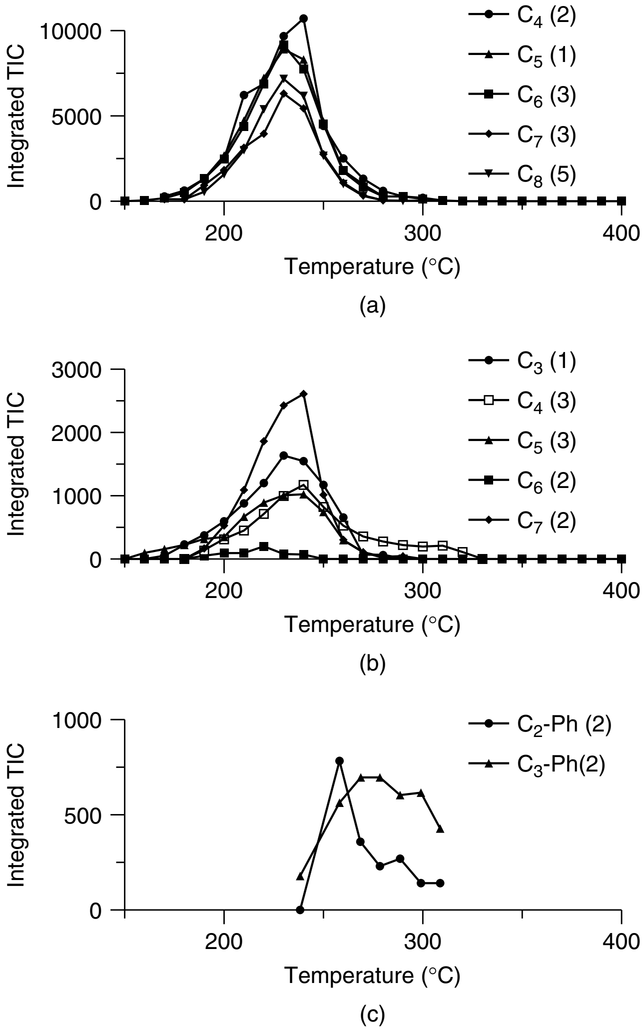


Figure 2.5 Species-specific evolution profiles for: (a) paraffin, (b) olefin; (c) alkyl aromatic products obtained when a PE-HY sample was heated. (Reproduced by permission of John Wiley & Sons, Ltd)

These chain reactions describe how paraffin and olefin cracking products are formed, but do not explain residue or aromatic product formation. Like the other reactions, aromatic- and coke-forming reactions involve surface carbenium ions. Carbenium ion thermal cracking can result in olefin ions, which may undergo dehydrogenation and cyclization reactions that are suspected to be the source of aromatic products from straight-chain paraffin feeds. When unsaturated ions are protonated, di-ions are produced. Doubly charged ions can also be formed by disproportionation reactions between adjacent surface carbenium ions. Multiply charged ions are strongly bound to surface conjugate base sites and are less likely to participate in reactions with feed than singly charged carbenium ions. Consequently,

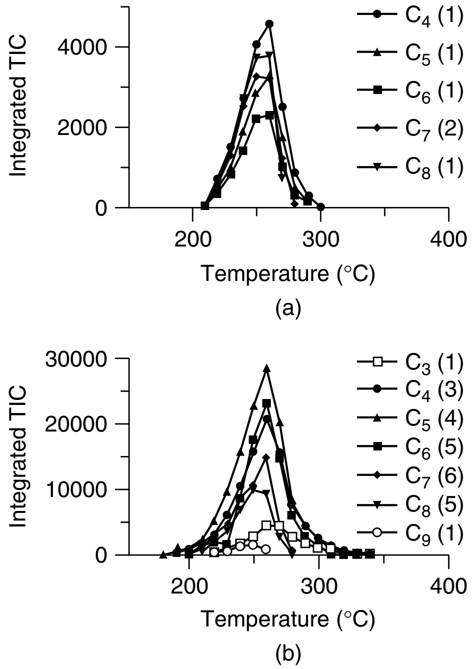


Figure 2.6 Species-specific evolution profiles for: (a) paraffin; (b) olefin products obtained when a PE-MCM-41 sample was heated. (Reproduced by permission of John Wiley & Sons, Ltd)

catalyst sites occupied by polyions are unavailable for further reaction. Catalyst acidity and pore size dictate the relative rates of protolysis, disproportionation, β-scission, and termination reactions, which determine the abundance of volatile paraffin, olefin, aromatic, and nonvolatile hydrocarbon products.

Disproportionation reaction rates depend on carbenium ion reactivities, which are determined by catalyst site acid strength. Carbenium ions produced at strong acid sites are less likely to undergo β-scission or desorption. Compared with HY, the smaller pores in HZSM-5 inhibit bimolecular disproportionation reactions. In contrast, the low paraffin/olefin volatile product ratio for the PE-MCM-41 sample is likely due to the low acidity of the catalyst. Although the MCM-41 pore size is large enough to facilitate disproportionation, catalytic site acidity is too low for this reaction pathway to be dominant.

Aromatic products were detected at temperatures above those at which paraffin and olefin evolutions maximized. The shift in alkyl aromatic evolution profiles to higher temperatures relative to paraffins and olefins is consistent with a mechanism in which unsaturated surface ions are precursors for alkyl aromatic formation. Alkyl aromatic yields decrease in the order: PE-HZSM-5 > PE-HY > PE-MCM-41, which follows a trend in increasing pore size. Steric restrictions on reaction volume afforded by HY and HZSM-5 promote aromatic ring formation from conjugated unsaturated polymer segments. The smaller pore HZSM-5 is significantly more effective at forming alkyl aromatics than HY.

Unsaturated residue formed during catalytic reactions that produced paraffins and olefins is the source of alkyl aromatics and nonvolatile residue. When HZSM-5 catalyst is employed, aromatic alkyl chain sizes are restricted to C_4 or smaller. The pores of HZSM-5 are large enough to allow formation of small alkyl aromatics by cyclization and dehydrogenation of surface species, but formation of fused unsaturated coke precursors are inhibited. Unlike HZSM-5, larger HY pores facilitate the formation of larger nonvolatile unsaturated coke precursors.

Trends in volatile paraffin/olefin ratios and alkyl aromatic yields observed when polyethylene is cracked by aluminosilicate catalysts cannot be correlated with catalyst acidity or pore size variations alone. Instead, product slate differences occur because relative rates of specific carbenium ion reactions are affected by the combined effects of catalyst acidity and pore size.

3 POLYSTYRENE CRACKING

Radical depolymerization of neat PS samples produces large quantities of monomer (styrene) and chain-end backbiting yields substantial amounts of dimer and trimer. Polymer decomposition proceeds by entirely different processes when a catalyst is present. Repetitive injection GC/MS was employed to investigate the primary reaction processes that occur when PS is cracked by silica–alumina, sulfated zirconia, and HZSM-5 [74]. These catalysts exhibit a wide range of acidity, but only the HZSM-5 catalyst has a regular pore structure. The most abundant volatile species detected from PS-catalyst samples was benzene. About 30% of the volatile material produced from the PS-Si/Al and PS-ZrO_2/SO_4 samples was benzene. For PS-HZSM-5, the relative yield of benzene was over 50%. Other volatile products detected from the PS-catalyst samples in substantial yield included: alkyl benzenes, indanes, and naphthalenes. The relative yields of alkyl benzenes were greatest for the samples containing Si/Al and ZrO_2/SO_4 catalysts. In contrast, PS-HZSM-5 produced fewer alkyl benzenes, but significantly larger quantities of indenes.

Figure 2.7 contains plots of repetitive injection GC/MS chromatographic peak areas (integrated total ion current) as a function of sample temperature for benzene and styrene as well as selected products representing alkyl aromatics (ethyl benzene), indanes (methyl indane) and indenes (indene) evolved from PS-catalyst samples. The plots show that benzene is by far the most abundant volatile product. All of the PS-catalyst samples produce alkyl benzenes and indanes, however samples containing HZSM-5 catalyst generate significantly lower relative yields of these products.

The formation of the primary PS catalytic cracking volatile products can be explained by initial electrophilic attack on polymer aromatic rings by protons [60, 75]. Protons preferentially attack the *ortho* and *para* ring positions because the aliphatic polymer backbone is an electron-releasing group for the aromatic rings. Most volatile products can be derived from mechanisms beginning with ring protonation. Thermal decomposition of *ortho*-protonated aromatic rings in the polymer chain (1) can lead directly to

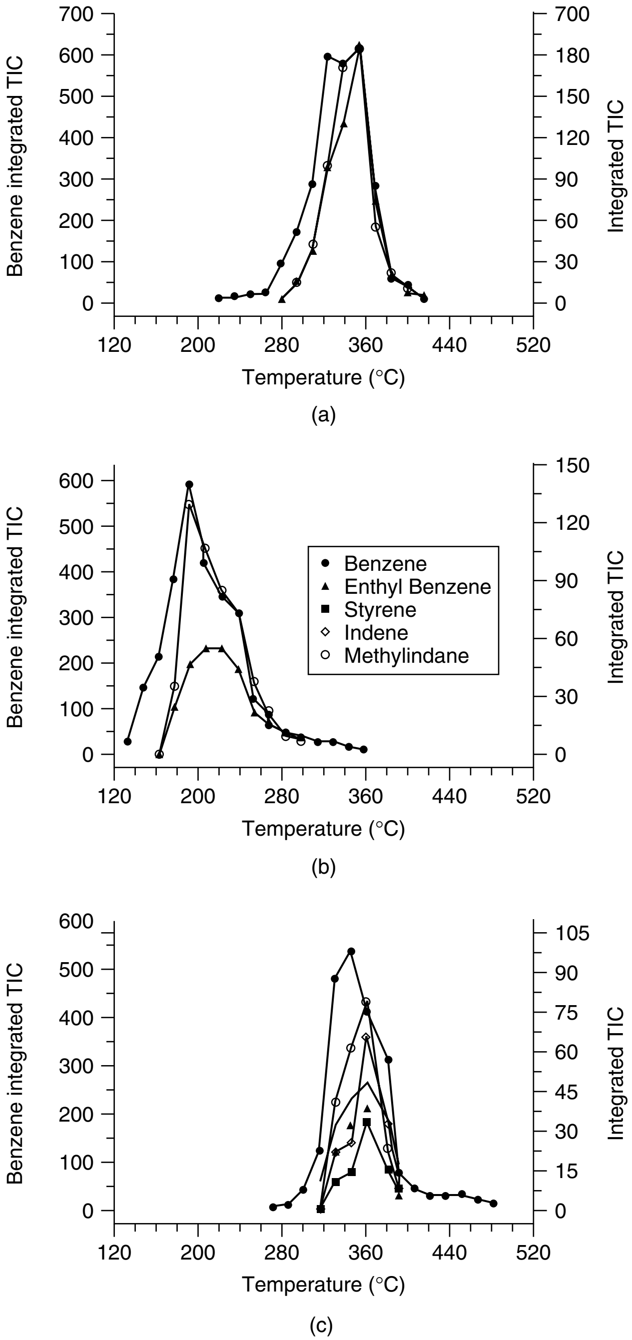
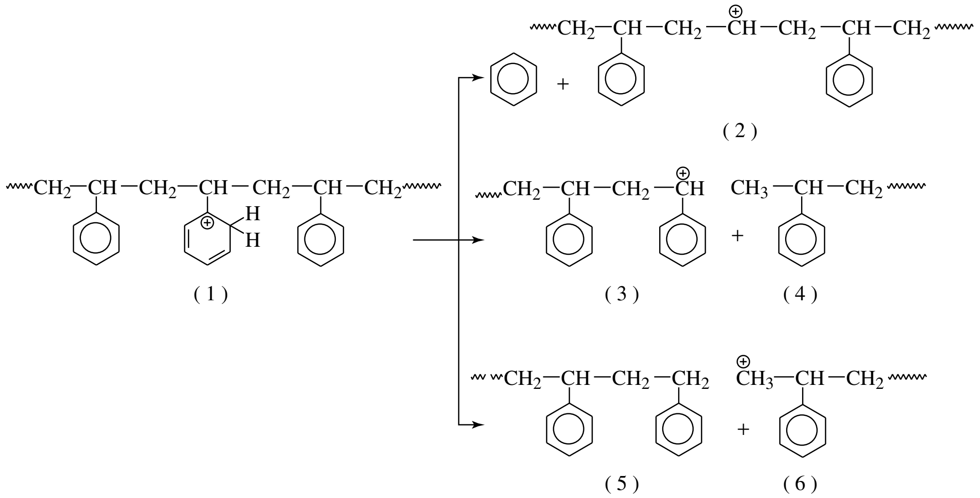


Figure 2.7 Species-specific evolution profiles for various PS-catalyst samples: (a) PS-Si/Al, (b) PS-ZrO_2/SO_4; (c) PS-HZSM-5. The left axis scale represents benzene chromatographic peak areas and the right axis scale represents all other peak areas. (Reproduced by permission of John Wiley & Sons, Ltd)

the liberation of benzene, the primary catalytic cracking product, or may result in chain shortening.



Benzene cannot be obtained directly from *para*-protonated aromatic rings in the polymer. However, *para*-protonated rings can react with neighboring polymer chains to yield the same chain scission products that are formed by *ortho*-protonation.

The macro cation remaining after benzene evolution (2) may undergo chain shortening β-scission to produce (3) and an unsaturated chain end, rearrange to form an internal double bond and protonate a neighboring aromatic ring (either by intra- or intermolecular proton transfer), cyclize to form an indane structure, or abstract a hydride to produce a saturated chain segment. The substantial quantities of indanes obtained by PS catalytic cracking suggests that cyclization of (2) to form indane structures is a favored process. This is supported by Nanbu *et al.*, who reported that benzene and indane structures were the only products detected when PS was cracked by using a strong acid catalyst at 50°C [75]. A consequence of chain unsaturation resulting from (2) might be the formation of conjugated polyene segments that may subsequently cyclize to form naphthalenes. A minimum of three conjugated double bonds must be created in polymer chains before naphthalenes can be formed. As a result, naphthalene evolution is delayed relative to the evolution of alkyl benzenes and indanes, which can be formed from polymer segments without conjugated unsaturation. This is illustrated by Figure 2.8, which shows the temperature-dependent yields of methyl indane (open circles) and naphthalene (open squares) derived from analysis of the PS-ZrO_2/SO_4 sample.

Decomposition of (3), which might be formed from (1) or (2), can result in the formation of styrene or may lead to chain end unsaturation and neighboring ring protonation. Hydride abstraction by (3) would result in a saturated chain end. The lack of significant styrene production from any of the PS-catalyst samples suggests that β-scission of (3) to form styrene is not a dominant decomposition pathway at low temperatures. Chain end unsaturation derived from (3) may result in formation of indenes, which were detected in substantial amounts only when HZSM-5 catalyst was present. The restricted volume

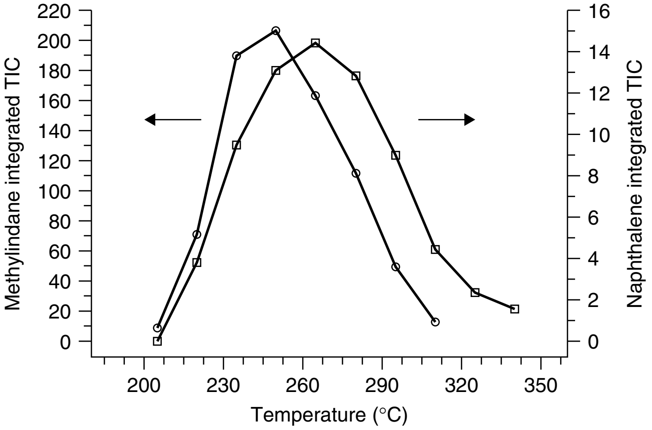
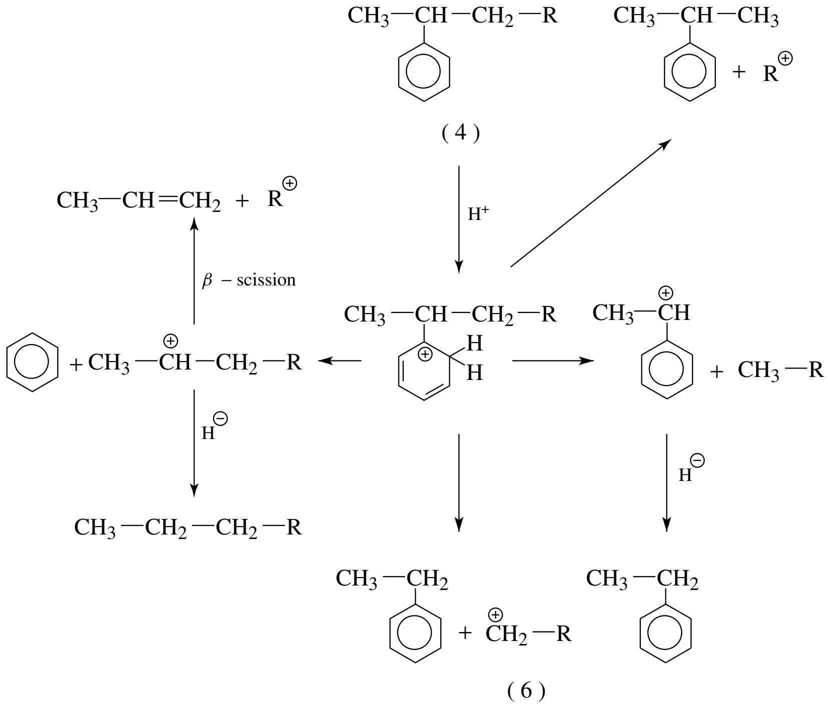


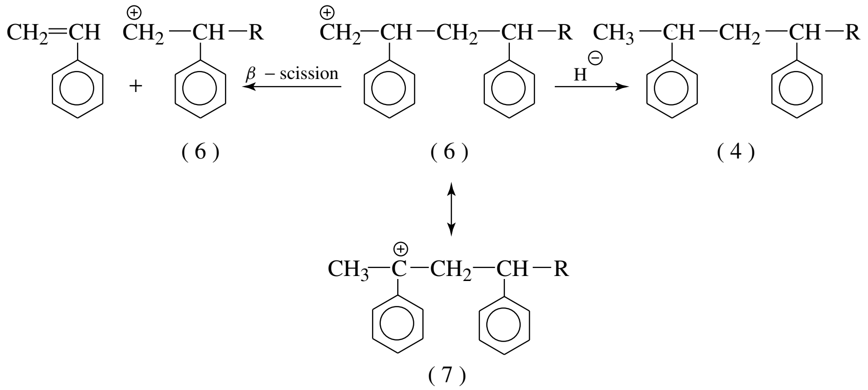
Figure 2.8 Species-specific evolution profiles for methyl indane (open circles) and naphthalene (open squares) derived from a PS-ZrO_2/SO_4 sample. (Reproduced by permission of John Wiley & Sons, Ltd)

of the HZSM-5 channels apparently inhibits hydride abstraction pathways for (3), which results in increased production of indenes and styrene for PS-HZSM-5.

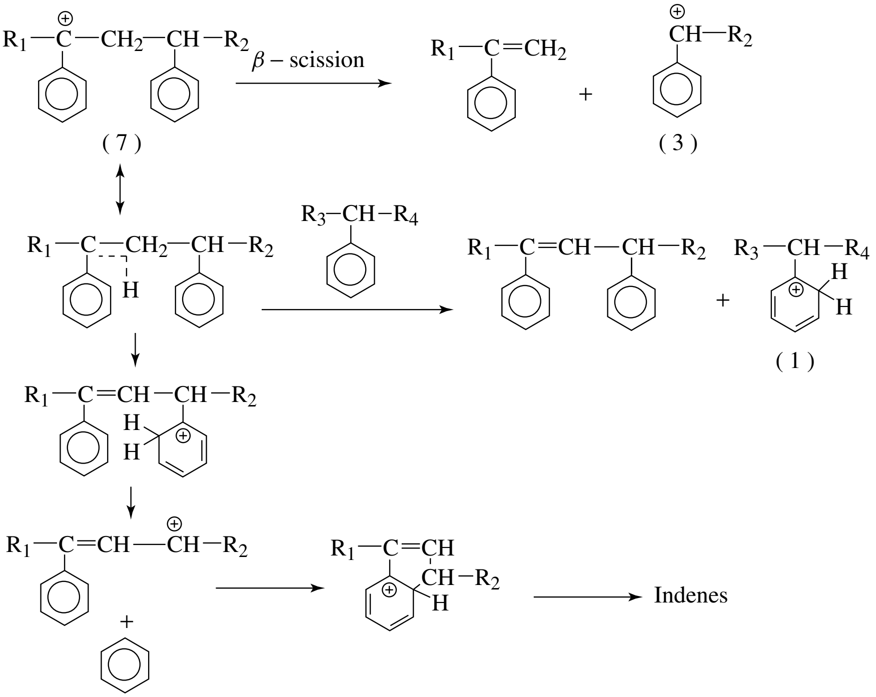
Protonation of aromatic rings adjacent to methyl-terminated chain ends (4) can result in the formation of alkyl benzenes, propene, and benzene, depending on how the macro cation decomposes.



Macro cation (6), which can be formed from (1), (4), or (5), can undergo β-scission to form styrene, rearrange to form a tertiary benzyl cation (7), or may abstract a hydride to form (4).



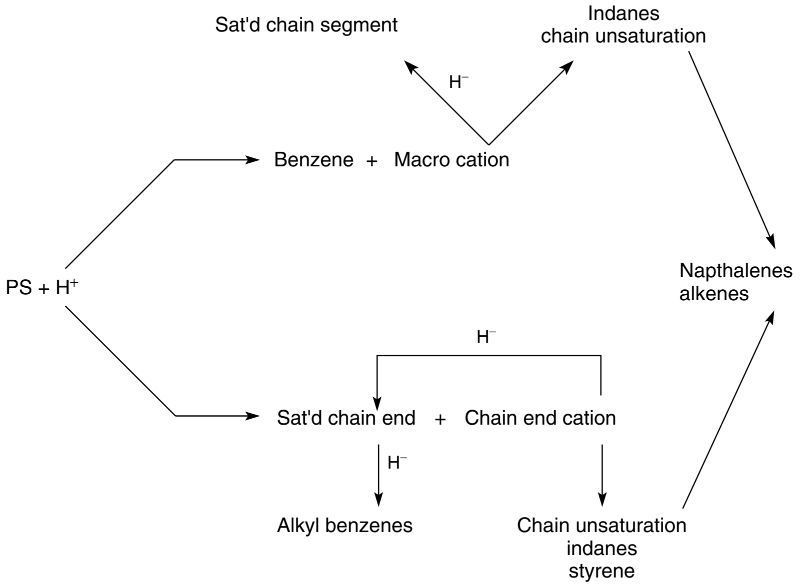
The tertiary benzyl cation (7), which would be preferentially formed by hydride abstractions in addition to rearrangement of (6), may be a precursor for chain unsaturation and for the formation of indenes.



If rearrangement of (7) results in chain unsaturation and intramolecular ring protonation, volatile indenes ultimately result. If intermolecular ring protonation occurs, macro cation (1) would likely be formed.

Figure 2.7(b) shows that benzene can be obtained by PS catalytic cracking at temperatures as low as 130°C. The fact that the temperature at which volatile decomposition products were detected from PS-catalyst samples was dependent on the catalyst acidity suggests that the rate-limiting step in the acid catalyzed decomposition of PS was aromatic ring protonation. For all PS-catalyst samples, benzene was the first volatile product detected when samples were heated, which suggests that processes leading to benzene liberation were favored over those that resulted in the products detected at higher temperatures. This is consistent with the reaction schemes shown here, which suggest that benzene can be easily formed from (1), but that formation of other volatile decomposition products is more difficult and may require macro cation rearrangement, hydride abstraction, or successive protonations.

Although acid catalyzed PS cracking appears to involve many different parallel reactions and is quite complicated, the following general reaction scheme can be used to represent the primary reaction pathways. The initial step in PS cracking is protonation of polymer aromatic rings, which may result in chain shortening, yielding a chain end cation and a saturated chain end. *Ortho*-protonation can readily lead to benzene evolution and the formation of a secondary macro cation, which may subsequently cyclize to form an indane structure. The fact that Nanbu *et al.* [75] detected only benzene and indane structures from acid catalyzed PS cracking at 50°C suggests that reactions that form these species are favored and that *ortho* ring protonation is the rate limiting step for the evolution of benzene. Hydride abstraction appears to be an important reaction pathway for chain end cations, except when the catalyst restricts the movement of polymer chains (e.g. HZSM-5). Saturated chain ends are the likely source of alkyl benzenes, which can be formed after protonation of chain end aromatic rings. Rearrangements and β-scissions of macro cations can lead to chain unsaturation, or, for chain end cations, the formation of unsaturated volatile products such as styrene and indenes. Conjugated polyene chain segments resulting from macro cation rearrangements can backbite to form naphthalenes.



4 HYDROCRACKING PROCESSES

The yield of unsaturated catalytic cracking products can be reduced by the addition of hydrogen to cracking atmospheres. Dufaud and Basset demonstrated this by employing a zirconium hydride Ziegler–Natta catalyst to crack PE in a hydrogen atmosphere [25]. Ding *et al.* studied the hydroconversion of PE with sulfided Ni and NiMo silica–alumina and compared these catalysts with HZSM-5 [76]. They found that Ni/silica–alumina produced higher quality liquid products (i.e. more isoparaffins and fewer aromatics). Walendziewski *et al.* studied PE hydrocracking in autoclaves and reported that the addition of catalysts decreased the boiling range and unsaturation of liquid products compared with thermal and catalytic cracking [40, 48].

Although most previous reports focus on correlating variations in product slate with catalyst properties, some studies have attempted to compare catalyst activation energies obtained by using thermal analysis techniques. Garforth *et al.* used activation energies derived from thermogravimetry (TG) measurements to compare the cracking properties of ZSM-5, HY, and MCM-41 [22]. They found that coking was most significant for HY and that MCM-41 exhibited the lowest cracking activation energy. In a similar study, Fernandes *et al.* compared the TG derived activation energy for PE thermal decomposition with that for HZSM-5 catalytic cracking and found that the catalyst reduced the activation energy by more than a factor of two [23, 77]. Lin and co-workers characterized the deactivation of US-Y zeolite by monitoring changes in the TG properties of polymer/catalyst mixtures [21].

A detailed study of PE hydrocracking by PtHZSM-5, PtHY, and PtHMCM-41 bifunctional aluminosilicate catalysts was recently reported [78]. Repetitive injection chromatogram mass spectra were employed to identify class-specific fragment ions for use in effective activation energy calculations. By comparing selected ion profiles with total ion current chromatograms, it was determined that *m/z* 57, 55, and 91 could be used to represent paraffins, olefins, and alkyl aromatics, respectively. Virtually all of the mass spectrometer *m/z* 91 ion signal could be attributed to alkyl aromatics. Unfortunately, the *m/z* 57 and 55 ion signals could not always be attributed solely to paraffins and olefins, respectively. To assess the ‘selectivity’ of these ions for their respective product classes, a selectivity value was calculated by computing the ratio of the ion signal contribution from the desired class to the total ion signal for the target m/z value. This calculation was repeated for each repetitive injection chromatogram to obtain selectivity profiles as a function of sample temperature.

4.1 PE-PTHZSM-5

Figure 2.9 shows the species-specific evolution profiles for: (a) paraffin; (b) olefin; and (c) alkyl aromatic volatile products for the PE-PtHZSM-5 sample heated in hydrogen. As expected, paraffins dominated the hydrocracking volatile product slate and olefin and alkyl aromatic yields were greatly reduced compared with results obtained when the same sample was heated in helium. The paraffin profile for the PE-PtHZSM-5 sample heated in hydrogen exhibited two maxima. Below 200°C, volatile product mixtures were composed entirely of paraffins. As the sample temperature increased, a wide range of

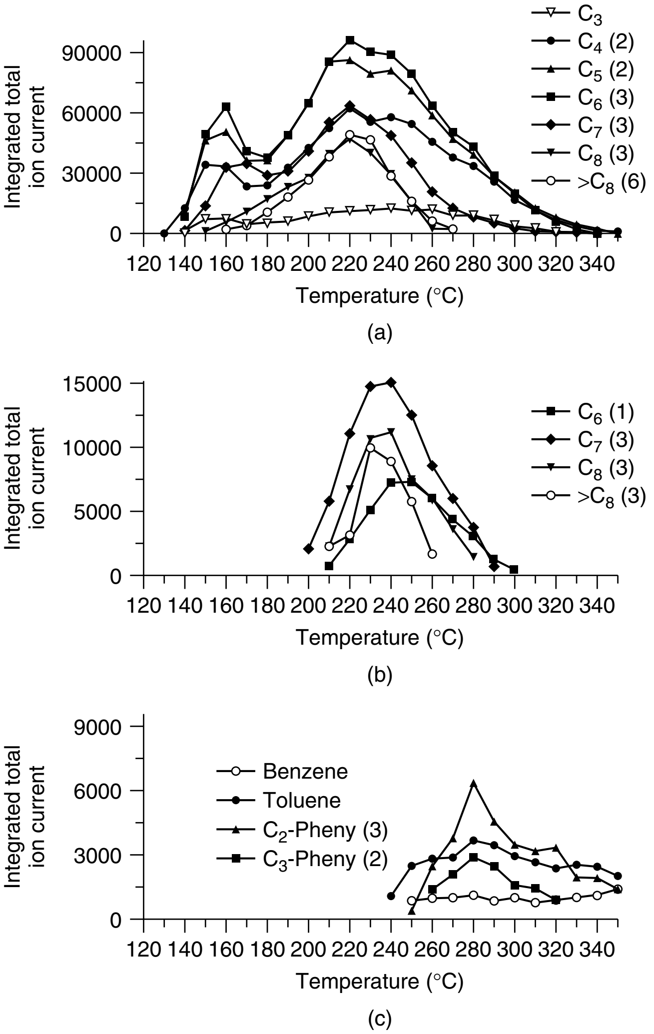
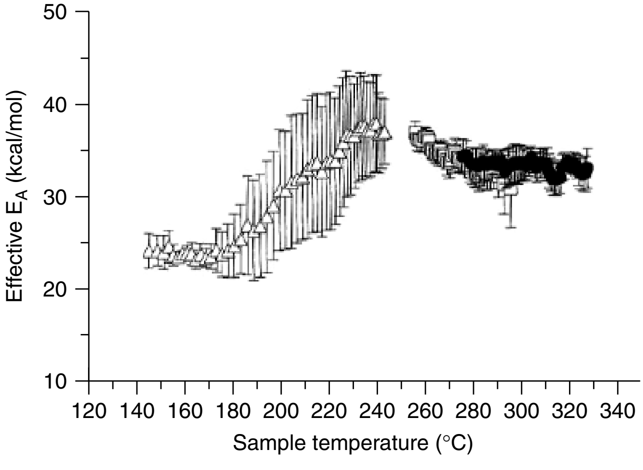


Figure 2.9 Evolution profiles for: (a) paraffins; (b) olefins; (c) alkyl aromatics for a PE-PtHZSM-5 sample heated in hydrogen. (Reproduced by permission of John Wiley & Sons, Ltd)

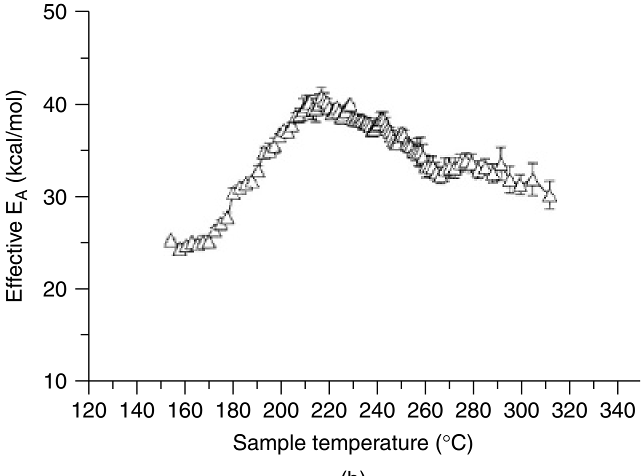
C_3–C_{10} volatile paraffins were formed, with C_5 and C_6 paraffins being the most abundant volatile products detected.

Figure 2.10(a) shows class-specific effective activation energy E_a versus temperature plots generated for the evolution of paraffins (*m*/*z* 57), olefins (*m*/*z* 55), and alkyl aromatics (*m*/*z* 91) when the PE-PtHZSM-5 sample was heated in helium. The selectivity of *m*/*z* 57 for paraffins was about 90% between 140 and 240°C. Paraffin evolution E_a values above 240°C were not included in Figure 2.10(a) because the *m*/*z* 57 selectivity for paraffins decreased dramatically above this temperature due to increased contributions to the *m*/*z* 57 ion signal from olefins. The selectivities of *m*/*z* 55 for olefins and *m*/*z* 91 for alkyl aromatics were at least 99% for the values plotted in Figure 2.10(a). Olefin E_a values below 250°C were not included in Figure 2.10(a) because the *m*/*z* 55 selectivity for olefins was significantly reduced due to contributions to the *m*/*z* 55 ion signal from paraffins.

Figure 2.10(b) shows the paraffin-specific effective E_a versus temperature plot for the PE-PtHZSM-5 sample heated in hydrogen. The *m*/*z* 57 ion signal selectivity for paraffins was 99%. Smaller error bars in Figure 2.10(b) compared with Figure 2.10(a) reflect the fact that paraffins were by far the dominant volatile product when the PE-PtHZSM-5 sample was heated in hydrogen. As a result, the *m*/*z* 57 ion signals were larger than those detected in helium and the *m*/*z* 57 selectivity for paraffins was much greater when the sample was heated in hydrogen.



(a)



(b)

Figure 2.10 PE-PtHZSM-5 effective activation energy profiles for: (a) paraffins (triangles), olefins (squares), and alkyl aromatics (full circles) in helium; (b) paraffins (triangles) in hydrogen. (Reproduced by permission of John Wiley & Sons, Ltd)

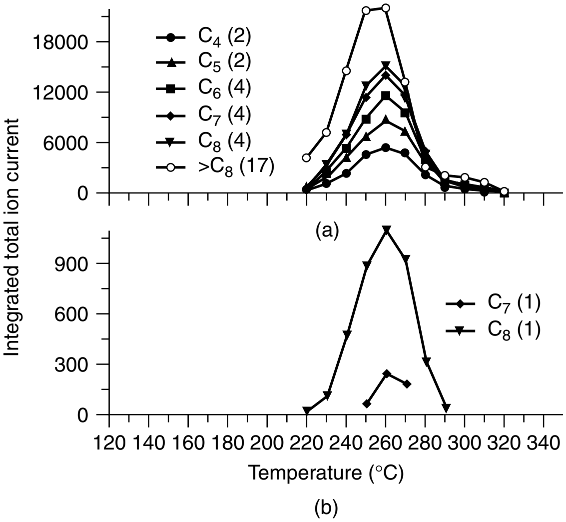


Figure 2.11 Evolution profiles for: (a) paraffins; (b) olefins for the PE-PtHY sample heated in hydrogen. (Reproduced by permission of John Wiley & Sons, Ltd)

4.2 PE-PTHY

Figure 2.11 shows species-specific evolution profiles for: (a) paraffin; and (b) olefin volatile products for the PE-PtHY sample heated in hydrogen. Seventeen different paraffins with at least nine carbon atoms dominanted the volatile products. Volatile alkyl aromatic yields were insignificant compared to the paraffin and olefin yields.

Figure 2.12(a) shows the E_a versus temperature profiles for paraffin and alkyl aromatic evolutions when the PE-PtHY sample was heated in helium. The m/z 57 and m/z 91 ion signal selectivities for paraffins and alkyl aromatics were at least 99%. The alkyl aromatic E_a value calculated for the PE-PtHY sample heated in helium was 10 kcal/mol lower than that for the PE-PtHZSM-5 sample. Figure 2.12(b) shows the paraffin E_a versus temperature profile for the PE-PtHY sample heated in hydrogen. The m/z 57 ion signal selectivity for paraffins was at least 99%. The E_a value for paraffin formation was 38 kcal/mol at 230°C and decreased to 28 kcal/mol by 300°C. The initial paraffin E_a value for the PE-PtHY sample heated in hydrogen was 10 kcal/mol higher than the E_a value for the same sample heated in helium.

4.3 PE-PTHMCM-41

Figure 2.13 shows species-specific evolution profiles for paraffin volatile products for the PE-PtHMCM-41 sample heated in hydrogen. Volatile paraffins with more than eight carbon atoms dominated the product slate. Volatile alkyl aromatic products were not detected for the PE-PtHMCM-41 sample heated in either helium or hydrogen.

Figure 2.14(a) shows the olefin evolution E_a versus temperature plot for the PE-PtHMCM-41 sample heated in helium. The m/z 55 ion signal selectivity for olefins was

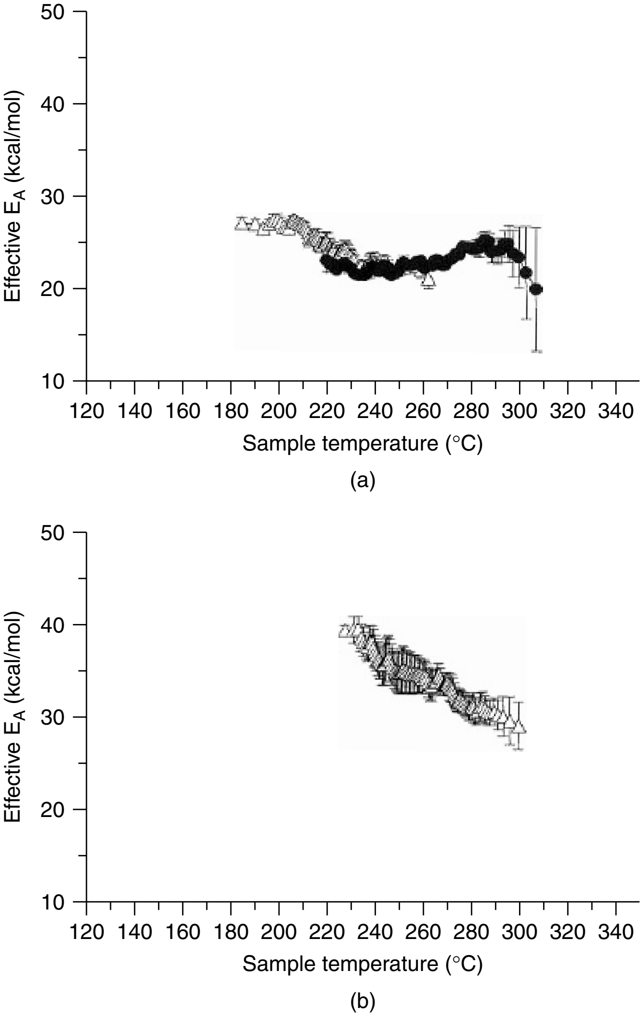


Figure 2.12 PE-PtHY effective activation energy profiles for: (a) paraffins (triangles) and alkyl aromatics (full circles) in helium; (b) paraffins (triangles) in hydrogen. (Reproduced by permission of John Wiley & Sons, Ltd)

99%. Figure 2.14(b) shows the paraffin E_a versus temperature plot for the PE-PtHMCM-41 sample heated in hydrogen. The *m*/*z* 57 ion signal selectivity for paraffins was 99% for the data plotted.

The hydrocracking effect on PE decomposition is clearly evident in the make-up of the volatile product slates for the three bifunctional catalysts. As expected, olefin and alkyl aromatic yields diminished and paraffin yields increased substantially when hydrogen was added to the cracking atmosphere. The most dramatic change to the paraffin/olefin ratio was found for the PtHMCM-41 catalyst. The presence of hydrogen also significantly reduced the quantity of residue remaining after catalytic cracking. These effects

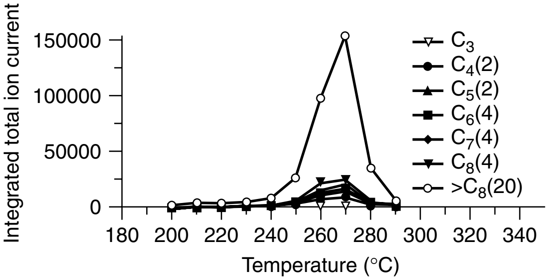


Figure 2.13 Paraffin evolution profiles for the PE-PtHMCM-41 sample heated in hydrogen. (Reproduced by permission of John Wiley & Sons, Ltd)

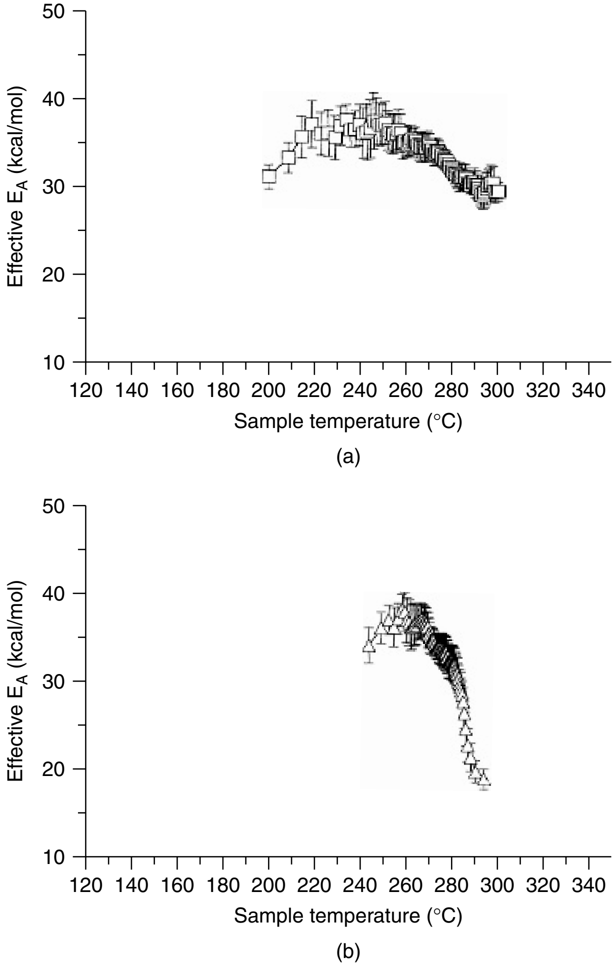


Figure 2.14 PE-PtHMCM-41 effective activation energy profiles for: (a) olefins (squares) in helium; (b) paraffins (triangles) in hydrogen. (Reproduced by permission of John Wiley & Sons, Ltd)

are well-known consequences of hydrocracking with bifunctional catalysts containing platinum [79–81].

Paraffin evolution profiles for the PtHZSM-5 catalyst in helium and hydrogen exhibited bimodal features. The presence of two maxima in paraffin evolution profiles suggests that there were two PE cracking pathways leading to volatile paraffins and that these pathways were available in helium and hydrogen. If the first evolution maximum is associated with cracking outside of catalyst pores, the second maximum might be due to additional cracking that occurs when the zeolite pores became accessible to polymer melt. Above 180°C, short polymer segments could more easily enter zeolite channels. In contrast to the paraffin profiles, the evolution profiles for olefins in helium and hydrogen exhibit only a single maximum with much lower yields at low temperature. Evidently, low-temperature carbocation disproportionation reactions, which yield paraffins, occur more readily than β-scission reactions, which are thought to be responsible for most olefin products [72]. The substantial reduction in alkyl aromatic yields in hydrogen compared to helium is evidence that formation of conjugated unsaturation in the polymer melt was hindered by the hydrogenation activity of the bifunctional catalyst.

Paraffin effective activation energy plots for the PtHZSM-5 catalyst reflect the bimodal nature of the evolution profiles The increase in activation energy may be due to increased steric hindrance for cracking reactions that take place within HZSM-5 channels.

The temperature range for alkyl aromatics evolution for the PtHY catalyst in helium was similar to that for the PtHZSM-5 catalyst. However, the effective activation energy for alkyl aromatics evolution was about 10 kcal/mol lower for PtHY compared with PtHZSM-5. The higher activation energy for PtHZSM-5 may have been due to the smaller channels of HZSM-5 compared with HY. Although the HZSM-5 channels may facilitate conjugated bond cyclization reactions, the smaller HZSM-5 channels may also hinder the release of aromatic products from the catalyst. The larger zeolite channel diameter of HY is also likely responsible for the fact that the most abundant PtHY aromatic products in helium were C_3-phenyl species whereas C_2-phenyl products dominated the PtHZSM-5 product slate. The PtHY volatile paraffin and olefin evolution profiles in hydrogen are narrower and shifted to higher temperature by about 50°C compared with the profiles obtained in helium. This is consistent with the higher paraffin evolution effective activation energies in hydrogen compared with helium. Increased effective activation energies for catalytic hydrocracking compared with catalytic cracking have been reported previously [82, 83].

The primary volatile products of PE cracking in helium by the PtHMCM-41 catalyst were olefins. Unlike the other catalysts, alkyl aromatics were not detected for the PtHMCM-41 catalyst. The effect of hydrogenation on the catalytic cracking ability of PtHMCM-41 was dramatic. Volatile paraffins were the sole products detected in hydrogen and only 5% of the initial polymer mass remained as residue. The reduced catalytic cracking capacity of PtHMCM-41 arising from its lower acidity resulted in the dominance of large paraffins ($>C_8$) in the hydrocracking product slate.

Hydrocracking effective activation energy plots for the three catalysts used in this study all exhibit a decrease with increasing temperature above 240°C. The magnitude of the drop in activation energy follows the trend: PtHMCM-41 > PtHY > PtHZSM-5. It has been previously reported that the strength of olefin adsorption on catalyst surfaces determines the kinetics of platinum-catalyzed hydrogenation[84]. The strength of olefin adsorption would be expected to decrease with an increase in catalyst temperature, which would explain the observed decrease in activation energy for each catalyst. The activation energy decrease is much greater for PtHMCM-41 than the other catalysts. The attraction of olefins to PtHMCM-41 catalyst surfaces would be expected to be much less than the other catalysts because of its relatively low acidity. Apparently, interactions between olefins and PtHMCM-41 catalyst surfaces diminish more rapidly with increased temperature than the other catalysts. Hydrocracking reactions dominated when poly(ethylene) was catalytically cracked in the presence of hydrogen. The length of volatile paraffins was found to depend on the catalyst pore size and acidity and followed the trend: PtHMCM-41 > PtHY > PtHZSM-5. Volatile product slate and effective activation energy trends cannot be explained by a single catalyst characteristic. Instead, the combined influence of acidity, pore size, and preferred cracking mechanism(s) for each volatile product must be considered.

5 CONCLUSIONS

The reaction pathways involved in acid-catalyzed cracking of PE and PS are numerous. Subtle changes in catalyst structure or operating conditions can significantly alter which reaction pathways are favored. Catalytic reactor design can further affect relative product yields by facilitating secondary reactions. The results described here were obtained by using samples containing a large excess of catalyst. Because polymer–catalyst samples contained much more catalyst than polymer, results primarily reflect innate catalyst activities and any effects from catalyst deactivation processes were minimal. The primary reaction pathways described here will serve as benchmarks for understanding the dynamics of steady-state reactor performance, which will indeed be a challenging endeavor. To fully explain steady-state reactor processes, the effects of secondary reactions and catalyst deactivation must also be considered. A full understanding of practical applications of plastic waste catalytic cracking will be even more difficult because reaction pathways for multiple polymer types must be simultaneously considered.

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3

Catalytic Upgrading of Plastic Wastes

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1 INTRODUCTION

Upgrading of plastic wastes by catalytic cracking is a subject of growing interest in the last years as a feasible way for promoting the feedstock recycling of these residues towards either raw chemicals or fuels [1]. According to 2002 data, the total plastic consumption in Western Europe accounts for 38.1 million tonnes while the amount of plastic wastes collected was around 20.4 Mt [2]. This growing amount of residues has raised a deep public concern due to the depletion of landfills, their effect in our life quality and the loss of potentially valuable raw materials. In 1994, the European Union launched the 94/62/CE directive on waste packaging that established minimum rates of recycling per material (15%). Since then, the percentages of recycling and energy recovery have increased to 14.8 and 23% respectively (2002 data). Nevertheless, 62 wt% of plastic wastes are still being disposed of by landfilling in Western Europe.

A great proportion of plastics end its lifetime as a part of the overall solid waste stream where they represent roughly 10 wt%. The typical distribution of plastics in household wastes is shown in Figure 3.1 [3]. The main components are polyolefins: low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE) and polypropylene (PP), accounting for about 67% of the total amount of plastic wastes. Other important components in plastic wastes are polystyrene (PS), poly(vinyl chloride) (PVC) and poly(ethylene terephthalate) (PET).

Pyrolysis treatments are interesting regarding the aforementioned plastic refuse makeup. Other successful treatments for feedstock recycling of condensation polymers (PET, ABS, etc.), that allows for the depolymerization and recovery of their constituent monomers (e.g. hydrolysis, alcoholysis, methanolysis, etc.), cannot be applied for polyolefin plastics recycling. In contrast, pyrolysis of polyolefins yields valuable hydrocarbon mixtures of

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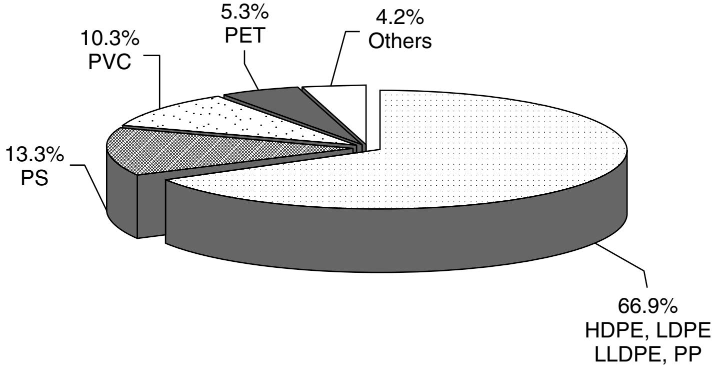


Figure 3.1 Typical distribution of plastics in household wastes in Europe [3]

different composition, depending on the operating conditions [4, 5]. For the particular cases of some plastics (e.g. the thermal cracking of PMMA), wherein depolymerization really occurs on heating, the original raw monomer (MMA) can be obtained with high yields (up to 97%) [6]. Catalytic cracking can be considered as an advantageous treatment in regard to other competing procedures for feedstock recycling of plastic wastes such as gasification towards synthesis gas ($CO + H_2$) [7–9] and its recent use as coke substitute in steel making industry [2]. Unlike them, catalytic cracking is a versatile process since a variety of valuable products can be attained through a proper choice of both the process conditions and catalysts. Moreover, it does not require the construction of large-capacity plants to be profitable as it is the case for gasification. However, most industries have remained reluctant to employ catalytic cracking of plastic wastes due to the limitations posed by the heterogeneous nature of plastic wastes (presence of heteroatoms, additives and other wastes) and their high viscosity and low thermal conductivity. This situation has started to change, with several plants in operation in Poland [10] and Japan [11] based on the use of catalytic cracking processes for converting plastic wastes into fuels. This progress can be considered a result of the development of better sorting procedures [12], increasing public opinion cooperation, the modification of plastic product design in order to promote their separation, identification and recycling [13] and the regulation pressure. Recently, a life-cycle assessment of plastic waste catalytic cracking process has been published showing the environmental and economic benefits that can be derived in regard to other waste management alternatives [14]. In addition, a large number of scientific papers and patents have appeared in recent years upon plastic catalytic degradation and considerable scientific advances have been performed, so many technical problems have already been overcome. In this regard, the present work is aimed at reviewing the main scientific breakthroughs produced in the field of catalytic cracking and conversion of plastic wastes.

1.1 CATALYTIC VERSUS THERMAL CRACKING

Thermal and catalytic treatments of plastic wastes present meaningful differences. In terms of mechanism, thermal degradation proceeds according to a radical chain reaction pathway comprising hydrogen transfer steps along with the progressive breaking of the polymer backbone. The detailed mechanism can be found elsewhere and involves the classical initiation, propagation and termination steps [4, 15]. In general terms, the initiation reactions comprise the homolytic cleavage of a carbon–carbon bond by either random or end chain scission giving rise to the appearance of two radicals. This may be followed by intramolecular/intermolecular hydrogen chain transfer reactions forming more stable secondary radicals. Additionally, these intermediate radicals may undergo C–C bond rupture by β-scission to produce olefins (ethylene and propylene) and new radicals. Finally, termination reactions such as disproportionation towards different olefins and alkanes or bimolecular coupling between radicals might take place. One important feature of thermal cracking reactions stems from their radical nature since no radical rearrangement reactions occur which restricts the number of potential products to be attained. In this regard, branched products may only be formed as a result of either the interaction between two secondary radicals or between a secondary and a primary radical. As a consequence of this mechanism, thermal cracking of polyethylenes leads towards a broad distribution of hydrocarbons within the C_5–C_{80} range, each fraction being mainly formed by the corresponding diene, 1-olefin and *n*-paraffin, as it can be appreciated in the gas chromatogram shown in Figure 3.2. At high temperature, hydrogen is also formed in significant amounts [15]. The products of thermal cracking of polyolefins are of limited commercial value, being mainly applied as fuels. In some cases, the heavy fraction has been proposed to be applied as a wax [16]. A different approach for the thermal conversion of plastic wastes is the one based on steam cracking processes at high temperatures and low residence times, which leads to the production of light hydrocarbons (ethylene, propylene, butenes) [17].

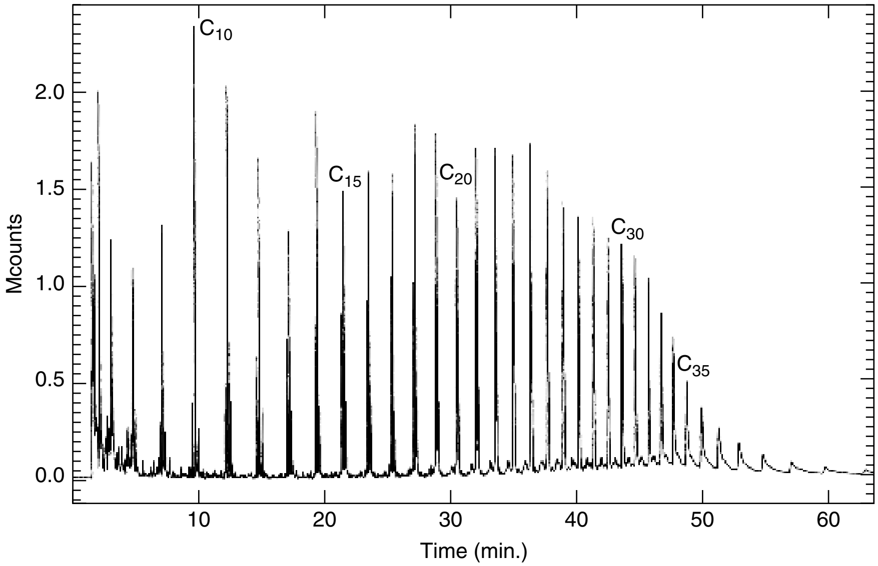


Figure 3.2 GC analysis of the products obtained in the LDPE thermal degradation. (Reproduced with permission from Elsevier)

In contrast, catalytic cracking takes place following a carbocationic mechanism [18, 19] although the simultaneous occurrence of thermal degradation reactions is usually observed, whose relative extent depends mainly on the temperature. In fact, many of the reported procedures for catalytic cracking of plastics are indeed a reforming of the products coming from a previous thermal cracking [20]. In most systems, the catalytic cracking mechanism proceeds with the formation of a carbocation, either by hydride abstraction on a Lewis site or by generating a carbonium ion over a Brönsted acid site. In addition, polymers usually present some double bonds (e.g. vinylidene moieties resulting from the polymerization process) and branchings that are more reactive points for the carbocation formation. Subsequently, the polymer is fragmented by β-scission and disproportionation reactions, the former leading to olefins. Unlike the previously commented radical pathway for thermal cracking, skeletal isomerization occurs simultaneously with the cracking reactions giving rise to branched products. Additionally, oligomerization, cyclization and aromatization reactions may proceed together with the cracking. The adequate choice of the catalyst allows the cracking and reforming reactions to be addressed towards a limited range of products, as it may be appreciated in the gas chromatogram shown in Figure 3.3, corresponding to the catalytic cracking of low-density polyethylene over HZSM-5 zeolite with a high catalyst loading. In this case, many of the components are aromatic hydrocarbons, whereas linear compounds, typical of the thermal degradation, are present in negligible amounts.

The following advantages can be envisaged for catalytic cracking processes compared with simple thermal treatments:

- lowering of the reaction temperature, which leads to a decrease of the energy consumed in the process;

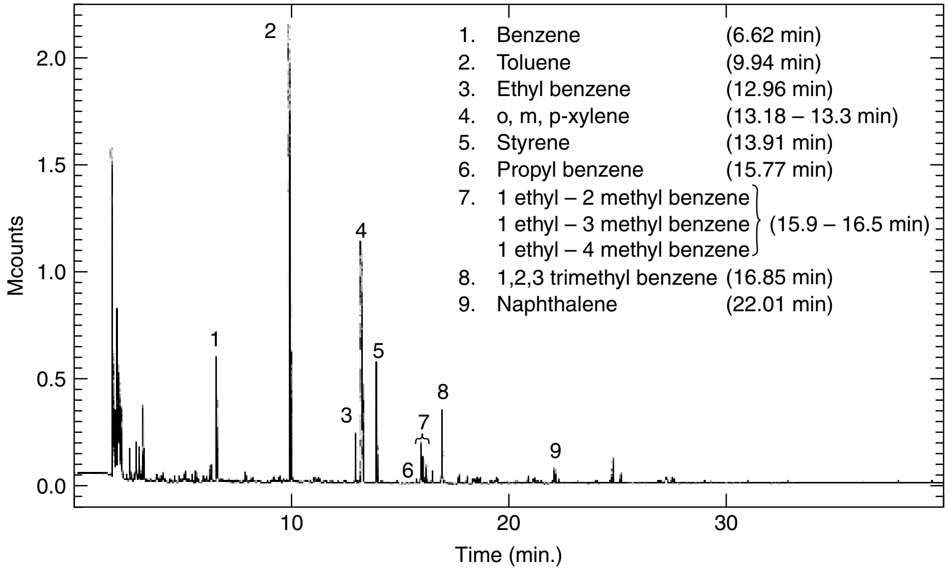


Figure 3.3 GC analysis of the products obtained in the LDPE catalytic cracking over HZSM-5 zeolite. (Reproduced with permission from Elsevier)

- the cracking reactions proceed faster, bringing about shorter residence times and lower reactor volumes;
- selectivity may be tailored towards different valuable products by a judicious choice of both the catalyst and process conditions;
- in the case of polyolefins, the products derived from the catalytic cracking contain mainly cyclic, branched and aromatic hydrocarbons, which increase the quality of the potential fuels;
- inhibition of the formation of undesired products (e.g. chlorinated hydrocarbons), which is a feature especially interesting in the presence of PVC. It has been observed that catalysts based on some metals (aluminium, zinc, iron) and metal oxides with large ionic radius (ferric oxide and titanium oxide) reduce the temperature of hydrochlorination onset by attracting chlorine [21].

However, along with the reported advantages of the catalytic processes, there are also some important drawbacks, stemming mainly from the heterogeneous makeup of the plastic waste mixtures. Thus it must be pointed out that most of the studies on plastic cracking have been carried out using virgin plastics as raw materials. The situation is completely different when real polymer wastes are to be degraded. On the other hand, the above mentioned presence of chlorine from polyvinylchloride (PVC) may cause corrosion problems as well as the formation of toxic chlorine containing compounds. Additionally, other heteroatoms such as nitrogen, coming from acrylonitrile–butadiene-styrene plastics (ABS) (among other sources), and sulphur, from oils, rubber and some additives, are usually present in plastic wastes. Both nitrogen and sulphur compounds are known poisons for acid solids catalysts and decrease their activity to a large extent [22]. In this regard, the use of previous separation steps in order to eliminate the source of these heteroatoms (e.g. flotation stage) and/or the heteroatom in the process itself (e.g. a dechlorination stage) must be considered. On the other hand, acid solid catalysts can be deactivated by coke deposition and by the occurrence of different cross-linking reactions favoured by the presence of some plastics, as it is the case of ethylene–vinylacetate copolymers [23]. Finally, plastics are bulky macromolecules, which usually present steric/diffusional hindrances to access to the internal acid sites of conventional microporous acid catalysts such as zeolites [24]. However, all these bounds constitute a challenge for the development of more active and deactivation resistant catalytic systems.

1.2 PLASTICS SUSCEPTIBLE TO UPGRADING BY CATALYTIC CRACKING

Catalytic cracking has been extensively applied to polyolefinic plastics (HDPE, LDPE, PP) and PS, mostly because of their abundance and similar elemental composition. For other plastics, there are currently competing successful recycling process for the recovery of the original plastic (Vinyloop process for PVC) or the monomers (PETCORE process for PET) [25], so the cracking route seems not to be a recommended way. The number of publications devoted to the study of the catalytic cracking of other pure plastics (EVA, PET, ABS) [23, 26, 27] and their mixtures with polyolefins [23] has increased in the last years, although the latter are mostly addressed to ascertain the influence exerted by these minor components present in the plastic waste stream upon the catalyst cracking performance.

Thus, the catalytic cracking of PET has been recently a subject of interest [26]. Several acid solids (zeolites 4A and 13X and alumina) as well as metal salts ($CuCl_2$, $MgCl_2$ and Zn, Sn, Mg, Mn acetates) have been tested as catalysts at 400–500°C. Copper chloride has been found as the most effective catalyst, reducing the degradation time by almost 3.5 times in regard to the thermal treatment and minimizing the amount of carbonaceous residues.

Thermal and catalytic cracking of ABS has been studied by Brebu *et al.* [27] over silica–alumina and three silica–alumina/iron oxide combinations. The introduction of iron into the catalyst formulation allows for degrading the heavy nitrogen-containing compounds into light aliphatic nitriles that can be eliminated from the oils simply by distillation. Thus, the concentration of the most abundant nitrogen-containing compound (4-phenylbutyronitrile) was reduced from 17.5 to 1.7 wt%. This example highlights the importance of the catalyst formulation not only for the degradation of the polymer, but also for the removal of heteroatoms.

1.3 PRODUCTS DERIVED FROM THE CATALYTIC CRACKING

The products obtained in the catalytic cracking of plastics depend on numerous experimental variables. The possible products derived from the cracking of a polyolefin plastic wastes mixture over acid solid catalysts are summarized in the mechanism depicted in Figure 3.4 [28]. Depending mostly on the acid strength of the catalyst, cracking proceeds mainly by either random (medium or weak acidity) or end-chain scission (strong acidity) giving rise to waxes and middle distillates (gasoil, gasoline) or light hydrocarbons (C_3–C_5 olefins), respectively. These primary cracking products can be removed from the reaction medium or undergo secondary reactions (oligomerization, cyclization, aromatization). The relative extent of these reactions is bound up with the acid and textural properties of the catalysts, but also with the employed experimental variables (e.g. reactor type, temperature, residence time, etc.).

From the aforementioned products, light olefins are potentially valuable feedstocks, especially the C_3–C_5 fractions [29], which may be used as raw chemicals while the paraffin components may be used as a fuel. In addition, they can be easily separated as the number of isomers in these low carbon number fractions is fairly low. In contrast,

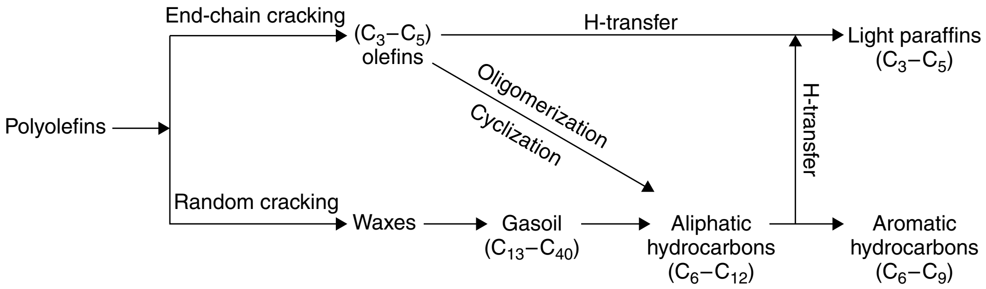


Figure 3.4 Mechanism of catalytic cracking of polyolefins over acid solid catalysts [28]. (Reproduced by permission of the American Chemical Society)

middle distillates fractions (C_6–C_{40}) are usually of limited applicability because of the huge number of isomers obtained obliges them to be used solely as fuels. In this case, the catalyst is usually tailored in order to obtain better quality fuels such as gasoline and diesel. However, some catalysts have been developed in order to attain high selectivities towards specific raw chemicals, e.g. BTX (benzene, toluene, xylenes).

2 CATALYTIC SYSTEMS

Both homogeneous and heterogeneous systems have been used in the literature for studying the catalytic cracking of polymers. In general, heterogeneous catalysts are the preferred choice due to their easy separation and recovery from the reacting medium.

2.1 HOMOGENEOUS CATALYSTS

Homogeneous catalysts used for polyolefin degradation have mostly been classical Lewis acids such as $AlCl_3$, metal tetrachloroaluminates melts and more recently, new catalytic systems based on organic ionic liquids.

Ivanova *et al.* [30] degraded polyethylene catalytically with $AlCl_3$ and electrophilic complexes at 370°C giving rise to higher yields of gaseous compounds (88.2 wt%) than thermal cracking of this same polymer (40 wt% of gases at 400°C). The main gaseous compounds obtained in the catalytic cracking were isobutane (42.5%) and isobutene (21.8%) and the amount of hydrocarbons heavier than C_5 was practically negligible. Tetrachloroaluminate melts $M(AlCl_4)_n$ ($M = Li$, Na, K, Mg, Ca, Ba; $n = 1$–2), which constitute ionic media, were also applied as catalysts for polyethylene cracking leading to 90–95% of C_4 hydrocarbons.

Catalytic systems over ionic liquids are gaining increased attention worldwide as benign solvents for green chemistry processes due to their low volatility and ease of product separation. Recently, catalytic cracking of polyethylene (HDPE, LDPE) has also been carried out using organic ionic liquids, such as 1-ethyl-3-methylimidazolium chloride-aluminum (III) chloride [31]. Light alkenes (C_3–C_5), such as isobutene, and branched and cyclic alkanes were the major product components. The reported working temperatures are meaningfully lower (90–250°C) than those used over conventional heterogeneous catalysts although times of 1–6 days of reaction were needed to obtain yields of 60–95 wt%.

2.2 HETEROGENEOUS CATALYSTS

A wide variety of heterogeneous catalysts have been tested for the catalytic cracking of polyolefins and polystyrene, which can be summarized as follows:

- conventional acid solids used in the catalytic cracking of hydrocarbon feedstocks: zeolites, silica–alumina, aluminas, fresh and spent FCC catalysts [32–42];
- mesostructured catalysts: MCM-41, FSM-16, Al-SBA-15 [5, 43–48];
- aluminium pillared clays [49–51];
- nanocrystalline zeolites (*n*-HZSM-5) [52];

- superacid solids (ZrO_2/SO_4^{2-}) [53];
- gallosilicates [54, 55];
- metals supported on carbon [56, 57];
- basic oxides (BaO, K_2O, etc.), mainly for polystyrene cracking [58, 59].

Among the above-mentioned solids, zeolites have been certainly the most studied catalysts for polyolefin cracking. Zeolites are crystalline microporous aluminosilicates of groups IA or IIA elements (mainly sodium, potassium, magnesium, calcium) whose chemical composition may be represented by the following formula [60]:

$$M_{2/n}O.Al_2O_3.ySiO_2.wH_2O$$

where $2 < y < 10$, n is the cation valence and w represents the amount of water.

The zeolite framework is built from the combination of SiO_4 and AlO_4 tetrahedra linked by sharing oxygen atoms which extend tridimensionally. The presence of aluminium into the framework brings about the appearance of a negative net charge which must be balanced by an extra-framework cation. This charged nature of zeolites provides them with the capacity for ion exchange as well as acid properties when the extra-framework cation is a proton. The required acidity may be tuned by a proper choice of the zeolite structure as well as their aluminium content [60]. Zeolites may exhibit a mono-, bi- or tridimensional channel network with pore sizes of definite dimensions (below 1.0 nm) and even interconnected microporous cavities depending on their topology. In this regard, zeolites are considered as molecular sieves since their pore dimensions are close to those of many molecules (usually 0.4–1.0 nm) showing the property called 'shape selectivity' which allows them to discriminate among different reactants, transition states or products.

At present more than 100 zeolitic structures (both natural and synthetic) have been reported and their number grows annually as new structures are continuously being discovered which opens up a wide range of possible applications [61, 62]. However, from a practical viewpoint, only a few zeolites are used as industrial catalysts such as Y, ZSM-5, Beta and mordenite (Table 3.1), mainly due to the cost and difficulties inherent to their preparation [60]. When zeolites are applied for the catalytic cracking of polymers, their microporous structure causes important diffusional and steric hindrances for the access of the bulky plastic molecules to the internal acid sites [5, 24].

Amorphous silica–alumina ($SiO_2–Al_2O_3$) has been also tested for the catalytic cracking of polyolefins [36, 37, 43]. This acid solid is featured by having a broad distribution of pore sizes, which is determined by the synthesis procedure. Moreover, the occurrence of a bimodal pore size distribution (e.g. meso-macroporous) is usually present. The aluminium

Table 3.1 Structural features of common zeolites used as catalysts in plastic cracking

Zeolite	Structure	Pore size (nm)	Si/Al ratio
ZSM-5	MFI	0.53 × 0.56, 0.51 × 0.55	10–1000
Y	FAU	0.74	1.5–3
Beta	BEA	0.64 × 0.76, 0.55 × 0.55	8–1000
Mordenite	MOR	0.65 × 0.7	5

content of these materials can be varied within a broad range (0.1–30 wt%) and their acid strength is of medium type, lower than that of the majority of zeolites, containing acid sites of both Brönsted and Lewis nature. Amorphous silica–alumina is also employed as a component of the formulation of FCC catalysts for the cracking of heavy feedstocks as these macromolecules can enter through the large meso/macropores of this material.

Both fresh and especially spent FCC catalysts have been the object of recent attention for polymer cracking [41, 42]. Although they are less active than silica–alumina or mesoporous catalysts [41], spent FCC catalysts still maintain enough activity to be considered as a good choice regarding the fact that their cost is basically zero and they are continuously being disposed of from FCC units. In addition, it has been proved [42] that the unavoidable metal contamination coming from their accumulation after the processing of heavy feedstocks (mostly Ni and V in amounts within 3000–6000 ppm) catalysts did not affect the obtained products over spent FCC catalysts. These same authors carry out an economic evaluation of a catalytic system based on used FCC catalysts, concluding that the cost seems comparable to that of a commercial thermal cracking plant.

The design of catalysts capable of overcoming steric hindrances by having more accessible acid sites located either into larger pores (mesoporous catalysts, pillared clays) [5, 43–51] or over the external surface (nanozeolites) [52] have been successfully tested for the cracking of polyolefins. The first mesoporous aluminosilicates (M41S) were discovered in the early 1990s by Mobil Oil researchers [63]. These aluminosilicates show a uniform mesopore size which can be tailored within the 1.5–10.0 nm range by a suitable choice of synthesis conditions (template, temperature and medium composition). Their BET surface areas are around 1000 $m^2\ g^{-1}$ and their pore volumes about 0.8 $cm^3\ g^{-1}$. MCM-41, which exhibits a hexagonal array of unidimensional mesopores, has been the most studied catalyst of the M41S family. Other mesoporous aluminosilicates such as FSM-16 have also been tested for the catalytic cracking of polyethylene. FSM-16 shows textural properties close to those of MCM-41 materials in terms of BET surface area and pore size, the main difference residing in that a layered silicate (kanemite) is used as silica source in its synthesis [46]. Both MCM-41 and FSM-16 have shown activity for the cracking of polyethylene even in their pure silica form [46, 47, 64]. Recently, another mesoporous silicate (SBA-15) was synthesized with BET surface areas around 600–800 $m^2\ g^{-1}$ and uniform mesopores of dimensions adjustable within the 3.0–30.0 nm range [65]. SBA-15 has the advantage of its wider pore walls (>2.0 nm), that provides this material with higher hydrothermal and thermal stability compared to MCM-41, an important feature from the point of view of the catalyst regeneration. Catalytic cracking of polyethylene over Al-SBA-15 has also been carried out, yielding similar results in terms of product distribution to those of Al-MCM-41 catalysts [48]. Figure 3.5 shows the transmission electron micrographs of both Al-MCM-41 and Al-SBA-15 wherein their respective hexagonal array of mesopores is clearly appreciated. All the reported mesoporous aluminosilicates possess amorphous pore walls and a medium acid strength distribution, quite similar to that of silica–alumina.

Both natural clays and their aluminium oxide pillared analogues have also been tested for the catalytic cracking of polyethylene [49–51]. The clays investigated include montmorillonite and saponite. They possess a layered structure which can be converted into a two-dimensional network of interconnected micropores by intercalation of molecular moieties. In the case of aluminium pillared clays, these materials show a mild acidity

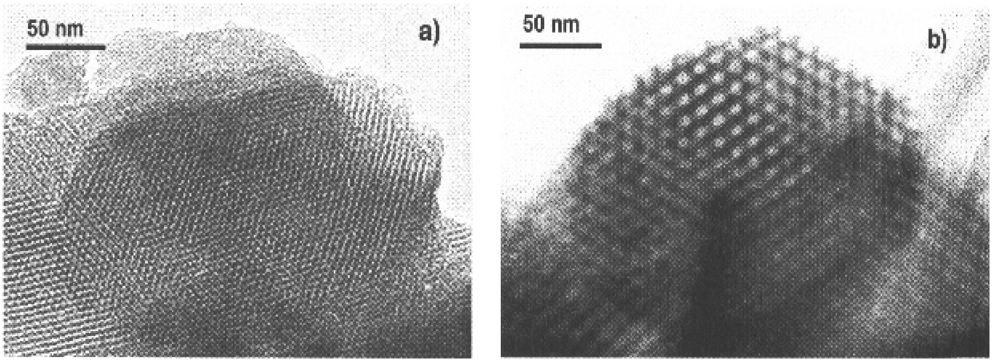


Figure 3.5 TEM micrographs of MCM-41 (a) and SBA-15 (b) mesoporous materials

and an accessible pore size structure. The consideration of pillared clays as possible catalysts for plastic cracking is mainly supported by the fact that their acidity is weaker in strength than that of zeolites. Accordingly, they show a lower cracking activity, but also the catalyst deactivation by coke formation takes place to a lower extent compared with zeolitic catalysts. Moreover, the liquid products obtained over the clay catalysts are heavier, as the strong acidity of zeolites is responsible for plastic overcracking reactions with the production of light hydrocarbons. Likewise, the mild clay acidity leads to a lower occurrence of hydrogen-transfer reactions compared with US-Y zeolite, which in turn causes the formation of alkenes as the main products of the polyethylene cracking over clay catalysts.

Nanocrystalline zeolites, mainly HZSM-5, have also shown remarkable activity for polyolefin cracking [52]. These materials are zeolites synthesized by procedures leading to nanometer crystal size (<100 nm), which provides them with a high share of external surface area fully accessible to the whole of the bulky polymer macromolecules. For instance, nanocrystalline HZSM-5 (*n*-HZSM-5) with a crystal size around 60 nm presents an external surface area of 82 m^2 g^{-1} (almost 20% of the total surface area) and consequently, a high amount of external acid sites. This catalyst has shown a high activity in the cracking of polyolefins, even when working at temperatures as low as 340°C and high plastic/catalyst ratios (P/C = 100).

Catalytic degradation of a standard polyolefin mixture made up of LDPE (46.5%), HDPE (25%) and PP (28.5%) was performed in a semi-batch reactor over a variety of acid solids, differing both in textural properties and acid strength distribution [43]. The conversions and the selectivities by groups and carbon atom number obtained in the cracking of the polyolefin mixture at 400°C for 0.5 h and using a plastic/catalyst mass ratio (P/C) of 50 are illustrated in Figures 3.6, 3.7 and 3.8, respectively. The highest conversions were obtained in the following order: *n*-HZSM-5 > HBeta > HMCM-41 > HZSM-5. However, the acid strength of the catalysts decreased as follows: HZSM-5 > *n*-HZSM-5 > HBeta > HMCM-41 > HY $\sim$ $SiO_2 - Al_2O_3$. The high performance of HMCM-41 was ascribed to both its large surface area and mesopore size while for the case of zeolite HBeta, its relatively large micropore size and medium acid strength are the main reasons to explain its good catalytic behaviour. It is noteworthy to observe the huge differences between the conversions obtained over the micrometer-size (HZSM-5) and nanocrystalline

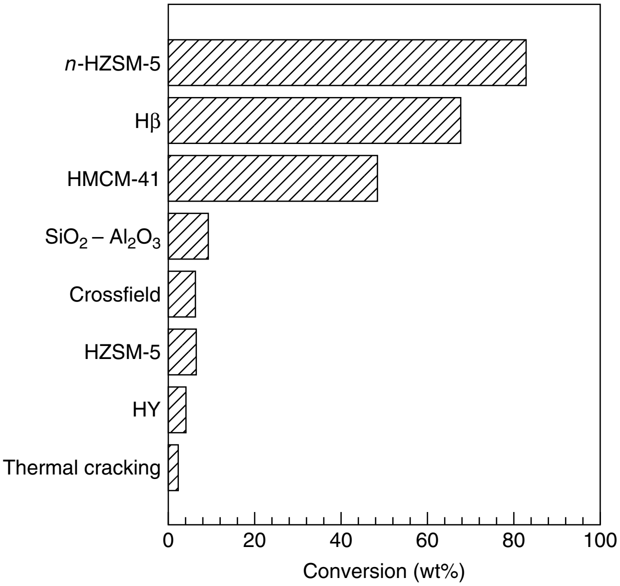


Figure 3.6 Conversions obtained in the catalytic cracking of a model polyolefin mixture (semi-batch reactor, $P/C = 50$; $T = 400°C$, $t = 30$ min) [43]. (Reproduced by permission of the American Chemical Society)

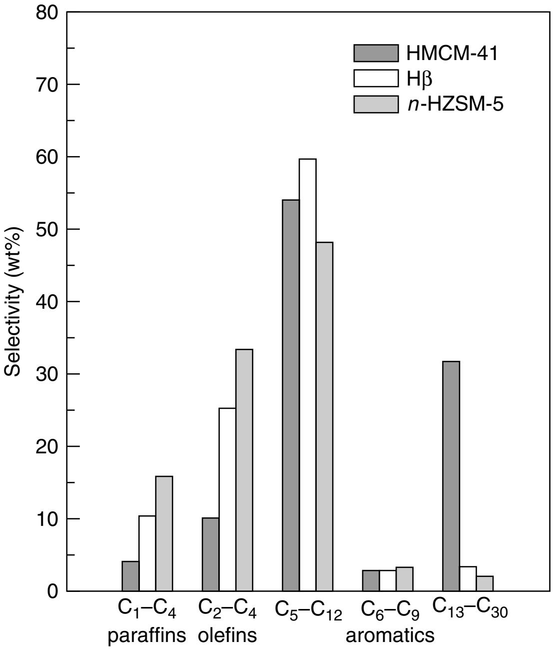


Figure 3.7 Selectivities by groups obtained in the catalytic cracking of a model polyolefin mixture (semi-batch reactor, $P/C = 50$; $T = 400°C$, $t = 30$ min) [43]. (Reproduced by permission of the American Chemical Society)

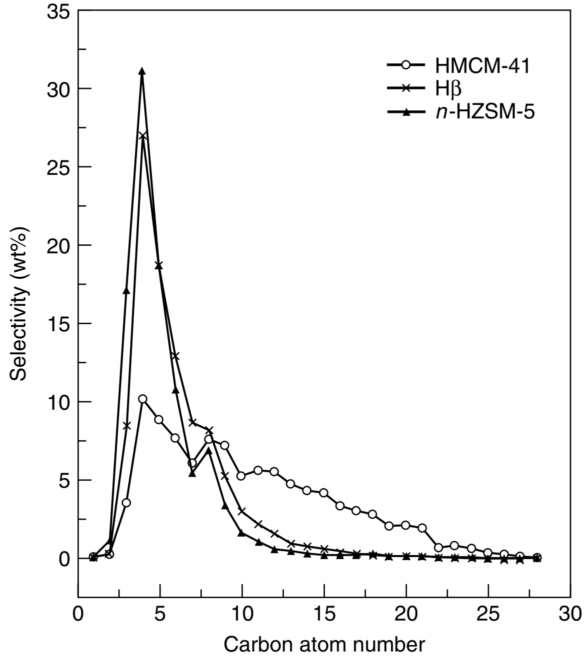


Figure 3.8 Selectivities by carbon atom number obtained in the catalytic cracking of a model polyolefin mixture (semi-batch reactor, $P/C = 50$; $T = 400°C$, $t = 30$ min) [43]. (Reproduced by permission of the American Chemical Society)

(*n*-HZSM-5) zeolites, which have been directly related with the higher accessibility of the acid sites in this last material. The selectivity by groups and atom carbon number distribution of the products (Figures 3.7 and 3.8, respectively) are mainly related to the catalyst acid strength. The stronger the acid sites, the higher the amount of gaseous C_1–C_4 formed by the end chain scission mechanism (mainly C_3–C_4). In contrast, the amount of C_5–C_{12} hydrocarbons increases over catalysts with medium acid strength as they promote random scission reactions of the polymer backbone.

Super acid solids (ZrO_2/SO_4^{2-}) have been tested [53] in the catalytic cracking of HDPE using a thermogravimetric equipment (TG). These solids present higher acidity than 100% sulphuric acid and it is also superior to that of zeolites. The results obtained pointed out the following reactivity order: ZrO_2/SO_4^{2-} > zeolite HZSM-5 > silica-alumina, with a high share of volatile hydrocarbons, mainly C_4–C_5 alkenes, being obtained.

A different approach was followed by Uemichi *et al.* [56] that used metals (Pt, Fe, Mo, Zn, Co, etc.) supported over activated carbons as catalysts for the catalytic degradation of polyethylene at 300°C towards aromatic compounds (mostly benzene). The most effective metals being Pt, Fe and Mo that produced around a 45% yield of aromatics. The role played by the metals was the hydrogen desorption while its abstraction occurs primarily over the carbon sites. In line with the same target products (aromatics), gallosilicates were also employed for the catalytic cracking of polyethylenes at 425°C [54]. The catalyst was actually an HZSM-5 zeolite with Ga incorporated into the framework as heteroatom

(Si/Ga = 25) instead of aluminium, and proved to be highly effective for the production of aromatics (BTX yields ~ 50%).

3 REACTORS

The low thermal conductivity of the molten polymers and their extremely high viscosity are the major problems for the catalytic cracking reactor design. The most widely used reactor systems have been:

- batch/semi-batch;
- fixed bed;
- fluidized bed;
- spouted bed;
- screw kiln.

Apart from these reactors, thermogravimetric techniques (TG) have been widely applied for the study of the thermal and catalytic cracking of several plastics over different acid solids, determining relative activity of the catalysts and kinetic parameters under both isothermal and dynamic conditions [45, 66–69]. Thus, Figure 3.9 illustrates the TG curves corresponding to the degradation of a commercial EVA copolymer by just thermal treatment or when mixed with a MCM-41 catalyst at two different heating rates [45]. It is observed that the catalytic cracking starts at lower temperatures than the thermal process. In fact for a heating rate of 10°C/min, the catalytic cracking has gone to completion at 450°C, whereas the thermal degradation requires a temperature of around 490°C to obtain total plastic conversion. TG experiments have been shown to be a fast method

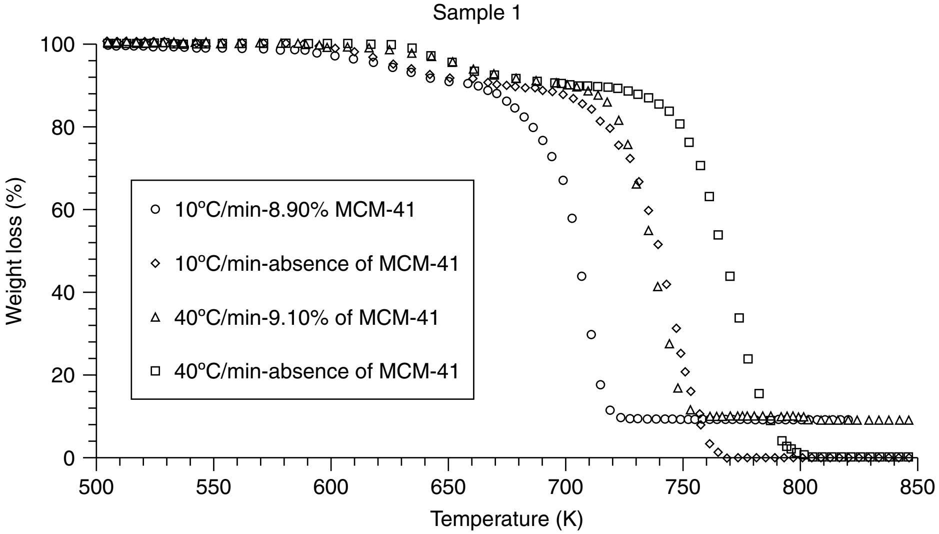


Figure 3.9 TG analyses of EVA polymer degradation by both thermal treatment and catalytic cracking over a MCM-41 material [45]. (Reproduced with permission from Elsevier)

for evaluating the activity of different catalysts or to study the catalyst deactivation, although the results must be carefully interpreted as they are not carried out under realistic conditions, whereas no information about the product distribution is usually derived.

3.1 BATCH/SEMI-BATCH REACTORS

The literature is full of studies that use either a batch or a semi-batch reactor for the catalytic cracking of plastics provided (but not always) with a stirring device [28, 38, 41, 55, 70]. The main reason is the ease of their design and operation. However, there is a significant difference between them. The semi-batch reactor is swept by a continuous flow of an inert gas (usually nitrogen) that removes the volatile products from the medium at the reacting temperature. The removal of the volatile compounds causes the secondary reactions of the primary cracking products (e.g. oligomerization, cyclization and aromatization) to take place only to a little extent. This does not occur in batch reactors where secondary reactions are supposed to be promoted [54].

One recent example of the use of a stirred semi-batch reactor for the catalytic degradation of plastics wastes (HDPE, LDPE, PP and PS) over spent FCC catalysts has been reported by Lee *at al.* [70]. The yields of liquid products at 400°C obtained with the different plastics follows the order: PS $>$ PP $>$ PE (HDPE, LDPE), with values in all cases above 80%. The amount of solids deposited over the catalysts was below 1 wt% except for PS (about 5%). In the last case, small cyclic intermediate precursors are first formed, which subsequently polymerize leading towards the observed solid residues. These authors also studied the composition of the liquids coming from the cracking of the different plastics by PONA analysis (paraffins, olefins, naphthenes, aromatics). Figure 3.10(a, b) compares the composition of the liquids obtained in the cracking of HDPE and LDPE, respectively. Olefins were the main components of the liquids obtained with both polyolefins, especially in the case of HDPE ($>$80%), while this share dropped with LDPE below 60%. The observed high selectivity towards olefins (primary products) and the lower one towards the remaining products agrees well with the initially reported features of this stirred semi-batch reactor.

3.2 FIXED-BED REACTORS

The fixed bed is likely the most classical catalytic reactor. However, its usage with plastics as feed is not straightforward since the high viscosity and low thermal conductivity of plastics pose serious problems for being loaded into the reactor. In some systems, the molten polymer is introduced into the reactor through a capillary tube from a pressurized tank [71]. The most usual technical solution is to carry out a previous thermal cracking of the plastic. Then, the liquid or gaseous compounds resulting from the thermal process can be fed easily into the fixed bed [72–75].

According to this concept, Masuda *et al.* [75] studied the catalytic cracking of the oil coming from a previous thermal pyrolysis step of polyethylene at 450°C in the bench-scale fixed-bed reactor shown in Figure 3.11. The catalysts employed were different zeolite types: REY (rare earth exchanged zeolite Y), Ni-REY (nickel and rare earth

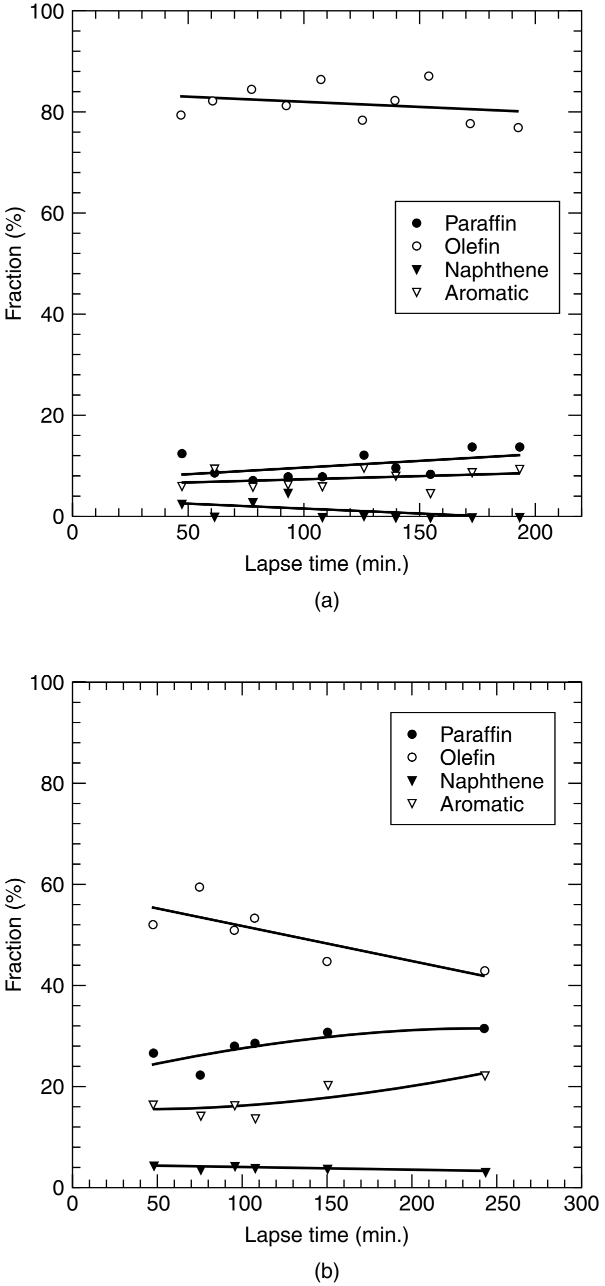


Figure 3.10 Fractions of paraffins, olefins, naphthene and aromatic products from the catalytic degradation of plastics over spent FCC catalyst in a semi-batch reactor (400°C, $P/C = 10$, $N = 200$ rpm): (a) HDPE; (b) LDPE [70]. (Reproduced with permission from Elsevier)

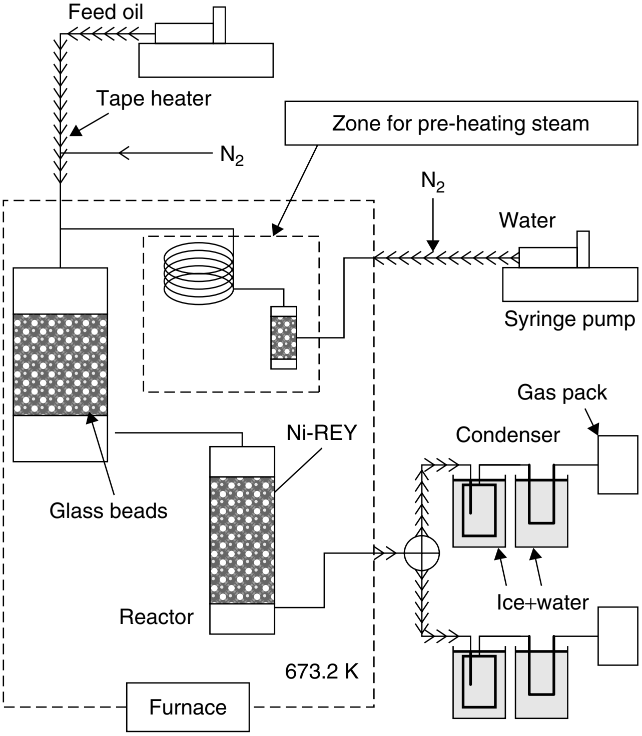


Figure 3.11 Bench-scale fixed-bed reactor used for the catalytic reforming of products coming from the thermal degradation of polyethylene [75]. (Reproduced with permission from Elsevier)

metal exchanged Y-type zeolite) and HZSM-5. The reactions were carried out under a steam or nitrogen atmosphere at 400°C. Nickel was included in the catalyst formulation in order to promote the transport of hydrogen atoms by spillover from steam to adsorbed olefinic hydrocarbons over the acid sites. When steam is used as the carrier, the strong acid sites of the catalysts are partially covered by hydrogen. As these strong acid sites are responsible for the formation of coke, catalyst activity is maintained for a longer time. Optimum nickel level in Ni-REY zeolite was about 0.5%. Conversions above 70% of the heavy oil and selectivities towards gasoline close to 80% were attained and maintained constant over Ni-REY after five sequences of reaction and regeneration. When HZSM-5 zeolite was used as catalyst, a fast deactivation was observed as a consequence of a dealumination process caused by the steam presence.

3.3 FLUIDIZED-BED REACTORS

Fluidized-bed reactors are featured by presenting both temperature and composition homogeneity. This is a remarkable advantage for the cracking of polymers due to their low thermal conductivity and high viscosity that usually lead to the appearance of temperature

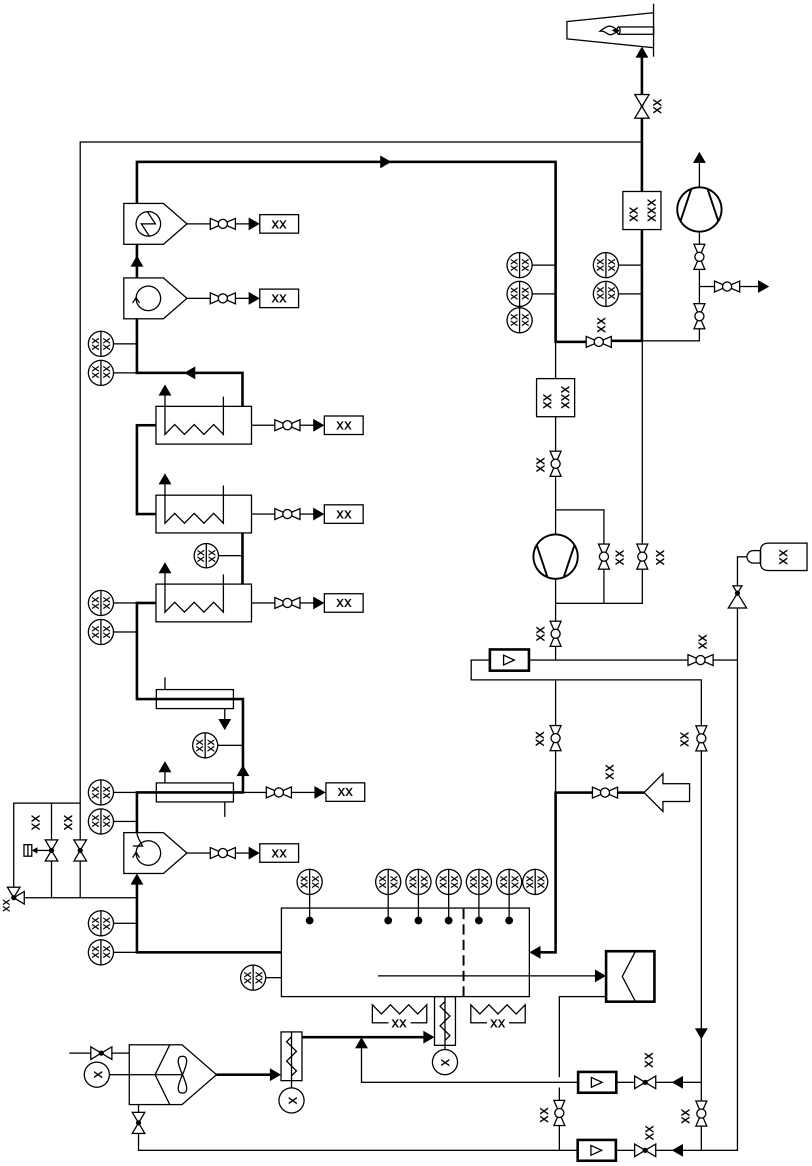


Figure 3.12 Flow scheme of a fluidized-bed reactor (Hamburg process) [76]. (Reproduced by permission of Wiley VCH)

gradients in other reaction systems wherein heat is not as properly transferred. One of the best known process for pyrolysis of plastic wastes is the Hamburg process developed by Kaminsky *et al.* [76] which is depicted in Figure 3.12. The fluidized bed consists of a 154 mm diameter, 670 mm height tube of stainless steel filled with 9 kg of sand and a gas distributor at the bottom formed by a steel plate with 108 tubes. The reactor is heated by 5 kW filaments and the input material is fed into the reactor by two screw conveyors. The products obtained are separated in several stages comprising a cyclone, coolers and electrostatic separators. Initially, this system was exclusively applied for the thermal cracking of polymer wastes using as fluidizing agent nitrogen or preheated steam. Thus, by pyrolysing at 510°C a mixed plastic waste mainly formed by polyolefins, a 90 wt% conversion towards oil and waxy products was attained while at higher temperatures (690–735°C) an oil consisting of 40% of BTX (benzene, toluene and xylenes), was obtained [77]. When PS and PMMA were used as feed, actual depolymerization towards the constituting monomers took place since they were obtained with high selectivity (61% of styrene and 97% of methyl methacrylate). On the other hand, if steam was used as fluidizing agent at 700–750°C, high yields of light olefins such as ethylene (21–29%), propylene (16–21%) and butadiene (5.6–6.6%) are achieved [17].

Mertinkat *et al.* [78] modified the Hamburg process for performing the catalytic cracking of the polymers by using as fluidizing medium an FCC catalyst instead of the inert sand or quartz employed in the thermal process. The amount of catalyst and plastic fed to the reactor was roughly 1 $\mathrm{kg\,h^{-1}}$ each and the residence time was varied within 3–12 s. Catalytic cracking of polyethylene at 450–515°C yielded gases (50%) and aliphatic oils (40%), while for polystyrene degradation, the main products were ethylbenzene (18–26%) and benzene (9–22%), with a significant reduction in styrene share (1–7%). Other researchers have also studied the catalytic pyrolysis of PS over HZSM-5 zeolite [79] and of different polyolefins over several acid solids using fluidized beds [80–82].

3.4 SPOUTED-BED REACTORS

One of the firstly proposed approach for the feedstock recycling of plastic waste was to merge them with standard FCC feedstocks and to submit them to cracking directly in FCC refinery units. According to this idea, a new reaction system denoted as spouted bed or riser simulator was proposed that allows for reproducing the conditions existing in an actual FCC unit [83–85]. The feed is usually a blend of 5–10 wt% plastic (PE, PP, PS) in an oil such as light cycle oil (LCO), vacuum gas oil (VGO) or even pure benzene. The scheme of the reactor is shown in Figure 3.13. It is an internal recycle reactor which can operate at low contact times (1–10 s) and with a suitable catalyst/oil ratio (e.g. C/O = 6). As inferred from Figure 3.13, the catalyst is placed in a basket and the gases are impelled

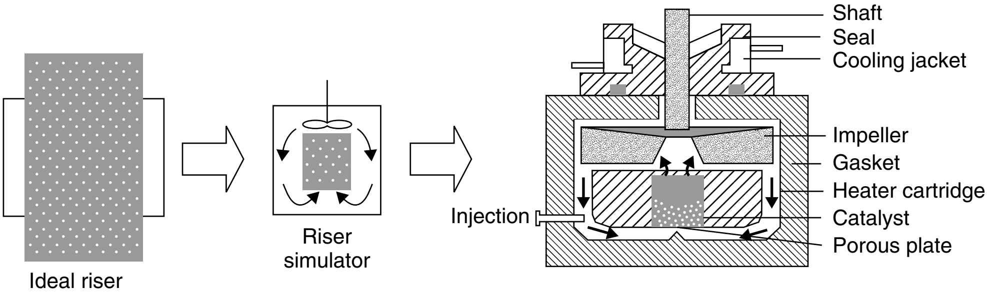


Figure 3.13 Scheme of a riser simulator reactor for plastic conversion [83]. (Reproduced by permission of Javier Bilbao)

by a turbine located in the upper part, circulating through the basket. At zero time, the feed is injected and when the reaction is completed, a valve is open, releasing the products into a vacuum chamber, being subsequently analysed.

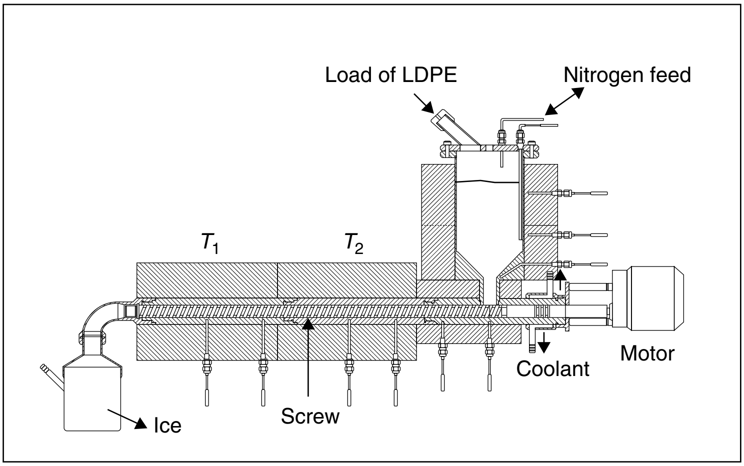
The cracking of PE/LCO and PP/LCO blends over HZSM-5 zeolite catalysts in the riser simulator at 450°C led towards mainly a C_5-C_{12} hydrocarbon fraction of aromatic nature and a low yield of C_1-C_2 gases and coke.

3.5 SCREW KILN REACTORS

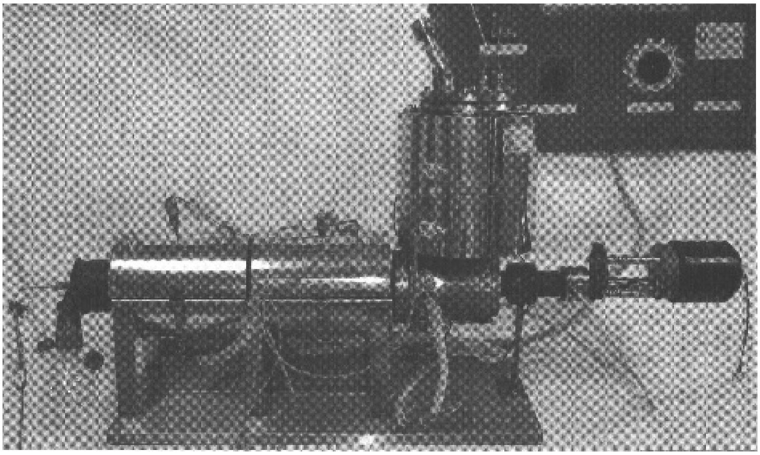
Recently, a new reaction system has been designed for the thermal and/or catalytic degradation of plastics and plastics–oil mixtures [86–88]. The reactor is named screw kiln reactor and its design reminds that of the extruders widely applied for polymer processing. The scheme and a photograph of this system are shown in Figure 3.14. Basically, the reactor is provided with a hopper wherein the plastics or plastics–oil mixtures are fed and heated at temperatures within 250–300°C by two external furnaces under a nitrogen atmosphere (at slightly higher pressure than atmospheric). The melted reacting mixture is subsequently fed into the reactor by means of a screw located inside a 52-cm-long stainless steel tube with 2 cm internal diameter, which is the actual reaction zone. The tube is heated externally by two furnaces whose temperature can be adjusted independently, the reactor being divided effectively into two heating sections (denoted as T_1/T_2). Temperature is continuously controlled by a set of built-in thermocouples through the reactor in order to avoid the appearance of cold spots and the subsequent plastics solidification. Screw speed can be varied within 0.5–25 rpm, thereby changing the residence time of the plastics. The small diameter of the screw assures that the radial temperature profiles are practically negligible. The catalyst is mixed up with the plastic at the hopper in order to attain a homogeneous reacting mixture and it follows the same flow as the polymer through the whole system, being recovered at the outlet simply by filtration.

As an example, catalytic cracking of pure LDPE was carried out in the screw kiln reactor over mesoporous Al-MCM-41 (plastic/catalyst mass ratio of 50) at $T_1/T_2 = 400/450°C$, respectively. The reported yields of hydrocarbons within the gasoline range (C_5-C_{12}) amounts to 80% with a high content of C_7-C_8 hydrocarbons, stemming likely from the occurrence of secondary catalytic oligomerization reactions affecting to the initially formed C_3 and C_4 fractions.

Unlike other reacting systems, this reactor is not bound by the usual viscosity problems of polymers as the extruder is used to displace the plastics, so pure plastics can be fed without any flow trouble. This is a significant advantage with regard to conventional fixed-bed reactors as in most of them the plastics just fall by gravity or the feed is indeed the product coming from a previous thermal pyrolysis, not the polymer itself. Compared with a conventional batch reactor, the screw kiln reactor leads to a lower formation of gaseous products and reduces the overcracking of the heavier fractions. These results were ascribed to secondary reactions occurring in the reactor due to the intimate contact of the primary cracking products (mostly light gases) and the partially cracked plastics, since no selective removal of the volatile hydrocarbons takes place inside the reactor, as it occurred in the semi-batch reactors. Moreover, all the hydrocarbon fractions present similar residence times within the screw kiln reactor, which also leads to a narrow product distribution.



(a)



(b)

Figure 3.14 Screw kiln reactor for the conversion of plastic and plastic-oil mixtures [87]: (a) scheme; (b) photograph of a laboratory reactor. (Reproduced by permission from Elsevier)

4 INFLUENCE OF THE MAIN OPERATION VARIABLES

Both the activity and selectivity of the catalysts heavily depend on the following reaction variables:

- temperature;
- catalyst amount;
- time;
- plastic composition.

Henceforth, their respective effect over the catalytic cracking of plastics is described:

4.1 TEMPERATURE

Temperature is likely the most important variable affecting the catalytic cracking of plastics. Reaction temperatures are usually in the range 300–450°C. In general, a temperature increase leads towards a parallel activity enhancement of the catalysts. Nevertheless, it must be taken into account that at high temperatures the simultaneous occurrence of thermal cracking reactions is favoured, which may modify the product selectivity.

Additionally, the temperature affects in a different way the reactions involved in the carbocationic chain pathway (initiation, propagation, termination) as they can be either mono or bimolecular, also changing the selectivity attained. Several studies have been performed reporting the effect of temperature in the catalytic cracking of plastics [28, 35, 89]. Sharratt *et al.* [35] observed, in their catalytic cracking experiments of high-density polyethylene (HDPE) over HZSM-5 zeolite in a fluidized bed within the 290–430°C range, that as temperature rises, the yield of lighter hydrocarbons increases as well as that of BTX and coke. In addition, these authors observed a decrease of the olefin/paraffin ratio in the gaseous fraction from 5.4 to 3.6. In another study performed in a semi-batch reactor, the influence of the temperature on the catalytic cracking of a model plastic mixture (46.5% LDPE, 25% HDPE and 28.5% PP) over both nanocrystalline HZSM-5 and Al-MCM-41 was also studied in the range 375–450°C [28]. The conversion increased with temperature leading to total conversion at 450°C for a plastic/catalyst mass ratio of 100. However, the share of heavier hydrocarbons augmented with temperature (see Figure 3.15

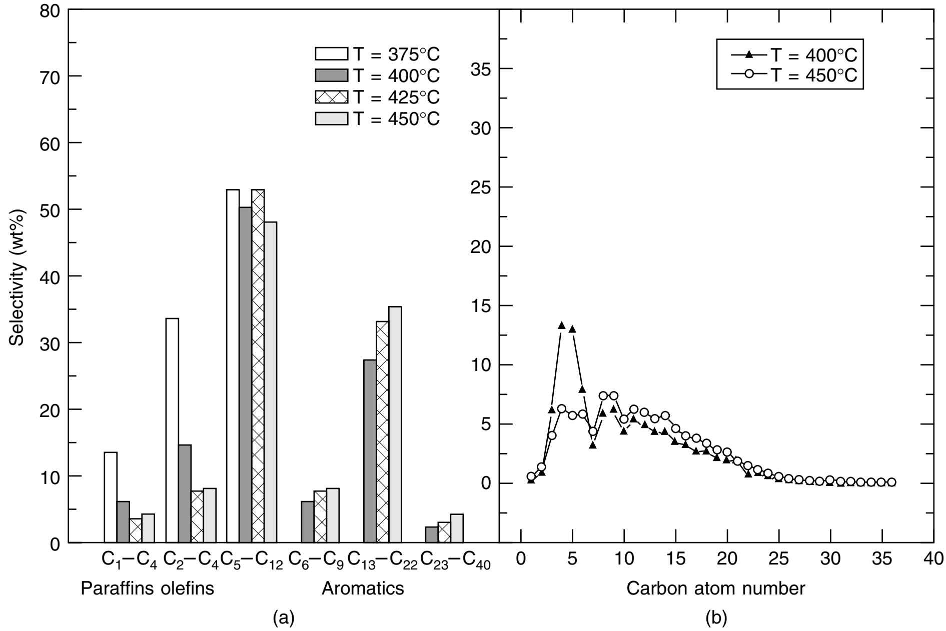


Figure 3.15 Product distributions obtained in the catalytic cracking of a polyolefin mixture over HMCM-41 at different temperatures ($P/C = 100$; $t = 30$ min): (a) selectivity by groups; (b) selectivity by carbon atom number [28]. (Reproduced by permission of the American Chemical Society)

for the products obtained over Al-MCM-41), which was ascribed to the larger extent of thermal cracking reactions and also to the vaporization of these heavier compounds at the highest reacting temperature, leaving subsequently the reaction medium. In addition, for nanocrystalline HZSM-5, a decrease in both C_4 and C_5 selectivity, while C_3 remained almost constant, was observed on going from 400 to 450°C, which was explained in terms of the higher extent of direct scission reactions at the end of polymer chains instead of previous rearrangements. Similar results were appreciated by Ishihara *et al.* [89]; at low temperature, the main products of polyethylene degradation were both isobutane and isobutene, but at higher temperature, propylene begins to be formed in meaningful amounts.

4.2 CATALYST AMOUNT

Sharratt *et al.* [35] investigated the catalytic cracking of HDPE over HZSM-5 zeolite varying the polymer-catalyst mass ratio from 1:10 to 1:1 at 360°C in a fluidized-bed reactor. The obtained conversions were always above 90%. However, some differences were appreciated regarding the product distribution. The increase in polymer/catalyst mass ratio led towards higher yields of gaseous C_1-C_4 hydrocarbons (61–69%) and coke. This is an expected result since primary cracking reactions leading towards the formation of C_3-C_4 are favoured as the amount of catalyst is increased, whereas the secondary reactions involving these olefinic gases occur in a minor extension, due to the really short residence time in the fluidized-bed reactor.

On the other hand, the catalytic cracking of a model plastic mixture (46.5% LDPE, 25% HDPE and 28.5% PP) at 400°C in a semi-batch reactor was carried out varying the plastic/catalyst mass ratio (P/C) from 200 to 4 [28]. When nanocrystalline HZSM-5 zeolite was employed as catalyst, the selectivity towards gases (C_1-C_4) and gasoline (C_5-C_{12}) was always within 45–50%, irrespective of the P/C ratio used. However, the composition of both gaseous and gasoline fractions changed significantly. The paraffin/olefin proportion in gaseous hydrocarbons increased on diminishing the plastic/catalyst mass ratio. The same trend was observed for the aromatic content in the gasoline fraction, as shown in Table 3.2. These results suggest that secondary reactions involving the olefins produced directly from the plastic cracking take place in a growing extent as the amount of catalyst is increased.

Table 3.2 Aromatic hydrocarbon content in the gasoline fraction resulting from the cracking of a polyolefin mixture at 400°C over *n*-HZSM-5 zeolite at different P/C ratios [28]

P/C ratio (w/w)	Benzene (%)	Toluene (%)	Ethylbenzene (%)	Xylenes (%)	Trimethylbenzenes (%)
200	0.33	0.41	0.25	0.91	0.64
100	0.60	0.34	0.28	0.99	0.44
50	0.81	0.87	0.54	3.39	0.23
10	0.98	3.46	1.28	6.90	0.81
4	1.03	5.32	1.74	9.19	2.28

Both examples illustrate clearly the influence of the catalyst amount in the product selectivity. Therefore, an adequate tuning of both primary/secondary reactions is required to achieve the desired product distribution.

4.3 TIME

Changes in the performance of catalysts with time are directly related to their deactivation kinetics. However, work aimed at studying the catalyst deactivation in the cracking of polymers is scarce in literature. Lin *et al.* [90] have investigated the deactivation of USY zeolite in the catalytic cracking of HDPE using thermogravimetric analyses (TG). These authors observed that USY zeolite was deactivated by coke deposition and established a exponential relationship between the activity decay and the measured coke content. Similar conclusions were drawn by Uemichi *et al.* [91] in their study of the deactivation of several zeolites (HZSM-5, HY, H-mordenite) and silica–alumina in the cracking of LDPE in a fixed bed. The plastic, previously melted at 310°C, was fed into the catalytic bed by capillary pressure. Catalyst deactivation was studied within the temperature range 375–526°C using a space time (W/F) of 7–23 g catalyst min g^{-1} of polyethylene. HZSM-5 was observed to be the most effective catalyst for degrading the plastic into gasoline range hydrocarbons rich in isoparaffins and aromatics with very low deactivation by coke deposition during the time on stream. However, the mordenite and Y zeolites suffered of strong deactivation, leading to a fast fall in liquid production, probably due to the pore blockage by coke. In contrast, silica–alumina retains a good performance over time, probably due to their large pore size. The authors also studied the catalyst deactivation in polystyrene degradation. In this case, a strong deactivation was appreciated over all the catalysts because of the formation of unsaturated and polyaromatic compounds (indane and naphthalene derivatives) that were converted to coke, in keeping with previous observations [92].

4.4 PLASTICS WASTE COMPOSITION

The composition of the raw plastic wastes may have a huge influence on the performance of the catalysts. Hence, catalysts leading to high conversions for the cracking of pure polymers have often been observed to lose their activity to a large extent when cracking a real mixture of plastic wastes. In addition, plastic wastes makeup varies largely, depending on the origin of the waste, making difficult to foresee in a general way the performance of the different catalysts. This fact was observed in the cracking of plastic film waste coming from Spanish greenhouses [93]. Apart from the influence of non plastic components (additives, dirt, etc.), it was proven that the presence of a 4 wt% of EVA copolymer in LDPE decreases the activity of mesoporous catalysts (Al-MCM-41, Al-SBA-15) to values close to those of thermal cracking. Owing to these facts, several works have been recently published dealing with the cracking of standard mixtures of several plastics, in order to ascertain their influence on the cracking activity and product distribution. Yanik *et al.* [94] studied the catalytic degradation of polymer mixtures made up of PVC/PE, PVC/PP and PVC/PS (8:2 mass ratio) at 430°C. The tested catalysts were red mud (a waste from alumina production formed by a mixture of iron, aluminium, silicon, calcium, sodium, etc.) and a combination of silica–alumina and y-Fe_2O_3 (chlorine adsorbent). Red mud and iron oxides showed good properties for chlorine fixation although it was concluded that the catalyst promotes the formation of some organic chlorinated compounds, whose amount was markedly lower for thermal cracking.

Likewise, Tang *et al.* [95] have investigated the catalytic cracking of mixtures of several polyolefins and PVC (PP/PVC, PE/PVC, PS/PVC) at 360–380°C over a novel Al-Zn composite. These authors observed that the composite accelerated the degradation of the plastic mixtures and retained the chlorine resulting from PVC degradation.

5 PROCESSES

Initially, processing of plastic wastes was proposed to be carried out directly through their incorporation into the streams of oil refineries, since their main components (polyolefins) present several advantages that convert them into a desired feedstock for the different refinery units. These plastics possess a high hydrogen/carbon ratio (around 2) with a low tendency to form coke due to its aliphatic composition, showing also a reduced metal content. However, it was obvious fairly soon that this choice presented several important drawbacks coming from the own working specifications of the refinery [3], the main ones are quoted as follows:

- halogen content should be below 20 ppm;
- feed must be pumped as an oil or gaseous stream, free from solids;
- absence of filler materials, which may foul heat exchangers and plug pipes or other conduits;
- absence of condensable additives;
- Heavy metal content below 0.1 wt% to avoid deposits, coking and catalyst fouling.

During the last decade, there have been a significant increase in the number of patented processes that use catalytic cracking technologies for the upgrading of plastic wastes and/or the oils derived from a previous pyrolysis treatment. The number of patents has grown especially in the Asian countries, wherein the depletion of available landfills caused by the overpopulation has triggered a huge regulation pressure.

From a technical point of view, the great majority of the patented processes based on catalytic pyrolysis of plastic wastes are mainly addressed towards the preparation of different grade fuels (gasoline, kerosene, diesel). Two groups can be easily envisaged within these patented processes. The first one will be made up by those processes that cracked the plastic wastes directly, without any previous thermal treatment for precracking them and/or releasing unwanted products (e.g. hydrogen chloride from PVC). The only thermal step before the catalytic cracking is the melting of the plastic for feeding it continuously inside the catalytic reactor. The second group comprises those processes in which plastic wastes are first thermally cracked in a previous step. After the removal of undesired compounds (such as hydrochloric acid), the products resulting from the thermal treatment are fed to the catalytic stage, where they undergo a catalytic upgrading towards more valuable products so as to improve the whole economy of the process.

Additionally, some particular catalytic cracking processes for recovering specific raw chemicals from plastic wastes can be found in the literature. This is the case of the process patented by Mazda Motor for the recovery of phthalic anhydride from plastic materials (mainly PVC), containing phthalate ester as plasticizer [96]. The process comprises three main steps: (a) heating at temperature below 350°C to vaporize the desired product; (b) catalytic cracking over a solid acid (preferentially alumina); and (c) recovery of the obtained phthalic anhydride. The process also considers the recovery of the hydrogen chloride released on heating the PVC-containing plastic waste material.

5.1 DIRECT CATALYTIC CRACKING

In addition to requiring just one reactor, direct catalytic cracking of plastic wastes presents several advantages, mostly in terms of energy efficiency, with regards to the two stage processes (thermal degradation and subsequent catalytic reforming). Both residence time and reaction temperature might be lowered by the use of catalysts, which reduces energy costs significantly. Additionally, the nature of the obtained products might be tailored by a judicious choice of the catalysts, making unnecessary the use of a second catalytic reactor for reforming them.

However, this technology suffers of different limitations, the main one being related to the catalyst performance along the time on stream. The catalysts should be resistant to the heterogeneous nature of the plastic waste stream as well as to the presence of a large variety of additives. Additionally, the possibility of repeated regeneration cycles of the catalyst should be deeply regarded in the design of the process so as to achieve a better profitability. In the light of these facts, fluid catalytic cracking technology seems to be an interesting choice, provided that the specific fluidodynamic issues related to the macromolecular nature of plastic waste can be properly solved.

Despite these inconveniences, there can be found in the literature some patented processes for plastic waste cracking based on direct catalytic cracking in stirred semi-batch reactors [98, 99]. Corma *et al.* [98] designed a process of direct catalytic cracking of either pure or waste polyolefins (polyethylene, polypropylene, polystyrene), their mixtures and including also halogen-containing polymers. Both catalyst and waste plastics are put into contact in a stirred semi-batch reactor under a continuous gas flow (nitrogen and/or steam) at temperatures within 300–550°C. The volatile products at the reaction temperature leave the reactor, being separated and collected afterwards. Fresh FCC catalysts, balanced FCC catalysts or their mixtures can be used in the process. The reported conversions varied within the 30–96 wt% range, depending on the experimental conditions (amount of catalyst, time and temperature). High selectivities towards gasoline (70–80 wt%) are attained, with 10–20 wt% of diesel and fairly low amounts of gases (<10 wt%). The authors claim that the profitability of the whole process is improved by the use of spent FCC catalysts, which are meant to be a refuse from FCC units to be disposed of. Spent FCC catalysts still retain enough activity for promoting the catalytic cracking of the plastic wastes and are available in huge amounts after FCC shutdown.

An alternative process based on two sequential catalytic cracking stages aimed at obtaining gasoline and diesel from waste plastics or heavy oil/waste plastics mixtures is shown in Figure 3.16 [99]. The catalyst employed in the first step is made up of powder alumina, waterglass and HZSM-5 zeolite and is mixed up directly with the waste plastics in a screw reactor preferably at 600–700°C. The second catalytic step consists in a fixed bed containing zeolite ZSM-5, zeolite REY and flokite as major components, being operated at temperatures within the 300–600°C range to increase the output of gasoline and diesel. As inferred from Figure 3.16, the first catalyst is previously heated in a combustion chamber up to 600–700°C and thereafter, loaded into the first cracking reactor along with the waste plastics stream continuously fed by a screw extruder. The loaded materials are decomposed into gaseous hydrocarbons and an inorganic residue. The gaseous hydrocarbons are fed to a fixed bed to be decomposed into smaller molecules which are separated afterwards in a fractionation column into gasoline and diesel. On the other hand, both the residues and the first catalyst are collected at the bottom of the vaporizer and separated in two successive stages. The coke deposited over the first catalyst is finally burnt off in the combustion chamber before being added again into the first catalytic reactor. The yields obtained indicate that for a starting feed of 1400 kg of waste plastics formed by PP (25%), PS (25%) and PE (50%), 630 kg of gasoline (RON = 93.5; 48% olefins and 19.9% paraffins, 9.9% aromatics), 420 kg of diesel (cetane value = 52; 55% olefins, 10% aromatics), 140 kg of inorganic residues and 210 kg of flammable gas are attained. However, no data are provided about the effect of the heteroatoms content in the feed and their influence on the catalyst behaviour.

In agreement with the concept of using several catalytic stages, Kwak *et al.* [100] recently designed a method for converting waste plastics into gasoline, kerosene and

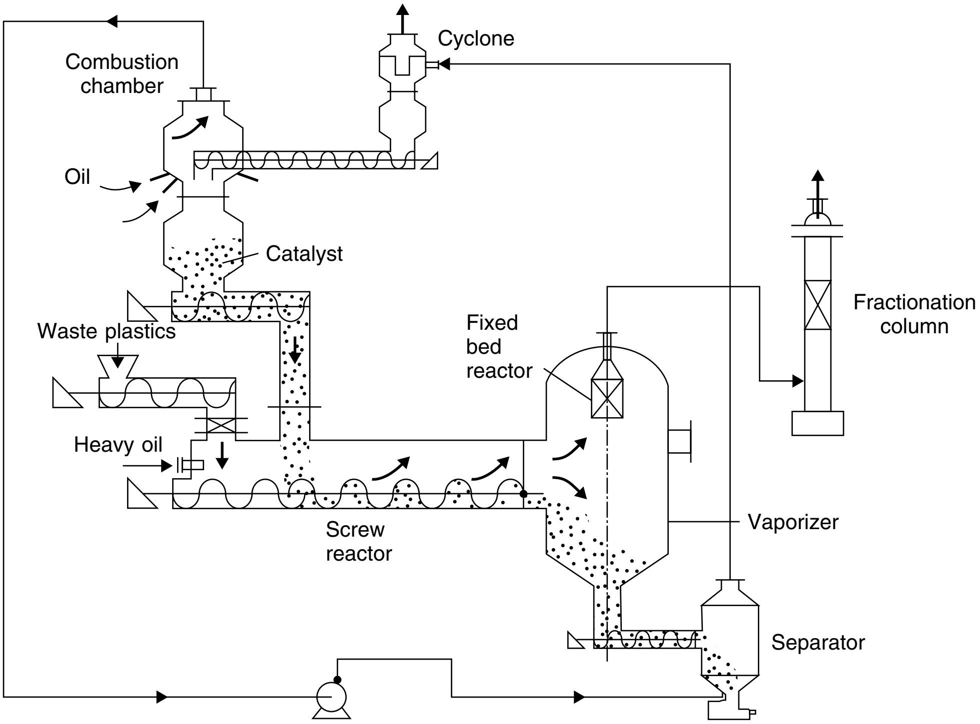


Figure 3.16 Scheme of a process for the direct catalytic cracking of plastic wastes in two steps [99]

diesel by means of a three-step catalytic process. In the first step, melted plastic wastes are subjected to a simultaneous dehydrogenation and decomposition treatment over a nickel-based catalyst at temperatures around 350–370°C for roughly 20 min. This treatment enables a reduction in the molecular weight between 1/8 and 1/12 of their starting values. The second catalytic step is carried out in a fluid catalytic cracking pipe at 500–550°C using a silica–alumina catalyst. Subsequently, steam is introduced to remove heavy oils present on the catalyst surface. The cracked products are separated by distillation into three fractions: gasoline, kerosene and diesel oil. The third catalytic step is solely applied to the gasoline fraction in order to reform it towards a higher quality product by contacting with an acid catalyst such as HCl, $AlCl_3$ and $SbCl_3$.

Another approach for overcoming the problems posed by conventional cracking catalysts has been disclosed recently by Reverso *et al.* [101]. In this case, direct cracking is performed by using as catalyst a molten bed of pure metal or a metal mixture (mainly lead, zinc, tin) at a temperature of 460–550°C wherein the waste polymer is loaded inside the reactor at a certain depth. The authors point out that the products are indeed a result of the combination of both thermal and catalytic cracking. The catalyst composition may also include some acidic component such as metal silicates, metal carbonates and their mixtures. The process can be applied to pure and mixed polymers (PE, PET, PP, PVC), as well as to the plastic fraction of municipal solid wastes.

5.2 THERMAL DEGRADATION AND SUBSEQUENT CATALYTIC UPGRADING

This type of process is the preferred choice for treating plastic wastes containing a high proportion of components that may affect negatively the catalyst performance. The occurrence of a previous thermal step allows for the removal of many of these components previously to the catalytic treatment.

Figure 3.17 illustrates the flow sheet of the process developed by the company Nippon Steel Corporation, being applied in Japan on a commercial scale [102]. The process may use as raw materials any kind of plastic wastes, including chlorine contents from PVC and limited amounts of nonplastic components, such as paper, fibres and aluminium foil. It includes a pretreatment to remove undesired materials (metals, paper, etc.). Then, the crushed plastic wastes are loaded by a screw conveyor into a mixing tank, being melted at 300°C. In this stage, PVC is thermally decomposed and more than 90% of chlorine is removed in the form of hydrogen chloride. The melted plastics are fed into the thermal cracking vessel operating at 400°C and pressures close to atmospheric. The gas stream derived from the thermal degradation is first purified from additional HCl, released in the thermal treatment, and subsequently reformed by contacting with a catalyst in a fixed bed reactor, leading to oils useful as fuel. The carbon residue precipitated in the thermal cracking reactor is discharged out of the process continuously by using a centrifugal separator and finally burnt at about 1100°C within an incinerator. Several pilot and semi-commercial plants are being setting up in Japan based on this technology.

Although the great majority of the aforementioned processes for giving added value to the product of a previous thermal cracking have been addressed towards the production of higher quality fuels, other alternatives have been proposed yielding completely different

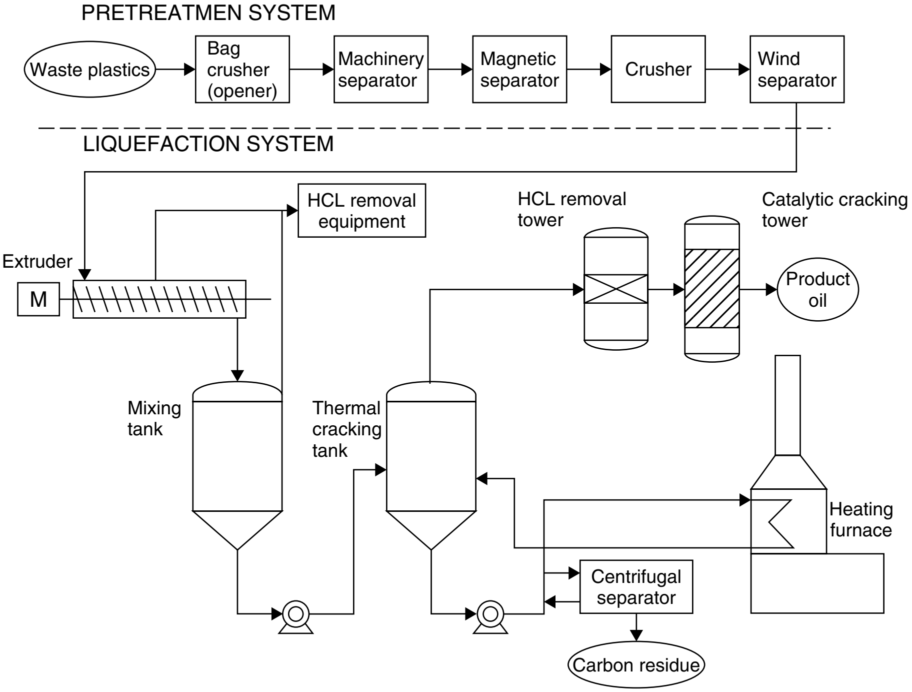


Figure 3.17 Flowsheet of a waste plastic liquefaction plant based on thermal cracking and subsequent catalytic reforming [102]. (Reproduced by permission of the International Solid Waste Association (ISWA))

products. In this regard, the upgrading of a polyethylene waste by its conversion into lubricating oils with high viscosity index has been patented by Chevron [103]. The process starts with the thermal conversion of pure or waste HDPE at 600–700°C giving rise to a mixture of *n*-paraffins and 1-olefins (25–75 wt%). The heavy fraction in this mixture (boiling point above 650°C) is separated and then passed through a hydrogenation zone to remove the N, S and O heteroatoms that might deactivate subsequently the dewaxing catalysts. Finally, the effluent of the hydrogenation zone is isomerized using a typical dewaxing catalyst such as an intermediate pore size molecular sieve (e.g. ZSM-22, ZSM-23, SSZ-32, SAPO-11). According to this patent, the lubricating oils obtained show pour and cloud points below −9.5°C and −3.9°C respectively, the oil yields being above 50 wt%.

Other interesting products that can be obtained from waste plastics using combined thermal and catalytic processes are alkylaromatic compounds, which possess industrial applications as automatic transmission fluids (ATF), detergents (linear alkyl benzenes, LAB), and improvers of cetane number in diesel fuels [104]. The process uses as raw material the olefins generated in a previous step of thermal and catalytic cracking, which represent a cheaper source of olefins alternative to the currently existing ones. No special details about the conditions applied for the olefin production are indicated, the emphasis being focused on the alkylation step. Alkylation catalysts comprise conventional Lewis acids ($AlCl_3$, $FeCl_3$, $TiCl_4$, $ZnCl_2$, etc.) and solid acids such as pillared clays, natural and synthetic zeolites (ZSM-5, ZSM-12, ZSM-23, USY), amorphous silica–alumina, etc.

6 RELATED TECHNOLOGIES: COPROCESSING

In addition to the above-mentioned catalytic processes, there are some other related technologies wherein the catalytic cracking of plastic wastes is combined with the coprocessing of other substances, mainly coal and petroleum feedstocks (lube oil, LCO, VGO) or even a solvent. Hereafter, these technologies are explained more in detail.

6.1 COAL

Coprocessing of plastics with coal in order to convert both of them into fuels is another promising option deeply studied by different authors [105–109]. The different chemical nature of plastics (mainly aliphatic due to its polyolefin character) and coal (aromatic) affect to the choice of a solvent, as well as of the reaction conditions, for their joint processing. To circumvent this bound, a two stage process was proposed by Luo *et al.* [106] for the coprocessing of commingled waste plastics and coal, which is depicted in Figure 3.18. The use of two separate stages allows for a better selection of the reaction conditions and catalysts so higher yields of the desired boiling points products were attained.

In the first step, the plastics mixture (either a model one made up of 50% HDPE, 30% PET and 20% PS or an actual mixture formed primarily of HDPE and PP) was catalytically degraded at 440°C under 2.8 MPa of H_2 over different catalysts (HZSM-5 zeolite and

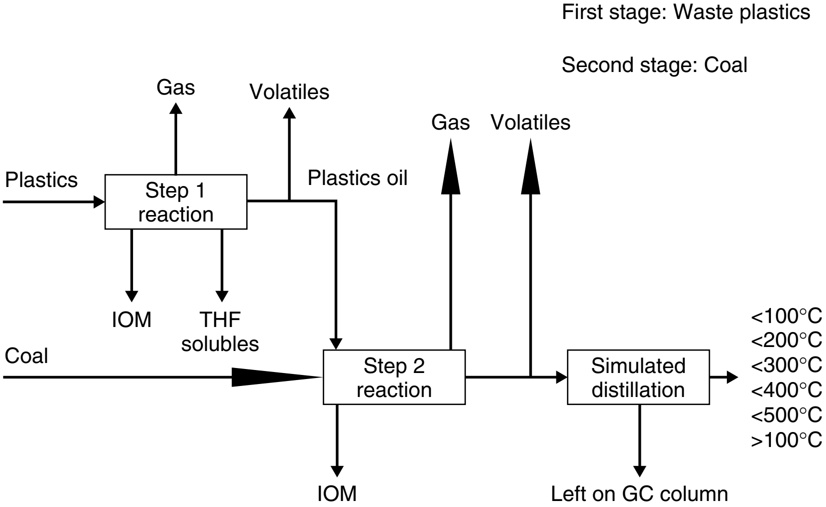


Figure 3.18 Scheme of a two-stage process for waste plastics and coal coprocessing [106]. (Reproduced with permission from Elsevier)

two commercial catalysts). The products resulting from the first stage were a gaseous hydrocarbon fraction, a liquid fraction soluble in hexane (plastics oil), other liquid fraction soluble in tetrahydrofuran (THF) and an inorganic matter insoluble fraction (IOM) formed mostly by ash. Conversions in this first stage was around 85–95% over all the studied catalysts, the highest amount of hexane-soluble oils compounds from the model plastic mixture being attained over zeolite HZSM-5 (75%). The hexane soluble fraction was used as solvent for the second stage wherein coal was hydrotreated at 400°C for 30 min under 5.6 MPa of H_2 using several slurry hydrotreating catalysts such as Mo naphthenate, Fe naphthenate (500–1000 ppm) or their combination plus sulphur (6000 ppm). Coal liquefaction is affected by the reactions conditions of the first stage that determine the composition of the produced solvent. These authors observed that the combination of HZSM-5 in the first stage and Mo-naphtenate and sulphur in the second one yielded both the highest conversion and production of hexane soluble fraction.

6.2 PETROLEUM CUTS

The possibility of cofeeding plastic wastes with petroleum cuts such as vacuum gas oil (VGO) [110], Arabian light petroleum residues [111], light cycle oil [84], lube oils [88] or even raw chemicals such as benzene [85] has been widely investigated in the literature. The underlying aim is to reduce the high viscosity of the molten plastics. However, there is a limit since the maximum amount of plastics in the mixture to achieve a convenient rheological behaviour must be at most within 5–10 wt%.

In this way, Ng [110] reported the catalytic cracking of blends made up of vacuum gas oil (VGO) and 5–10 wt% of high-density polyethylene in a fixed bed reactor at 510°C over a FCC catalyst. High conversion of HDPE was obtained although using large catalyst/oil mass ratios (in the range 2–6). The gasoline yields depended on the polyethylene content of the starting blend as well as on the operation conditions. The gasoline obtained with a 5% HDPE blend appears to be subsequently decomposed into gas and coke by secondary cracking reactions while with the 10% HDPE blend, a higher gasoline yield was attained (>50%).

Arandes *et al.* [84] studied the catalytic degradation of several plastics (polypropylene, polystyrene, polystyrene–polybutadiene) dissolved in a light cycle oil (LCO) in a riser simulator of a FCC unit using both a fresh and an equilibrated FCC catalysts. Similarly, De la Puente [85, 112] studied the catalytic degradation of styrene-based polymers dissolved in benzene streams in the same riser simulator. Although the reported results are promising, oil refiners are reluctant regarding the inherent risks for the normal operation of the refinery units.

Another alternative that has been recently reported considers the use of spent lube oil as cofeed in the catalytic cracking of plastics [88]. At present, there could be a bound because of the available amounts of used lubricating oils are lower than those necessary to reach the aforementioned limit of 5–10 wt% plastic content for an adequate viscosity of the mixture. However, the use of a screw kiln reactor has allowed LDPE–lubricating oil base mixtures with compositions ranging from 40/60 to 70/30 (%, w/w) to be cracked catalytically. This is a remarkable advantage, as plastic–lubricating oil mixtures with compositions more in line to those actually occurring in the market may be degraded.

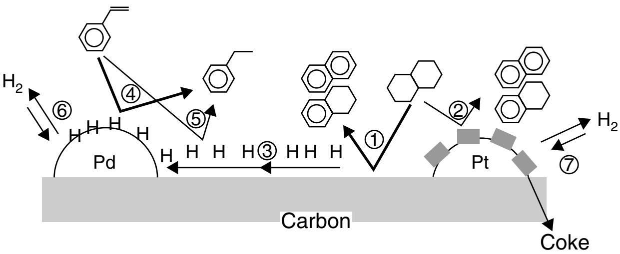


Figure 3.19 Reaction model of styrene based polymers over a carbon supported metal catalyst [57]: (1) Dehydrogenation on carbon; (2) dehydrogenation on metal; (3) hydrogen transfer; (4) hydrogenation on metal; (5) hydrogenation on carbon; (6) hydrogen desorption from metal; (7) hydrogen desorption with coking. (Reproduced by permission of Springer-Verlag GmbH)

Additionally, these authors also found that the presence of lube oil decreased the activity of the catalysts due to the presence of both sulphur- and nitrogen-containing compounds (4000 ppm of sulphur and 85 ppm of nitrogen) that poisoned the acid sites. Consequently, higher temperatures (450–500°C) should be employed to obtain complete conversion in the catalytic cracking of the LDPE-lubricating oil mixture over Al-MCM-41 and nanocrystalline HZSM-5 catalysts.

6.3 SOLVENTS

The use of solvents with hydrogen transfer properties offer interesting possibilities in the cracking of polymers. This was observed by Matsumoto [57] in the catalytic cracking of styrene-based polymers (polystyrene, poly-(4-methylstyrene), poly-(4-butylstyrene), poly-(α-methylstyrene) over metal supported carbon using decalin as solvent. Decalin possesses hydrogen transfer properties so the olefinic products derived from the catalytic cracking are thoroughly hydrogenated to the saturated form by hydrogen transfer reactions from the solvent, which is transformed into tetralin and naphthalene with simultaneous release of hydrogen (Figure 3.19). Plastic cracking in the presence of solvents with hydrogen donor ability allows for suppressing coke formation, being an advantageous choice for aromatic function-containing polymers.

7 CONCLUDING REMARKS

Catalytic cracking and conversion of plastics wastes is currently a field of intense research and open to innovative technologies to be discovered and applied. Significant advances have been carried out in recent years, with several commercial plants being already in operation based on the use of catalytic cracking for the plastic waste conversion into valuable products. However, there is still room for further developments. In this regard, the following fields of research can be foreseen in the next years:

- development of new catalysts capable of dealing with the heterogeneity of the plastic waste makeup and the diffusional/steric hindrances posed by their bulky nature;

- design of reaction systems appropriate to the high viscosity and low thermal conductivity of the plastics;
- study of the influence of the different additives and components in the performance of the catalytic process, regarding the diversity in origin of plastics wastes (urban, agriculture, etc.);
- improvement of the currently existing catalysts in order to achieve the preparation of specific and valuable raw chemicals (e.g. light olefins, aromatics, etc.) so as to get a better profitability of the whole plastic recycling system.

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4

Thermal and Catalytic Conversion of Polyolefins

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1 INTRODUCTION

Pyrolysis and cracking of waste polyolefins (plastics) can be categorized as the tertiary mode of recycling. Application of this type of recycling is reasonable especially in case of polyolefins when their further using in primary recycling (conversion into products similar in nature to the original product) and secondary recycling (conversion into products of different shape for less demanding products) is impossible. Pyrolysis and cracking are considered as alternative methods of the final processing of waste plastics such as polyolefins. In comparison with incineration, known as the quaternary mode of recycling, the tertiary mode of recycling is generally accepted. In thermal or catalytic cracking the main products of processing are gas, naphtha, both light and heavy gas oil fractions, and solid residue similar to coke. The main product of high-temperature pyrolysis process, 600–800°C, is C_2–C_4 olefins containing the gaseous fraction. Besides cracking and pyrolysis, other modes of the tertiary recycling can be applied: hydrolysis, ammonolysis or methanolysis for condensation polymers (polyethylene terephthalate, PET and polyurethane, PU) while gasification, hydrocracking, coking and visbreaking for additive polymers such as polyolefins, i.e. mainly polyethylene (PE), polypropylene (PP) and polystyrene (PS). Waste plastics cracking and pyrolysis can be especially profitable in the case of continuous increase in landfill taxes and the world cost of crude oil. This section presents some results of literature data on thermal and catalytic processing of waste polyolefins, types of applied processes, design of reactors and catalysts as well as possible products and their application and finally some economic considerations.

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2 GENERAL SCHEME OF WASTE POLYOLEFIN PROCESSING

Similarly to crude oil cracking the products of the waste polyolefin cracking process are hydrocarbon fractions. According to the process conditions different shares of gas, gasoline, light and vacuum gas oil fractions as well as solid residue (coke) can be obtained. The unsaturated character of these products makes the further treatment, i.e. hydrorefining or application as the feed in cracking or hydrocracking processes, necessary. Light gaseous fractions can be used as the source of C_2–C_4 olefins for polymerization or fuels for power generation. High-temperature processing of polyolefins, pyrolysis, similar to the petrochemical process can give gaseous olefins and liquid fractions composed of aromatics such as BTX fraction. Diverse applications of cracking products of waste plastics treatment proposed by BP are presented by Kastner and Kaminsky [1]. A modified scheme of waste polyolefin treatment is presented in Figure 4.1. According to the proposed technological scheme the prepared waste plastics (after selecting, washing if necessary and granulating) are submitted to the cracking process and the products obtained can be used with naphtha as feed for a steam cracker or with vacuum gas oil as feed for fluid catalytic cracking. Gasoline and light gas oil fractions can be delivered to a hydrorefining unit and processed with similar refinery fractions.

Chemical composition of waste plastic cracking products depends on shares of the individual polymers (PE, PP, PS) in the feed and process parameters. This fact decides the technological application of the final products. Important products of the cracking process, both petroleum fractions and waste plastics, are coke residues. Coke residue yield increases considerably, up to 10 wt%, in cracking of municipal and industrial waste plastics since they contain various inorganic impurities and additives. It can be applied as solid fuel, like brown coal. In the fluid cracking the solid residue is continuously removed from the process by combustion in a regenerator section.

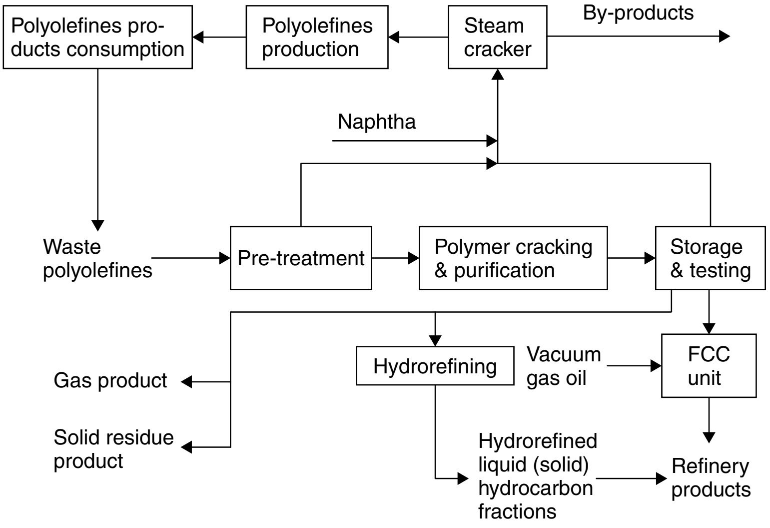

Figure 4.1 Cracking and pyrolysis of waste polyolefin processing, main products and their application [1]. (Reproduced by permission of Hydrocarbon Processing)

Waste plastics potentially can also be processed in hydrocracking process as an additional feed stream in mixture with vacuum gas oil or crude oil residues. Careful plastic segregation is then necessary since inorganic additives and impurities of plastics can foul the hydrocracking catalyst. Noncatalytic high-temperature olefin pyrolysis (700–800°C) and coking are insensitive to fouling.

3 WASTE PLASTICS SUITABLE FOR CRACKING AND PYROLYSIS

Cracking and pyrolysis are the suitable processes for the tertiary recycling of additive polymers such as polyolefins, mainly polyethylene (PE), polypropylene (PP), polybutadiene (PBD) and polystyrene (PS). Small admixtures of other plastics, such polyethylene terephthalate (PET), polyvinyl chloride (PVC), less than two 2%, are admissible yet not desirable. Taking into account the total share of polyolefins in plastics production (∼70 wt% including PS) they are the highest environmental problem. Their chemical composition (carbon and hydrogen) close to crude oil is the reason that this type of waste plastic can be processed simply by the refinery medium-temperature methods such as thermal and catalytic cracking, visbreaking or coking (temperature generally lower than 500°C) or high-temperature noncatalytic processes (600–800°C), i. e. pyrolysis. The relatively low density of PE, PP, PS in comparison with PVC and PET is the basis of water separation.

Commingled post-consumer or municipal waste plastics selected for cracking or pyrolysis also contain other elements such as oxygen, nitrogen, sulphur and about ten metals such as Al, Ca, Na (>100 ppm each) and Sb, Ba, Cr, Co, Cu, Fe, Pb, Mg, P, Zn, generally below 50 ppm each. Inorganic compounds in waste plastics are contained in the different types of additives and impurities (product remains). The total content of mineral components in waste plastics (approximate analysis) attains value 0.5–1 wt% (ash) [2, 3]. In our waste cracking experiments studies some PE samples selected from municipal wastes contained ∼0.6 while PS even more than 3 wt% of inorganic components [4]. Theoretical hydrogen content in PP and PE $(C_2H_2)_n$ is 14.28 wt%. The reduced hydrogen content in waste plastics, e.g. 13.7 wt% [2, 3] is a result of some oxygen or nitrogen content (admixture of PET or PA), inorganic components or PS (7.69 wt% H_2 content). Depending on the origin the hydrogen content in crude oil is 11–14 wt% [5]. Therefore from the cracking efficiency point of view, PE and PP are excellent feeds, better than PS since in the cracking processes they give a lower coke yield. In the course of cracking inorganic impurities and additives in waste plastics are deposited in coke (solid carbon residue). The high yield of coke in the cracking process diminishes the yield of light hydrocarbon fractions and complicates the process since it deactivates the catalyst and deposits over heat exchange surface of the reactor.

4 MECHANISM OF CRACKING PROCESSES

The main task of thermal and catalytic cracking is decomposition of large (long) hydrocarbon molecules into smaller ones. High-molecular feedstock, such as paraffin hydrocarbons and plastic chains produces lower molecular paraffins and α-olefins [5]:

$$\mathrm{R{-}CH_2{-}(CH_2)_x{-}CH_2{-}CH_3 \rightarrow R{-}(CH_2)_m{-}CH_3 + CH_3{-}(CH_2)_n{-}CH{=}CH_2}$$

Cracking of primary products, olefins, give higher molecular hydrocarbons by polymerization or tar and coke:

$$CH_2{=}CH_2 + CH_3{-}CH{=}CH_2 \rightarrow CH_3{-}CH_2{-}CH_2{-}CH{=}CH_2$$

$$R{-}CH_2{-}CH{=}CH_2 + R'{-}CH_2{-}CH{=}CH_2 \rightarrow \text{tar, coke}$$

It is generally accepted that thermal cracking is a free radical chain reaction (a free radical is an atom or group of atoms with an unpaired electron). Free radicals react with hydrocarbons and produce new hydrocarbons and new free radicals:

$$R{-}CH_2{-}CH_2{-}CH_2{-}CH_3 + CH_3^{\bullet} \rightarrow R{-}CH_2{-}CH_2{-}CH_2{-}CH_2^{\bullet} + CH_4$$

Free radicals can decompose by giving olefins and new radicals [6]:

$$CH_2{-}CH_2{-}CH_2{-}CH^{\bullet}{-}CH_2{-}CH_2{-} \rightarrow R{-}CH{=}CH_2 + CH_3{-}CH_2^{\bullet}$$

The mechanism of thermal cracking and pyrolysis is discussed by Buekens *et al.* [7]. They proposed four types of pyrolysis reaction. In the case of PE, PP and PS cracking only two type of the mechanisms were stated:

1. End-chain scission or depolymerization – production of monomers (stated for PS, polyethylstyrene, polyisobutene);
2. Random-chain scission, randomly cutting into fragments of various length (stated for PE, PP, PS, polyisobutene, polybutadiene).

In the PS cracking process both mechanisms are possible and therefore ~60 wt% of monomer can be recovered. Cracking of PP, PE and other polyolefins occurs by random-chain scission and therefore a broad hydrocarbon spectrum is produced.

At higher cracking temperature other reactions, i.e. cyclization and dehydrogenation of naphthenes and hydrocarbon pyrolysis with production of benzene and ethylene, butadiene and hydrogen are also possible.

Since cracking rate increases with molecular weight of the feed (average number of carbon atoms) then the rate of long-chain polyolefin cracking should be considerably higher in comparison with the typical cracking feeds (vacuum gas oils, 20–30 carbon atoms in chain) [6]. At the same cracking parameters, 500°C and presence of cracking catalyst, conversion of *n*-pentane attained a value less than 1 while conversion of *n*-hexadecane was 42 wt%.

The presence of catalyst is necessary in the catalytic cracking process. Acid cracking catalysts produce carbonium ions by protons addition to olefins or abstracting of hydride ions from hydrocarbon molecules:

$$\begin{aligned}&R_1{-}CH_2{-}(CH_2)_x{-}CH{=}CH{-}CH_2{-}R_2 + H^+\\&\quad\rightarrow R_1{-}CH_2{-}(CH_2)_x{-}{}^{+}CH{-}CH_2{-}CH_2{-}R_2\end{aligned}$$

$$\begin{aligned}&R_1{-}(CH_2)_x{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}R_2 + R^+\\&\quad\rightarrow R_1{-}CH_2{-}(CH_2)_x{-}{}^{+}CH{-}CH_2{-}CH_2{-}CH_2{-}R_2 + RH\end{aligned}$$

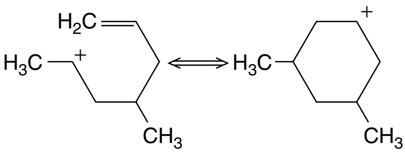

Figure 4.2 Intramolecular reaction between carbonium ions and double bond, cyclization

Polymer chains can be cracked through so called β-scission:

$$R_1\text{–}CH_2\text{–}(CH_2)_x\text{–}{}^{+}CH\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}R_2$$
$$\rightarrow R_1\text{–}CH_2\text{–}(CH_2)_x\text{–}CH{=}CH_2 + {}^{+}CH_2\text{–}CH_2\text{–}R_2$$

This is a mechanism of polyolefin cracking. The main polymer chains are reduced by reaction with protons or other carbonium ions, followed by chain scission giving C_{30}–C_{50} oligomeric hydrocarbons [7]. As a result of further, secondary cracking reactions by β-scission of C_{30}–C_{50} hydrocarbons, gas and lower-molecular liquid C_{10}–C_{25} hydrocarbons are produced. Other reactions are double bond and saturated hydrocarbon isomerization as well as methyl 'group shift'.

Production of carbonium ions gives the possibility to produce different hydrocarbons molecules, e.g. cycloparaffins and aromatics by cyclization and dehydrogenation reactions (Figure 4.2). In the first step presumably intramolecular reactions between carbonium ions and double bonds take place.

In the next step dehydrogenation reactions give aromatic derivatives. The application of cracking catalyst not only lowers the cracking temperature and increases the reaction rate, but also results in higher production of iso-alkanes and aromatics.

5 WASTE PLASTICS PROCESSING

5.1 *CATALYTIC AND THERMAL CRACKING PROCESSES: TYPICAL PRODUCTS*

The most exhaustive studies on waste plastics processing by cracking and pyrolysis methods were carried out at Hamburg University by Kaminsky and co-workers [e.g. 1, 8]. As a result of these studies various variants of the process were worked up. They used different types of the feed compositions and process parameters, starting from the low-temperature coking and cracking parameters (temperature lower than 500°C) and liquid and wax fraction as the main products up to pyrolysis parameters (600–700°C) and C_2–C_4 olefins and aromatic derivatives as the main products. The fundamental advantage of these studies is a continuous flow system and a fluidized-bed type of reactor (1–3 kg of waste plastic pellets per hour). Thermal cracking of PE in a fluidized-bed reactor gives higher-boiling products in comparison with PP cracking (50 and 70 wt% of <500°C boiling products, respectively). One can observe almost linear change of fraction product composition: gas, <500°C and >500°C boiling fractions when PP content in the feed changes from 0 to 100%. Small addition of PS to PP, PE or PE/PP mixture does not change product composition appreciably.

Other results obtained at Hamburg University [9] pointed out the advantages of application of spent FCC catalyst in the cracking process. It was found that processing of PS in the temperature range 370–515°C in the presence of FCC catalyst gives high yield of coke (up to 20%) and relatively low styrene yield. On the other hand a noncatalytic, thermal process gives above 60% styrene yield, accompanied by trace quantity of coke. At typical FCC cracking temperature (515°C) processing of PE results in almost 50% C_1–C_4 gaseous fraction yield, high shares of branched hydrocarbons and ~10 wt% of coke. Thermal PE cracking allows one to obtain low gas and coke yields (<2 wt%) while liquid and wax fractions reach over 97 wt%.

Efficient thermal or catalytic cracking of waste polyolefins can be realized in tube reactor with an internal mixer [10]. Depending on the type of raw material (commercial PE, PP and PS) application of this reactor system in thermal process makes it possible to obtain 85 wt% of liquid, semi-solid or solid product, 0.6–10 wt% gaseous product (mainly C_1–C_5 hydrocarbons) and 1–5 wt% of solid residue. In waste plastics cracking, yields of carbon residue and gas can increase up to 5–10 wt%. The main liquid products (or solid at ambient temperature) are characterized by high olefins content, bromine number more than 50 g Br_2/100 g and freezing point above 40°C for the feed with high PE content. The increase in PS and PP content in the feed is accompanied by lowering in freezing point of the main products, even below −15°C. High shares PP containing cracking feeds are especially suitable for production of light oil fractions of low freezing temperature (even −25°C) and high octane index (>50). Solid, coke-like residue, depending on the feed contains as much as 30–50 wt% of mineral components, including catalyst if used, and its calorific value, similar to brown coal, attains value ~20 MJ/kg.

The main difference between two types of the process, catalytic and thermal is in the different conversion levels and products yields. High gas (~50 wt%) and gasoline yields (~15 wt%) as well as low yield of gas oil and 10 wt% coke were found in the catalytic processes (commercial catalysts). On the other hand the thermal cracking processes give low gas, gasoline and light gas oil yields in connection with very high yield of waxes (over 87 wt%) and small yield of coke [9]. Low coke yield in thermal process is the result of the low cracking level of the polymer feed.

The high influence of cracking catalyst on PE conversion was confirmed by Aguado *et al.* [11] in a continuous screw kiln reactor. The application of a sophisticated laboratory Al-MCM-41 cracking catalyst and process temperature of 400–450°C led to 85–87% yield of gas and gasoline fractions (C_1–C_{12}). Besides olefins and *n*- and iso-paraffins some quantity of aromatics, 5 wt% was determined in the process products. In the same reactor system with a noncatalytic process the gas yield was halved while similarly as in case of the fluid reactor system yields of gas oil and heavy waxes fraction (C_{13}–C_{55}) attained values of ~62% (compared with 4 wt% in catalytic process) [12].

The considerably lower activity of other catalysts in PS cracking process, HZSM-5 and Al_2O_3-SiO_2 of higher acidity is explained by hydrocarbon cross-linking and heightened carbon residue yield. Similarly to the fluidized-bed process [9], the thermal PS cracking results mainly in styrene while HMCM-41 catalyzed process produces mainly benzene and ethyl benzene. Alkaline materials, e.g. magnesium or barium oxide, in PS cracking present high activity and selectivity to styrene [13]. This suggests quite different reaction mechanisms, i.e. that thermal cracking proceeds through a free radical chain mechanism while carbenium and anionic ions are involved in acid and alkaline catalysis cracking processes.

Increase in thermal process temperature up to 685–715°C in a fluidized-bed system (Hamburg University Pyrolysis Process-HUPP) and application of a mixture of municipal plastic wastes resulted mainly in gaseous products, over 41 wt%, of which olefins constituted 15%, and aromatic (BTX)-containing liquid products [14]. Considerably better results from the point of view of C_2 and C_3 olefins yield were obtained in other experiments. The application of steam as fluidization agent instead of circulation pyrolysis gas enabled an increase of C_2–C_3 olefins yield from 48 to 60%, accompanied by decrease in BTX yield from 24 to 11 wt% [15].

Analogous results were achieved in the fluidized-bed system by Williams *et al.* [16]. They found out that raising the PE pyrolysis temperature from 500 to 700°C gives an increase in gas yield from 11 to 71% and that C_2–C_4 olefins content increases from ~7 to above 53%. Hydrogen content in the gaseous fraction attained a level of 1%. At the same time oil and wax yields were diminished from 89 to 28.5 wt% in which 25% was identified as mono- and polyaromatic hydrocarbons. Noticeable quantities of aromatics (~2.5 wt%) in the products of the process at ~600°C were determined (Table 4.1).

Process temperature, as well as waste polyolefin composition and type of catalyst used are then the most important process parameters. It is evident that a process temperature below 500°C is the most suitable range for refinery fractions while 600°C and higher are appropriate for olefins production.

According to Bockhorn *et al.* [17], cracking of waste plastics can be carried out thermally in a three-step reactor cascade at laboratory scale in a reactor filled with special moving steel spheres. At the lower temperature (330°C) quantitative PVC dechlorination takes place, at 380°C polystyrene is decomposed with high styrene yield and 440°C is suitable for PE cracking into paraffins and olefins. The molecular weight of the cracking products obtained is a function of residence time of the feed in the reactor zone. In the presence of PE (or PVC) cracking PS gives ethylbenzene as a result of the hydrogen transfer from PE chains to styrene during the process.

In the range of higher temperatures, 475–525°C, commingled waste plastics conversion increased in laboratory autoclaves from 79 to 99.5%, gas oil yield decreased from 48 to 19% while yield of cracking gas increased from 32 to 66%. It is visible that increase in primary and secondary plastic conversion takes place. At the highest gas production the yield of coke attained 8%. Even at the lowest process temperature, i.e. 475°C almost total plastics conversion was attained in 15 min and the main cracking products were light and heavy gas oils at 1–2% coke and 20% gas yields. On the basis of kinetics analysis the authors concluded that cracking of polymers such as PE occurs to a greater extent near the end of the polymer chain rather than in the middle of it [2].

Table 4.1 Influence of process temperature on product yields from fluidized bed pyrolysis of LDPE [16]. (Reprinted from *Journal of Analytical and Applied Pyrolysis*, 1999: **51**: 107, P Williams & E Williams with permission from Elsevier)

Process products	Process temperature, (°C)				
	500	550	600	650	700
Gas (wt%)	10.8	21.4	24.2	40.1	71.4
Oil (wt%)	43.9	43.2	51.0	47.8	24.6
Wax (wt%)	45.3	35.4	24.8	12.1	4.0
Olefins in gas (wt%)	6.9	16.5	17.43	31.0	53.1

Comparative studies of thermal and catalytic PP cracking indicate a strong influence of catalyst on total conversion in the temperature range 340–380°C as well as gas and gasoline yield [18]. The results also point out the possibility of applying an equilibrium FCC catalyst [19]. Similar studies were carried out in other laboratories [7, 20]. The effect of the application of cracking catalyst, including equilibrium FCC catalyst is the increase in plastics conversion level, higher gas and liquid product yields as well as lower boiling temperature range and density of the liquid cracking products obtained. This seems to be a good solution. However, one has to remember that equilibrium FCC catalysts contain heavy metals (mainly V and Ni) and they are classified as environmentally dangerous materials. In the course of the cracking process they are collected in coke residues which have to be utilized.

High conversion level of waste plastics can be also attained in hydrocracking process with using of NiW-HY zeolite-based catalyst [20]. The main process products are good-quality gasoline fractions, with small olefins content. The basic drawback of hydrocracking is the necessity of using hydrogen, expensive catalysts and increased pressure (high cost of reactors and other plant equipment). Hydrocracking catalysts are also exposed to deactivation by mineral components in the plastic feed. Bergius – Pier hydrogenation technology was adopted by VEBA company for hydrocracking vacuum residue (waste plastics mixture at 450–490°C and pressure 150–250 bar, 40 000 tons per year output). The applied process catalyst and parameters gave ~90 wt% conversion [21].

Sophisticated catalysts, such as ZSM-5 or HZSM-5 [22] and other zeolites are also suggested in numerous papers, e.g. REY [23], HY and H-mordenite [24], Re-zeolite-based Engelhardt FCC commercial catalyst [25], and steamed commercial zeolite catalyst [26]. These investigations are mainly devoted to fundamental studies and the correlation between feed composition, catalyst properties, process parameters and efficiency connected with product distribution. Iron supported on silica–alumina, mesoporous silica and active carbons serves as the next example of materials applied in the waste plastics cracking [27, 28]. On the other hand, according to some results [29] application of cracking catalysts such as Zn-13X, Fe-5A and CoMo-HY are ineffective in waste plastics cracking.

The appropriate solution seems to be the application of cheap quartz, alumina and activated clays in this process [30, 31]. In some patents [e.g. 31] and papers [7] platinum or reforming catalysts are suggested as suitable for this process.

It is surprising that small-pore zeolites (pore size lower than 1 nm) are so frequently proposed as components of the catalysts of large-molecule waste polyolefin cracking [e.g. 22–24]. The very difficult transport of the melted plastics material into the catalyst pores is the fundamental problem with catalytic cracking of waste plastics. Therefore, cracking of long hydrocarbon chains can occur mainly at the external surface area of the catalyst grains while products of these primary reactions can be further cracked in the catalyst pores (secondary reactions). This is especially true in the case of PS with side phenyl groups in the polymer chain that create steric hindrance. Serano *et al.* state that this obstacle can be overcome by using large-pore materials such as (H)MCM-41 [12].

It seems that, from a practical point of view, equally or even more important than a type of potential cracking catalyst are impurities in real waste plastics. Only sparse research work has been devoted to problems such as possible PVC and heavy metals content in the cracking feeds. In the course of segregation and preparation of the feed some PVC can be included and then the cracking products obtained will contain chlorine or its compounds. According to Kaminsky *et al.* [14] and Simon *et al.* [32] gaseous cracking or pyrolysis products are free of chlorine if HCl is removed, e.g. by calcium carbonate, liquid products can contain up to 15 ppm chlorine while the largest quantity of chlorine is concentrated in tars or solid residues and mineral fluidization mediums. Relatively large quantities of chlorine can be concentrated in water (if present in the cracking products). At longer residence time or high process temperature chloroorganic compounds are totally decomposed into HCl and hydrocarbons. Heavy metals, such as Na, K, Cr, Mn, Zn, Cd, Sb derive from product residues and auxiliary agents used in polyolefins processing, such as stabilizers or plasticizers and others. They are mainly concentrated in soot or other solid residues, e.g. Zn content in soot attains even more than 1 wt %, while the oil fraction can contain about 20 ppm Zn [32].

5.2 COPROCESSING OF WASTE PLASTICS WITH OTHER RAW MATERIALS

Lubrication oil wastes and waste plastics are very similar materials from a chemical composition point of view; they are of organic origin and are composed mainly of carbon and hydrogen. Both feeds can be utilized by thermal or catalytic cracking or pyrolysis process. One of the differences is that annual waste oils amounts are considerably lower and account for about 15–20% of annual waste plastics amounts [33, 34]. Relatively high melting temperature, high viscosity and low thermal conductivity of waste plastics can cause difficulties in their direct feeding with the typical equipment. Mixing and diluting of waste plastics with waste oils and cracking is an optional method of common processing. Due to rheological properties, according to Lovett *et al.* [35], the maximum content of waste plastics in waste oils in commercial scale should not be higher than 10%. The further studies of Serrano *et al.* [34] showed that application of laboratory kiln reactor and thermal cracking temperature 450–500°C enables one to obtain over 95% degradation of LDPE–waste oil mixture (70/30–40/60) and gives mainly C_{13}–C_{22} and C_{23}–C_{40} fractions (*n*-paraffins and 1-olefins). It is evident that only partial waste oil conversion was attained (C_{28}–C_{41} hydrocarbons), since it is more thermally stable than LDPE. They obtained much better results by using HZSM-5 and Al-MCM-41 cracking catalysts at the same temperature range and 70 wt% LDPE content in waste oil. In this case 65 and 50% selectivity to C_5–C_{12} fraction was determined for Al-MCM-41 (mainly olefins) and HZSM-5 (olefins and aromatics), respectively. Kargöz *et al.* carried out similar experiments, but they applied municipal waste plastics and vacuum gas oil mixture under hydrogen pressure [36].

Light cycle oil, a highly aromatic FCC product (e.g. 67% aromatics content) can be used as solvent for PS and PS-BD (polystyrene–butadiene) mixture, component of synthetic rubber. Arandes *et al.* [37] proved that this feed can be further successfully thermally or catalytically cracked, giving mainly gasoline fractions. They contain a high quantity of valuable components for petrochemistry, styrene and C_4 olefins.

Gebauer *et al.* [38] suggest visbreaking of waste plastics with vacuum residue. This is a thermal process, applied in refineries in order to convert partially atmospheric vacuum residue and decrease viscosity and melting temperature. According to the authors, addition of 5% of waste plastics in laboratory tests does not influence noticeably the process parameters and final products properties. As in the case of LCO and VGO fractions the application of vacuum residue and mixture of waste plastics is applicable in refineries.

It is worthy mentioning two other possibilities of waste plastics processing, both based on gasification. In the first case, co-gasification of plastics and biomass, gives the possibility to utilize wastes accompanied by the control of hydrogen content in the synthesis gas produced [39]. According to Fink and Fink [40], synthesis gas from waste plastic gasification can be 'put in' pre-selected crude oil wells. These wells should be located near the gasification plant and the main goal of this method is to enhance crude oil recovery in the future.

Co-coking of waste plastics and coal-tar pitches in the temperature range 200–400°C yields reaction pitches which can be further applied as additives to coal blends and as a consequence improve their coking properties [41]. A quantity of lower-boiling products can be obtained as a result of the coking process. A similar process is presented in a German patent [42], but in the presence of granular calcium oxide in the temperature range 600–1400°C and at CaO: waste plastics ratio 1:1–3. The main products are calcium carbide and a gaseous fraction which can be used for power generation.

Some inventors suggest conversion of waste polyolefins and the waxy Fischer–Tropsch fraction into lube base oils in relatively mild thermal conditions, i.e. at 150–350°C and short residence time [43]. Both raw materials are submitted to pyrolysis and after thermal treatment the heavy liquid fractions can be hydrotreated and isodewaxed in order to obtain high viscosity index lubrication base oils while medium fractions after isodewaxing can be applied as the components of diesel or jet fuels. Polyolefins can be thermally or catalytically processed (Mn, V, Cu, Cr, Mo or W compounds as active phase) with natural or synthetic rubbers, paraffin or lignite waxes or other polymers [44]. Mixtures of PP and PE can be applied as good-quality feed for production of microcrystalline waxes [45]. At relatively low temperature, i.e. 350–430°C cracking is completed with partial melt recycling and destructive distillation (under normal pressure or vacuum).

6 REACTOR DESIGN

For acceptable efficiency waste polyolefin cracking process should be realized in continuous mode. For the same reason, as well as due to high coke and mineral residue yields, construction of reactor for waste plastics cracking has to enable continuous coke removal. The best solution is a fluidized-bed process, known in refineries as fluid catalytic cracking (FCC) in crude oil processing with cracking catalyst or fluid thermal cracking with coke or mineral grains as the fluidization medium [5]. In refinery implementations the coke-covered cracking catalyst (or inert material) is transported to a regenerator and after regeneration it is returned to the cracking reactor. Part of the deactivated catalyst is discharged from the system and the same quantity of fresh catalyst is put into the reactor. A thermal and catalytic fluid cracking reactor was applied in extensive studies by Kaminsky *et al.* [1] yet without catalyst regenerator operation.

According to a US patent [46], cracking or liquefaction of waste plastics is realized in a sequential three- or four-screw extruder system with increasing process temperature. Similarly, the catalyst (if used) is discharged with coke and mineral residue. At the end of the process, the distillable hydrocarbon fraction is separated from solid residue and coke.

In another US patent, [47], polyolefins and tires scrapes mixture is fed to the batch reactor equipped with a special mixer. A screw extruder or other device is used for feed supply. In this semi-continuous reactor raw material is fed to the reactor for some time and the main products are gaseous and liquid fractions as well as a mixture of soot, mineral impurities and coke. At the end of the production cycle the process is stopped and the direction of mixer rotation is reversed. In this cycle mixer arms are scraping coke from the reactor walls. The main disadvantage of this solution is a semi-continuous working mode, relatively low output and problems with application of the cracking catalyst.

In the next reactor design [48] mixer arms have exactly the same dimensions and shape as the internal reactor part and in the course of the run coke residue is scraped by mixer arms from the heated reactor walls. Scraped coke falls down and is collected at the bottom of the reactor and removed with part of the reaction mixture by a suction pipe. The main process products are the gas fraction (used for heating purpose), gasoline and light gas oil and paraffin fractions.

A batch-type reactor equipped with a screw feeder and mixer is offered by US patent [49]. A special grate is mounted inside the reactor, above the cracked melted waste plastics mixture. Scraped waste plastics which are submitted to the cracking reactor melt at the grate and fall down to the reaction mixture. As in the case of previous patent description, in the course of cracking process a mixer of a special construction scrapes coke form the reactor walls and then coke is removed from the specially shaped reactor bottom by a screw transporter. The process temperature attains level of 450°C.

Gasification of waste plastics in a plasma reactor and the application of the high calorific gas produced for production of electricity, followed by using waste heat from the turbine for steam generation, has been presented by German inventors [50]. There is no information about process efficiency and the main advantage of the solution is the possibility of using various feed compositions.

According to Polish inventors [51], semi-continuous reactor operation can be secured by special reactor construction equipped with an exchangeable heating coil. The heating coil, fired by flue gases, melts, heats and cracks waste plastics and as a result of the cracking process it becomes covered by solid carbon residue. The special construction of the cracking reactor enables it to coke remove by coil vibration. The heating coil can be easily dismantled and exchanged after stopping the process.

Because of inorganic components in waste plastics, thermal, noncatalytic processes present some advantages. In order to obtain high conversion Chinese inventors [52] propose a two-step process: thermal cracking in the first step in order to obtain partial cracking of waste plastics and to separate inorganic components, and in the next step catalytic cracking of the product over a fixed-bed catalyst.

Numerous cracking reactor constructions have been patented by Japanese and Chinese inventors. Similar cracking reactor construction is presented in two patents [53, 54]. Waste plastics are fed using a screw extruder followed by a parallel-shaped tube reactor with internal conveying and mixing divided sequentially for melting, cracking and evaporating zones. Japanese inventors have developed a tube cracking reactor with screw mixing and transport device [55]. Although the design idea of these reactors is not easily comprehensible it is evident that an important advantage of these cracking reactors is removal of coke, carbon residue, and catalyst (if used) from the reactor interior. There is no information about output of the reactor systems.

A tubular reactor of special design internal screw mixer has been developed at Wroclaw University of Technology [56, 57]. The melted plastics from a screw extruder are passed to the multi tube-cracking reactor where they are cracked in the temperature range 420–500°C. The role of the specially shaped internal mixer is to mix the melted plastics, to scrap coke from the internal surface of the tube reactor and to remove coke from the reactor. The removed coke grains drop down to the coke receiver at the end of the reactor tube while hydrocarbon vapor mixture flows sequentially to air and water coolers and next to the gas–liquid separators. Experiments carried out in the laboratory (0.3–2 kg) and pilot-scale plants with 20–30 kg per hour capacities showed that this type of reactor can find commercial application in the continuous process. Its basic advantage is continuous coke removal from the reactor tubes. It is planned that at the end of 2005 the first reactor unit of a commercial plant of ~2000 tons annual output will start its activity. The cracking reactor unit will be composed of 6 or more tubes with internal mixers and it will enable both thermal and catalytic cracking of waste polyolefins.

It seems that fluid-bed cracking reactor (thermal or catalytic) is the best solution for industrial scale. However, regeneration and circulation of so-called equilibrium cracking catalyst is possible for relatively pure feeds, for instance crude oil derived from vacuum gas oils. Municipal waste plastics contain different mineral impurities, trace of products and additives that can quickly deactivate the catalyst. In many cases regeneration of catalyst can be impossible. Therefore in waste plastics cracking cheap, disposable catalysts should be preferably applied. Expensive and sophisticated zeolite and other molecular sieves or noble-metal-based catalysts will find presumably limited application in this kind of process. The other solution is thermal process, with inert fluidization agent and a coke removal section or multi-tube reactor with internal mixers for smaller plants.

7 PILOT PLANTS AND COMMERCIAL PLANTS

Thermal or catalytic cracking are the typical refinery processes and therefore BP Chemicals built a fluid cracking plant for waste plastics at the Grangemouth refinery in England [58–60]. This was a pilot plant of 100 kg/h capacity for cracking of commingled waste plastics composed of 80% PE and PP, 15 wt% of PS, 3 wt% of PET and 2% of PVC. Sand was used as fluidizing agent and the process temperature was varied in the range 400–600°C, close to FCC temperature or higher, i.e. olefin pyrolysis. According to the pilot plant data the BP process is highly effective from the point of view of light C_2–C_4 olefins yield (~60%). The other process products are gasoline and coke yet there is no information about their yields. It was foreseen in 1993 that refinery plant of 500 000 ton per year output would be built in 2000 or even later. This would be local plant for cracking of waste plastics from the area of about 10 000 km^2. A two-stage variant of this technology was pursued by BASF in Germany [21, 62]. In the first step a low-temperature reactor dechlorination of PVC was realized and next the semi-product obtained was submitted to a thermal cracking reactor. Oil fraction was the main product; gaseous fraction product could be catalytic cracker feed while HCl from the dechlorination stage could be recycled to PVC production. It was planned in the 1990s to build a plant to process 300 000 tons of waste plastics per year.

A similar idea of waste plastics utilization was developed by Shell Research in Amsterdam. It was foreseen that a two-step thermal cracking plant for processing of ca 100 000 tons of wastes per year should be the receiver of waste plastics for local agglomeration [60]. There is no information about commercial implementation.

Various fluidized-bed processes were based on the discussed earlier HUPP design [1]. On the base of vast laboratory studies the fluid cracking pilot plant was built in Ebenhausen near Ingolstadt. This was a fluidized-bed process with ∼8-m high cracking reactor and capacity of 800 kg per hour as well as sand and pyrolitic gas as fluidizing agents, working in the temperature range 500–800°C. It was feasible to crack PS at 515–540°C in order to obtain styrene monomer and to pyrolyse PE at 780°C with C_2–C_4 olefins and mono- and polycyclic aromatics as the main products [58]. When PVC was a component in the waste plastic feed it was possible to add calcium oxide to wastes in order to remove hydrogen chloride or gaseous ammonium to fluidizing gas and remove HCl as ammonium chloride. According to the author's opinion waste plastics cracking in a fluid-bed reactor should be economically viable at a capacity of ∼40 000 tons per year. Tiltmann in his book [62] presents two experimental plants based on rotary kiln and fluidized bed reactors. Up till now there is no information on their application in industrial scale.

ZSM-5 based catalyst and continuous cracking process are the main features of the Fuji Process. In the temperature range 420–450°C and 80% polyolefins and polystyrene mixture as feed, gasoline and gas oil fractions are the main products. The special reactor design, similar to the H-Oil hydrocracking reactor with boiling catalyst bed and partially liquid product recycling, enables continuous catalyst exchange and regeneration [63].

The largest cracking plant for waste plastics processing in Poland (ca 10 000 tons waste plastics per year) is operated by Agrob Eko Company (Zabrze). The cracking reactors (six units, each ∼20 m^3) with mixers and internal heat exchangers are operated in the temperature range of 380–460°C. The feed for the plant is spent lubrication and technical oils as well as waste plastics (50 wt%), cracking products are liquid hydrocarbon fractions, bp$<$ 400°C, gas 7–8 wt% and coke 10–12 wt% [64]. Reactor construction allows for semi-continuous operation. After cracking of ∼60 tons of wastes reactor operation is stopped for cooling, and for vapor and coke removing (scrapping) from the internal surface of the cracking reactor. Six cracking reactors make continuous plant operating possible. It is a catalytic cracking process with silica–alumina as catalyst.

Although the idea of thermal or catalytic cracking or liquefaction of waste plastics seems to be simple and profitable, no successful and widely licensed technology is presented in the technical literature. Even if there is some press information about pilot-scale technology and its efficiency there is no further information about industrial implementation and/or transferring of the technology to other companies. The reason for is that up till now there has been no good and profitable commercial process. Any thermal processing of waste plastics, similarly to cracking or coking of heavy naphtha fraction, produces a considerable quantity of coke. It deactivates cracking catalyst in fixed beds and coke deposits on the surface of heat exchangers makes long-term operation of the process impossible. Therefore, as in case of refinery cracking processes the best solution is the application of the fluidized-bed operation. This type of process presents numerous advantages in large-scale crude oil fraction processing of hundreds thousands of tons per year or more. Continuous dosing of catalyst and continuous coke removal, together with the spent catalyst, accompanied by simultaneous catalyst regeneration and recycling ensures efficient process exploitation. This is not possible, or it is too expensive and commercially unaccepted, in the small plants. On the other hand the application of the other type of reactor, e.g. a batch one with mixers, can be exploited only semi-continuously. A few days working period has to be followed by a cleaning and coke removal period. A continuous mode of exploitation is possible in tube reactors with internal mixers and screw extruder feeding. However, this type of reactor can be exploited in rather small scale with waste plastic cracking output of 10 000 tons per year.

8 ECONOMIC ASPECTS

According to the Packaging Research Foundation (USA), costs of tertiary waste plastics recycling (fuel fractions or monomer production) can not be recovered with an oil price of ∼25–30 USD per barrel. Subramanian [65] comments on advanced, chemical plastics recycling in the USA (glycolysis, ammonolysis and pyrolysis). At the same time he also states that polyolefins are high-calorific solid fuels, similar to fuel oil and that 114 waste-to-energy (WTO) facilities were working in 32 states in the USA. In any economically viable recycling process the costs of collecting, sorting and washing should be repaid by reclaiming products from the collected wastes. There is no doubt that waste plastics have to be utilized. Then the main problem is whether they should be combusted in WTO facilities or pyrolyzed or cracked in order to obtain monomers or gaseous, liquid and solid hydrocarbon fractions. It is evident that from an economic point of view prices of waste plastics cracking products (gasoline, light gas oil and heavy wax fractions) have to be correlated with the crude oil world price. It is necessary to add that waste-plastics-derived products are sulfur-free, composed mainly of gasoline and light gas oil fractions, suitable for fuel production. For instance when the price of crude oil amounted $30 US per barrel, i.e. ∼$0.197 US per kg, Polish refineries offered a price equivalent to $0.35 US per kg for the liquid product of waste plastics cracking. This is almost as high as the crude oil price. This is possible since in Poland the economy of the utilization plants is aided by tax relief and lowering in excise duty as well as by ‘product payment’, i.e. obligatory payments for plastics package reclamation by their producers.

The results obtained by VEBA in a high-pressure hydrogenation plant [21] indicated an almost four times higher price of fuels from waste plastics than current fuel market prices. At the beginning of 1990s on the basis of pilot-plant-scale hydrogenation process the UK researchers stated that this process is not economically viable and they foresaw that it would not be available commercially until after 2000.

Economic efficiency of waste plastics processing depends on the methods of their selection and preparation for processing as well as the cost of thermal or catalytic treatment, i.e. the cost of investment and exploitation of the cracking plant. For instance the main characteristic of fluid-bed reactors is the possibility of exploitation of large-scale units (at least 50 000 tons or more per year), low cost of exploitation, but accompanied by large investment and feed delivery costs. And on the other hand, smaller reactors can be built on a smaller scale, a few thousand tons per year output, lower investment costs and lower feed deliveries (processing of local wastes in limited area), but operated with larger exploitation costs.

Finally, economic efficiency of waste plastics processing (tertiary recycling) can be influenced by state tax policy, e.g. by lowered income taxes and excise duty in the case of fuels produced from waste material. It will also be strongly influenced by continuous increasing of landfill costs and local legislation (local taxes lowered for waste plastics utilizing companies) as well as obligatory payments for package reclamation by their producers.

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5

Thermal and Catalytic Degradation of Waste HDPE

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1 INTRODUCTION

This chapter describes the thermal and catalytic degradation of waste high-density polyethylene (HDPE) in order to recover the fuel oil from waste plastics. Among waste plastics, the polyolefinic type that is a material of high potential for alternative oil production is more than 70% of the total plastic content in municipal solid waste (MSW). Waste HDPE in polyolefinic plastic is a difficult material in the pyrolysis process by treatment at high temperature, because of its high degradation temperature and high viscosity products such as low-quality wax.

In recycling methods, the thermal and catalytic degradation may provide a suitable means of recycling, of great interest both economically and environmentally [1, 2]. The advantage of this process is the low energy consumption, the handling of waste plastic that cannot be efficiently recycled by alternative means, and also the operation without the need for air or admixtures of hydrogen. This method has been studied by many researchers to recover valuable oil.

Thermal degradation is a simple process in which polymers at high temperature are melted and broken down to smaller molecules [3]. However, these products have a low practical use due to their low quality. Thus, the interesting method of polymer utilization is the catalytic degradation process. This is to convert the melted polymer to light carbon-derived materials with high-quality components, whereas the addition of catalyst in the pyrolysis process is accompanied by an increase in cost and also the development of a highly technical process. Moreover, the catalysts are deactivated during the process by the deposition of carbonaceous residues and other products, such as Cl and N compounds. For this reason, a pretreatment process is required to remove all the components

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that can negatively influence the catalyst. Catalytic degradation process enable lowering of reaction temperature, fast reaction with low activation energy and also a low boiling temperature range product with high quality such as branched, cyclic and aromatic structures, compared with the thermal degradation process. The product distribution over the catalytic degradation can be controlled by the selection of a suitable catalyst and its modification. As an example of the cracking catalyst, spent fluid catalytic cracking (FCC) catalyst is thrown away from the commercial FCC process in Korea as a few ten thousand tonnes per year, although it has high activity. This catalyst can be economically used in the liquid-phase cracking process for waste plastics into oil recovery, due to its low cost. On the other hand, the combination of pyrolysis and catalytic process can be a more efficient method for processing large amounts of waste plastics [4]. This method reduces the viscosity of the mixture products and enables the separation of unwanted components.

Also, in thermal and catalytic degradation of waste HDPE the influence of experimental variables, such as reaction temperature, catalyst type and other plastic addition, etc. is described in this chapter. Thus, the discussion focuses on waste HDPE as a reactant and the influence of various experimental variables and also a comparison of the thermal and catalytic degradation in detail.

2 THEORY OF PLASTICS PYROLYSIS

The decomposition of plastics can be considered as depolymerization of polymer into low-molecular product. The general reaction mechanism for the thermal degradation is described with the following steps, and also shown in Figure 5.1.

- Initiation may occur at random or end-chain positions.
- Depropagation is the release of olefinic monomeric fragments from primary radicals.
- Hydrogen chain transfer reaction, which may occur as intermolecular or intramolecular processes, leads to the formation of olefinic species and polymeric fragments. Moreover, secondary radicals can also be formed from hydrogen abstraction through an intermolecular transfer reaction between a primary radical and a polymeric fragment.
- β-cleavage of secondary radicals leads to an end-chain olefinic group and a primary radical.
- Termination takes place either in a bimolecular mode with the coupling of two primary radicals or by disproportion of the primary macroradicals.

The decomposition of plastics depends on the plastic type, with different reaction mechanisms of plastics proposed with four types [5].

- End-chain scission; the polymer is broken up from the end groups successively yielding the corresponding monomers. When this polymer degrades by depolymerization, the molecules undergo scission to produce unsaturated small molecules (monomers) and another terminal free radicals. (Polymethylmethacrylate, polytetrafluorethylene, polymethacrylonitrile, polyethylstyrene, polystyrene, polyisobutene)
- Random-chain scission; the polymer is broken up randomly into smaller molecules of varying chain lengths, producing a volatile with or without a double bonds. (Polystyrene, polyisobutene, polyethylene, polypropylene, polybutadiene)

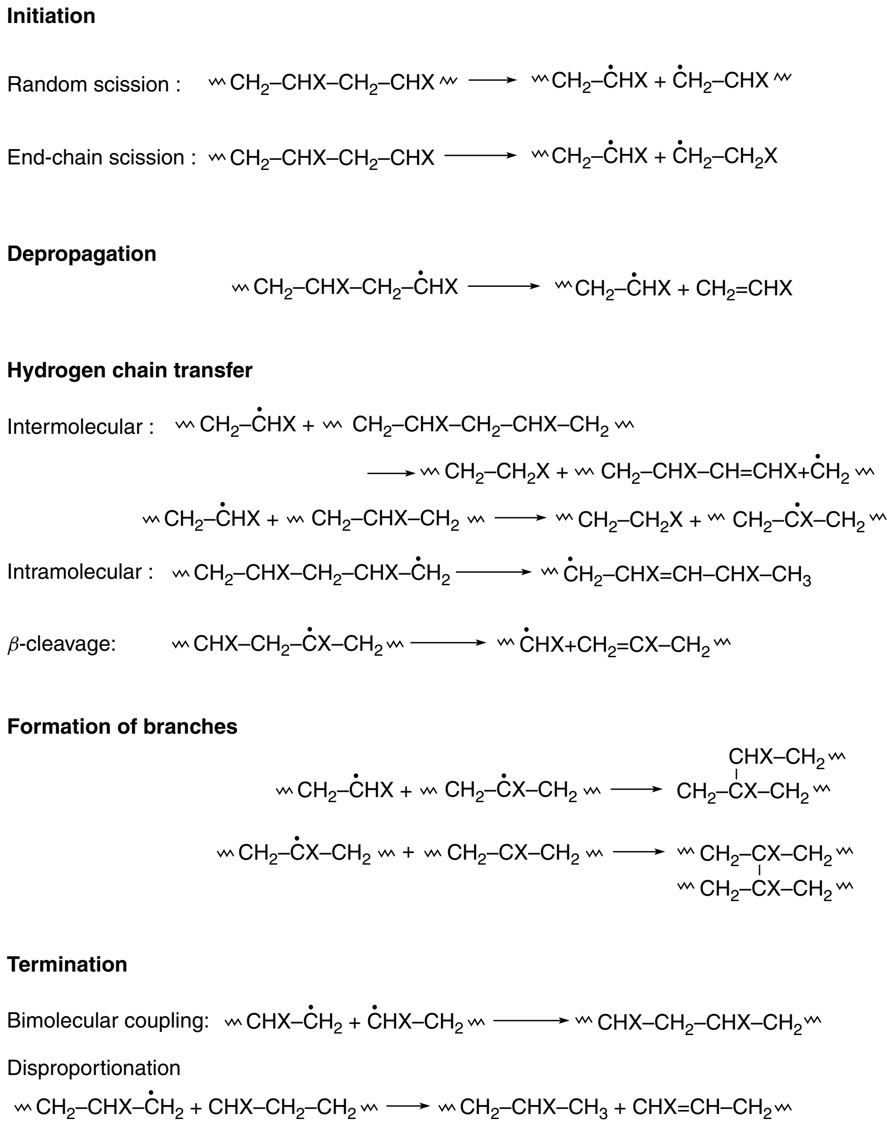


Figure 5.1 Reaction mechanism of polymer

- Chain-stripping; the reactive substituents or side groups on the polymer chain are eliminated, leaving an unsaturated chain. This polyene then undergoes further reaction, including β-scission, aromatization and coke formation. (Polyvinylchloride, polyvinyl fluoride, polyacrylonitrile)
- Cross-linking; the formation of a chain networks occur from thermosetting polymers, when heated at high temperature. This is pyrolytic condensation and rearrangement of carbon networks to form high-strength materials. (Thermosetting plastics)

These different mechanisms are related to the bond dissociation energies, the chain defects of the polymers, the aromatic degree and the presence of halogen and other hetero-atoms in the polymer chains. For the reaction mechanism of the main components in waste thermoplastics, the pyrolysis of PVC occurs by the chain-stripping mechanism with much less monomer recovery, whereas that of PS with cyclic structure occurs by both end-chain and random-chain scission mechanism and the monomer recovery is very high. Especially, PE and PP which comprise the main polymers in waste plastics pyrolyze by random-chain scission, which yields a wide range of hydrocarbon products. The oil products consist of higher-boiling-point hydrocarbons with low valuable products as well as lower-boiling-point hydrocarbons. Thus, in the pyrolysis process the more cracking of high-boiling-point hydrocarbons to obtain valuable light oil product with high yield must be taken into consideration in a large-scale plant.

A new macroscopic degradation mechanism of polymers studied by Murata *et al.* [6] was suggested with two distinct mechanism in the thermal degradation of PE, PP and PS. One is a random scission of polymer links that causes a decomposition of macromolecules into the intermediate reactants in liquid phase, and the other is a chain-end scission that caused a conversion of the intermediate reactants into volatile products at the gas–liquid interface. There are parallel reactions via two mechanisms. The random scission of polymer links causes a reduction in molecular weight of macromolecules and an increase of the number of oligomer molecules. The chain-end scission causes a dissipation of oligomer molecules and a generation of volatile products.

The cracking reactions of heavy hydrocarbons using a catalyst such as solid acid and bifunctional catalyst, etc. have been explained with the difference of simple thermal degradation of the polymer. In the depropagation of the polymer chain using the catalyst, the molecular weight of the main polymer chains may be rapidly reduced through successive attacks by acid sites on the catalyst, yielding a high fraction of low-molecular product. Also, the carbonium ion intermediates in the catalytic reaction progress can undergo rearrangement by hydrogen or carbon atom shifts with producing the isomers of high quality and can undergo cyclization reactions, by means of the intramolecular attack on the double bond of an olefinic carbonium ion.

In the case of a bifunctional catalyst playing different active site roles, this catalyst consists of both acidic and metal material as reforming catalyst. The metallic sites catalyze hydrogenation/dehydrogenation reactions, while the acidic sites on the support catalyze isomerization reactions, as shown in Figure 5.2. This catalyst can promote the isomerization of straight-chain paraffins into branched-chain molecules, the dehydrocyclization of straight-chain paraffins into cycloparaffins and also the dehydrogenation of naphthenes into

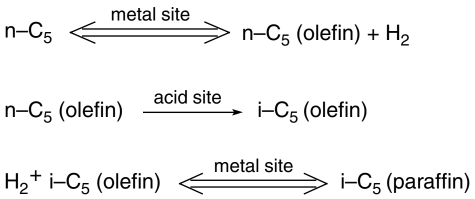


Figure 5.2 Reaction mechanism of hydrocarbon on bifunctional catalyst [5]. (Reproduced with permission from Elsevier)

aromatics. These reactions improve the octane numbers of light hydrocarbons. However, this catalyst is very expensive. Thus, its use in oil recovery from waste plastics containing contaminated material must be taken into careful consideration.

Characteristics of thermal and catalytic degradation of heavy hydrocarbons can be described with the following items, respectively.

- In the case of a thermal reaction
  1. High production of C_1s and C_2s in the gas product
  2. Olefins are less branched
  3. Some diolefins made at high temperature
  4. Gasoline selectivity is poor; that is, oil products are a wide distribution of molecular weight
  5. Gas and coke products are high
  6. Reactions are slow compared with catalytic reactions
- In the case of a catalytic reaction
  1. High production of C_3s and C_4s in the gas product
  2. Olefins are the primary product and more branched by isomerization
  3. Gasoline selectivity is high; that is, oil products are a short distribution in the gasoline range
  4. Aromatics are produced by naphthene dehydrogenation and olefin cyclization
  5. Larger molecules are more reactive
  6. Pure aromatics do not react
  7. Paraffins are produced by H_2 transfer
  8. Some isomerization occurs

3 PROCESS FLOW DIAGRAM

In this section we discuss the process flow diagram for the pyrolysis of waste plastics. This is required to be a compact process that can be controlled in a stable and continuous way, because of movement of the high-viscosity material for each unit system in the process. This material can block the flow line and make difficult the continuous control of unit process.

In order to obtain an oil product in the pyrolysis of waste plastics, the major steps for waste plastics that are derived from the household, industry, etc. are basically shown in Figure 5.3, Waste plastics as a reactant for obtaining the valuable products are invariably contaminated with materials such as soil, iron and wood etc. and also consist of various types of plastics. This material cannot be directly used in the pyrolysis process. Therefore, in the next step separation treatments must be applied to obtain waste plastic with a homogeneous composition. If it contains a lot of various contaminative materials in waste plastics, it leads to poor economics by increasing the recycling procedure cost. Thus, the important point for the pyrolysis process is the purification of waste thermoplastics, especially excluding PVC and PET in the reactant. Here, PVC and PET in the plastic feedstock can cause unfavourables emission due to the presence of Cl as well as high char/coke yields since they are not well degraded in the general pyrolysis process, respectively. The waste material must be separated into individual components, such as thermoplastic, PVC, PET, thermosetting, iron, aluminum and paper, etc.

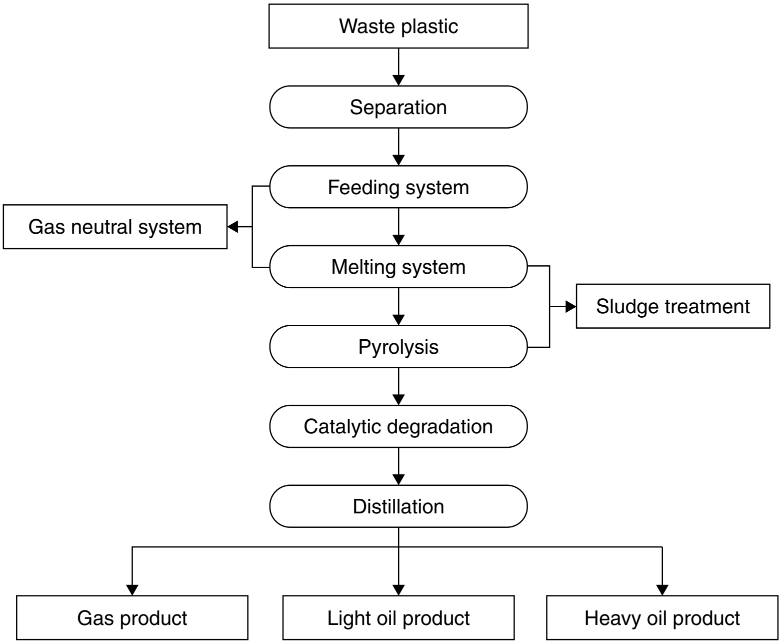


Figure 5.3 Continuous process flow diagrams for waste plastics into oil recovery

In the third step, the separated plastics are delivered by the feeding system such as the conveyer, hopper and extruder, etc. to the melting reactor, after cutting to a small size. The feeding system is continuously controlled with a constant reactant amount and classified as heated or nonheated case of the extruder. By preheating the plastic feedstock the melting time in the melting reactor can be shorted thus improving production rates. Moreover, the film type reactant is very bulky and voluminous, which makes it difficult to ensure continuous feeding, is easily dosed at the melting system after melting in the feeding system. In the unheated case, a hard reactant of several millimeter size is adequately controlled by a continuous feeding system. Thus, the feeding system will be determined by the profile of waste plastics that are exited from industry, agriculture and household, etc. Other important point is that if there is trouble in a continuous automatic feeding system, it can be quickly transferred to a manual system.

The next step is the melting system, where the solid plastic is changed to a low-viscosity melt. If there is sufficient time to melt the polymer in the melting reactor, the pyrolysis and/or catalytic degradation process as the next step of melting system will be well controlled without trouble in a continuous system. The residence time of plastics in the reactor depends on the plastic type and the desired viscosity extent. Thus, in order to reduce the melting time of reactant in the melting system, it needs be heated in the feeding system prior to the melting system. Moreover, as the system is scaled up to a big plant, this is a very important parameter for heating the feeding system.

In the pyrolysis and catalytic degradation of polymer at temperature 300–450°C the melted reactant is degraded into a smaller molecule and also upgraded to oil product with a high quality. Several processes of pyrolysis and catalytic degradation are available, such as pyrolysis process only, liquid-phase catalytic degradation after the melting process and catalytic degradation after the pyrolysis process, according to the characteristics of the oil produced.

For the processes of different reactor types, kiln and retort pyrolysis processes are characterized by a relatively low capital investment. However, they suffer from unfavorable economics, due to the high processing costs compared with the value of the oil product obtained. Also, the characteristics of this process are relatively long residence times of waste in the reactor, poor temperature control due to large temperature gradients across their internal dimensions, fouling walls of the reactor by carbon residue and low liquid product quality due to the production of a diverse number of pyrolysis products.

Fixed-bed pyrolysis–catalytic cracking process for oil recovery of waste plastic is in use at several commercial processes. The reactor type in the pyrolysis or/and catalytic cracking process is generally constant stirred tank reactor (CSTR) and plug flow reactor. The problem is the fact that carbon residues tend to foul the walls of the reactor and thus give poor heat transfer from the external wall to the center of the reactor. Furthermore, CSTR type can deal with a relatively high viscosity reactant, but the problem of heat transfer by a big reactor diameter can be more important, compared with that of plug flow reactor. Basically, waste plastics are melted to materials of low viscosity and then the liquefied reactant is thermally decomposed to low-molecular-weight hydrocarbons in the pyrolysis reactor. These reactants are cracked in a fixed-bed reactor using solid catalyst to yield the oil and gas products. The characteristics of this process are the quality of the oil product, very similar to that of conventional gasoline, kerosene and diesel oils, but the drawback of the catalyst is high cost and short life-cycle due to poisoning/deactivation.

The fluidized-bed process yields a uniform product and a high conversion during a short reaction time. In addition, the problem of low thermal conductivity of polymers is overcome by a fluidized system and thus heat transfer gradients are eliminated. Some advantages are high-quality product, low energy requirement supplied by combustion of a portion of the gas by-product, good temperature control, the efficient removal of impurities present in the waste plastic, application on a relatively small scale, and also a robust and relatively inexpensive process to establish. On the contrary, this process has problems with toleration in the chlorine produced, the removal of solid sludge from the fluidized bed and also its long-term durability.

In the pyrolysis process, one of the most important decision items is the degradation temperature in the reactor. The degradation temperature must be decided by the type and composition of plastics contained in mixed thermoplastics, because of their different degradation temperatures. For a reactor with a big diameter in a large-scale plant the temperature gradient must also be taken into consideration in determining the degradation temperature, because of heat transfer limitations for viscous fluids with low thermal conductivity in the large reactor. Moreover, the coke accumulated on the internal surface of reactor during a long reaction time hinders heat transfer between heat source and viscous fluid in the reactor. Thus, the heat supply of the plant is gradually increased with the progress of reaction time. Optimization process control for hindering the coke formation is an important key in a large-scale plant.

Also, the impact on the environment in the pyrolysis of waste plastics must be taken into consideration. If a PVC material is contained in the reactant, the hydrochloric acid is evolved during decomposition of PVC which causes air pollution. Thus, a system is needed in order to remove the chlorine components in gas products. The rest of the gas products consisting of light hydrocarbons can be used as fuel gas in the heating system. Also the nonvolatile material generated in the melting and pyrolysis process, which includes a small amount of volatile hydrocarbon components, is discharged to a sludge treatment system. After being sufficiently heated in the sludge system, the product obtained is used as a valuable oil, but the solid char/coke retained is landfilled or incinerated.

Finally, the product obtained is separated from the distillation tower, such as gas product, light oil product and heavy oil product. Our target is light oil product and/or heavy oil product, which is generally obtained by control of reactor temperature and distillation system such as temperature gradient, reflux ratio and reboiler temperature, etc. The distribution of the oil product must be decided by market circumstances.

4 TOTAL MASS BALANCE

Total mass balance is based on input and output amount in a simple process flow diagram, as shown in Figure 5.4. In this process, the optimization control condition is the maximum production of the oil product and the minimum production of the gas product and the sludge. Generally, the yields of gas and oil product are below 20% and above 70% respectively, based on 100% of feeding amount. Also, the sludge amount is much decreased to below 10%, which should be discharged in much smaller amounts, if possible. Increased amount of sludge discharged increases treatment cost and also decreases desired product yields, which has a great influence on economic decisions on the pyrolysis process of waste plastic.

As an example, the experimental data using stirred semi-batch laboratory-scale reactor [7] was obtained from the catalytic degradation of various plastics over spent FCC

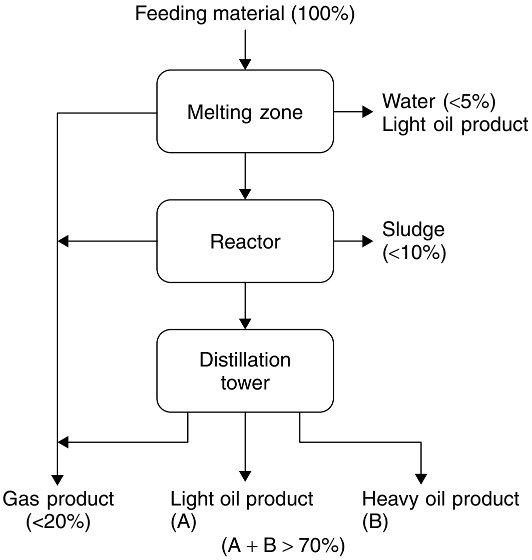


Figure 5.4 Total mass balance of a simple process flow diagram in the pyrolysis of waste plastics

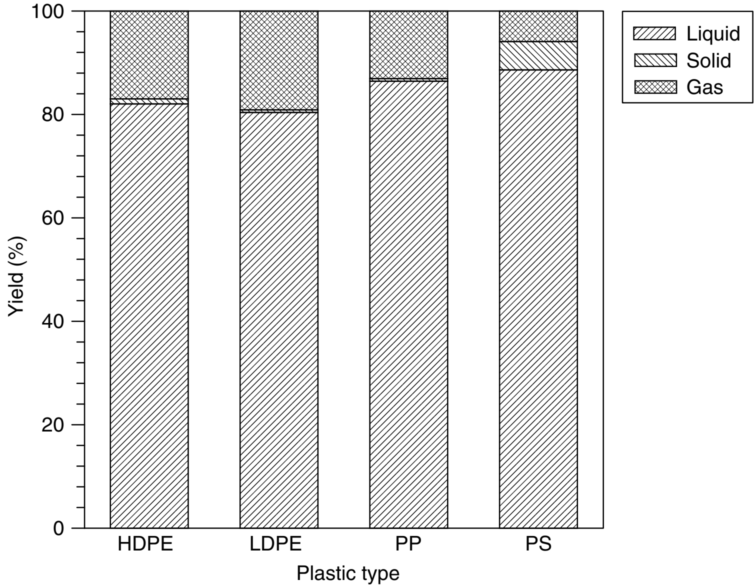


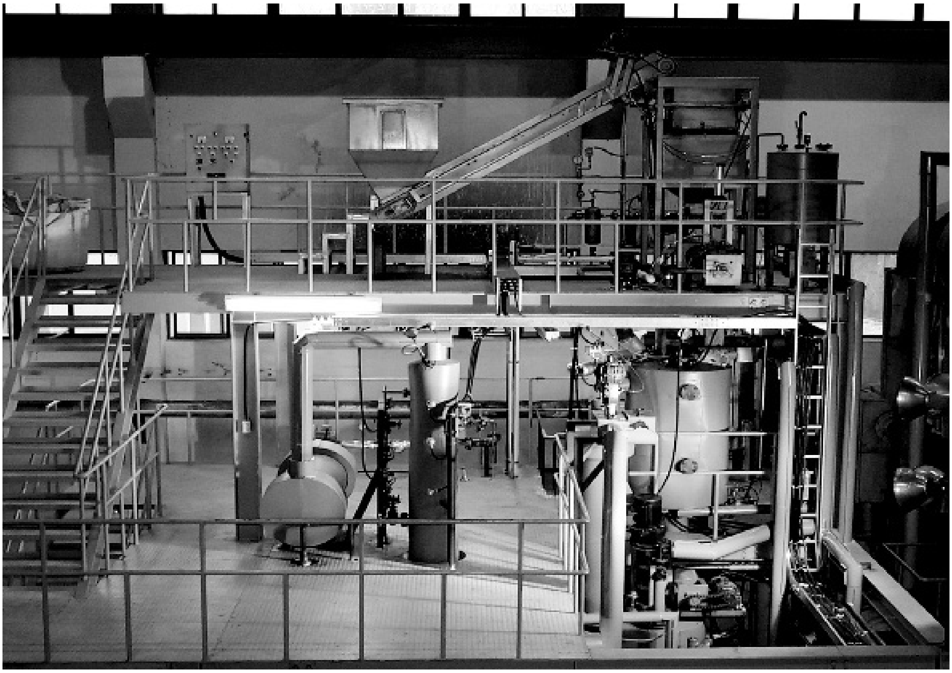
Figure 5.5 Yield of liquid, solid and gas products in catalytic degradation of various plastics using spent FCC catalyst. (Reproduced with permission from Elsevier)

catalyst at 400°C, as shown in Figure 5.5. In general thermoplastics, the yield of liquid products is 80% or over, which is the following order; PS > PP > PE. Plastics with a polycyclic structure have higher liquid yield than that of polyolefinic structures. On the contrary, the gas yields in these types of plastics are in reverse order compared with those of liquid, which is below 20% yield. Also, the solid is much more produced from polycyclic polymer than polyolefinic polymer. Accordingly, the product distribution is very influenced by the type of plastic.

The pyrolysis of mixed waste thermoplastics in a pilot plant of 360 ton/year at the Korea Institute of Energy Research (KIER), as shown in Figure 5.6, has an oil yield of about 82% for continuous process control over two days. The distribution of oil product is 27% gasoline product and 73% heavy oil product. Also the yield, of gas product is 10–15% and consists of about 18.1% C_1, 15.2% C_2, 30.3% C_3, 21.9% C_4 and 14.3% C_5 components. Similar results were obtained by other researchers, as shown in Table 5.1.

5 EFFECT OF TEMPERATURE

In the thermal and catalytic degradation of waste thermoplastics, the product yields such as liquid, gas and solid products change depending on the degradation temperature. Walendziewski and Steininger [8] reported the thermal and catalytic degradation of polyethylene in the temperature range 370–450°C. In the case of thermal degradation of polyethylene, an increase in degradation temperature led to an increase of gas and liquid products, but a decrease of residue (bp >360°C). However, according to the increase of degradation temperature, the yield of gas products resulted in not too large increase and that of residue decreased sharply. Similar results were obtained in the catalytic degradation and hydrocracking process.



(3rd and 4th floor)

(1st and 2nd floor)

Figure 5.6 Overall view of pyrolysis plant of waste plastics in KIER process

Table 5.1 Composition of gas products obtained from cracking of polyethylene at 400°C

Component	Thermal (KIER)[a]	Thermal[b]	Catalytic[b]	Hydrocracking[b]
Methane	18.1	22.7	12.4	21.1
Ethane	12.3	27.4	20.4	21.2
Ethylene	2.9	1.4	2.3	0.1
C_3	30.3	26.6	30.4	23.7
C_4	21.9	11.0	20.3	20.7
C_5	14.3	6.9	5.6	7.3
C_6	0.2	2.1	3.3	3.8

[a] Reactant: mixed plastics
[b] Based on [8]

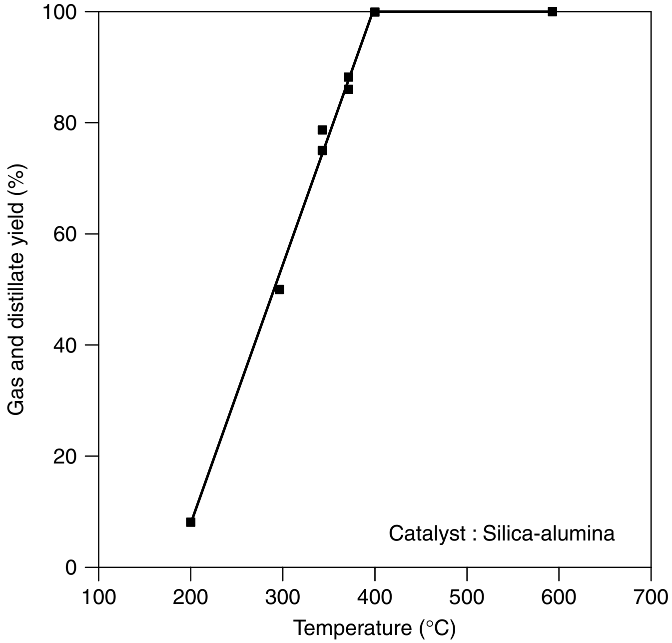


Figure 5.7 Influence of temperature on the catalytic degradation of polyethylene. (Reproduced with permission from Elsevier)

Beltrame *et al.* [9] have also studied polyethylene degradation over silica, alumina, silica–alumina and zeolites in a small pyrex vessel reactor without a stirring, in the reaction range 200–600°C. Thermal degradation and degradation catalyzed by alumina or silica leave the residue amount, even at 600°C. However, at this temperature the gas + distillate yield obtained in the presence of these two catalysts is much higher than that in the thermal degradation. For the silica–alumina with higher activity, the degradation gave much more gas and distillate fraction at 400°C, but at temperatures lower than 400°C it did not reach completion. In conclusion, the gas + distillate yield over silica–alumina, as a function of temperature, increased linearly up to 400°C, as shown in Figure 5.7. Production occurs even at 200°C and reaches 100% yield of gas + distillate at 400°C.

The catalytic upgrading of the pyrolysis gases derived from the pyrolysis of polyethylene at 500°C has been investigated by Bagri and Williams [10]. The catalytic upgrading was done over zeolite in the temperature range 400–600°C. As the zeolite bed temperature was increased, the gas yield increased with a decrease in oil yield. However, coke formation showed a small decrease with increase of catalyst temperature. Venuto and Habib [11] also showed that as the catalyst temperature was increased from 480 to 590°C, coke formation in the zeolite catalytic cracking of petroleum was reduced and also alkene gases in gas product increased. Sharratt *et al.* [12] carried out the catalytic degradation of high-density polyethylene using ZSM-5 zeolite. As the reaction temperature was increased from 290 to 430°C, the gas yield was increased, whereas the oil yields was decreased. The oil obtained in the pyrolysis of polyethylene contained a low concentration of aromatic compounds. After it was catalyzed, there was a marked increase in the concentration of aromatic compounds in the oil, which further increased in aromatic concentration as the temperature in catalyst bed reactor was raised.

Lee *et al.* [13] have described the cumulative amount distributions of liquid product by catalytic degradation of waste HDPE at different reaction temperatures and at a reactant amount of 200 g, as shown in Figure 5.8. These distributions were clearly dependent on reaction temperature. Thus the slope from the cumulative amount of liquid product versus the initial reaction time was defined as the initial rate of degradation, which is shown as a function of reaction temperature in Figure 5.9. The initial rate of degradation of waste HDPE was exponentially increased with increase of reaction temperature and moreover at

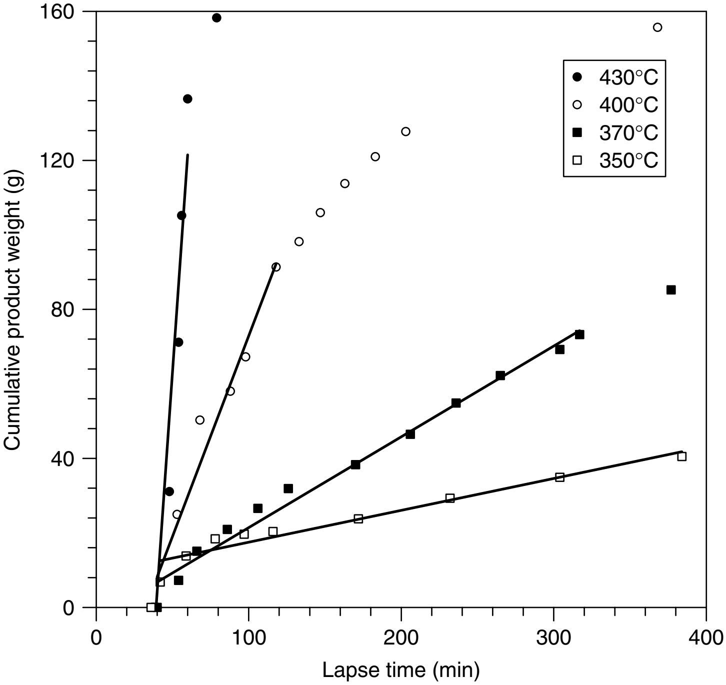


Figure 5.8 Cumulative amount of distillation as a function of reaction time for catalytic degradation of waste HDPE using spent FCC catalyst (catalyst content = 9.1 wt%)

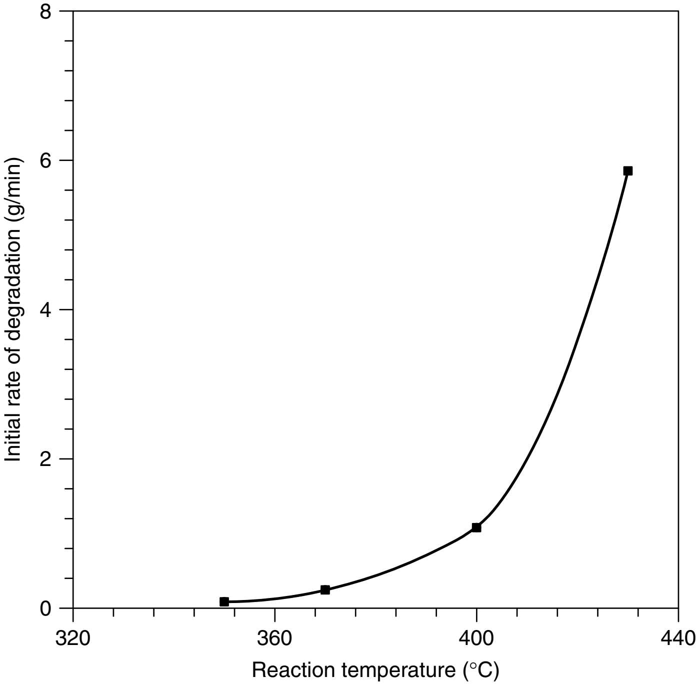


Figure 5.9 Initial rate of degradation as a function of reaction temperature for catalytic degradation of waste HDPE using spent FCC catalyst (catalyst content = 9.1 wt%)

a higher temperature was sharply increased from about 1 g/min (400°C) to about 6 g/min (430°C), a great influence of reaction temperature.

6 EFFECT OF CATALYST

Because the addition of catalyst in the pyrolysis process has many advantages, many researchers have looked for ways of improving light oil yield and oil quality from waste plastics. According to the catalyst addition in plastic pyrolysis, the degradation temperature for achieving a certain conversion is reduced drastically. Also, the increase of catalyst content in waste plastic further lowers the degradation temperature. In the liquid product from catalytic degradation, more products in the gasoline range and moreover more isoalkanes and aromatics in the C_5–C_{10} range can be produced. Also, the reaction rate is increased significantly. The product distribution over the catalytic degradation can be controlled by the selection of a suitable catalyst and its modification.

A simplified example [14] is illustrated by the difference in the product yields between thermal and catalytic degradation using spent FCC catalyst of waste HDPE in a stirred semi-batch reactor with on a laboratory scale, as shown in Table 5.2. Spent FCC catalyst can be supplied from commercial FCC process, which is very cheap and retained with adequate activity. Thus, it can be used as an alternative catalyst in liquid-phase catalytic degradation of polyolefin. Compared with thermal degradation, the catalytic degradation

Table 5.2 Yields of gas, liquid and residue obtained from thermal and catalytic degradation of waste HDPE at 430°C

	Gas (%)	Liquid (%)	Residue (%)
Thermal degradation	20.0	75.5	4.5
Catalytic degradation	19.4	79.7	0.9

showed an increase of liquid yield whereas that of residue was reduced, due to the decomposition of heavier residues into lighter oil product.

Furthermore, the difference of cumulative yield distribution in liquid product between thermal and catalytic degradation of waste HDPE was clearly apparent, as shown in Figure 5.10. The catalytic degradation produced initial liquid product with more rapid, higher degradation rate into liquid product and also much more liquid yield in comparison with thermal degradation. It is supposed that if waste plastic in the thermal degradation process is subject to short residence time in a continuous stirred tank reactor, partial degradation of plastic can occur, while the rest of the feed can produce high-viscosity product, such as wax.

The paraffins, olefins, naphthenes and aromatics (PONA) distribution of liquid product with time on stream for thermal and catalytic degradation of waste HDPE at 430°C is shown in Figure 5.11. In the case of thermal degradation, paraffin and olefin components are the main products and aromatic compounds hardly appear, without change by increase

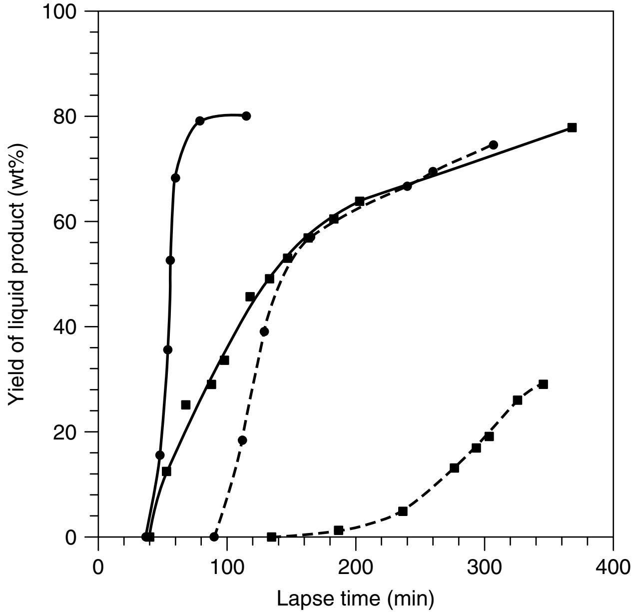
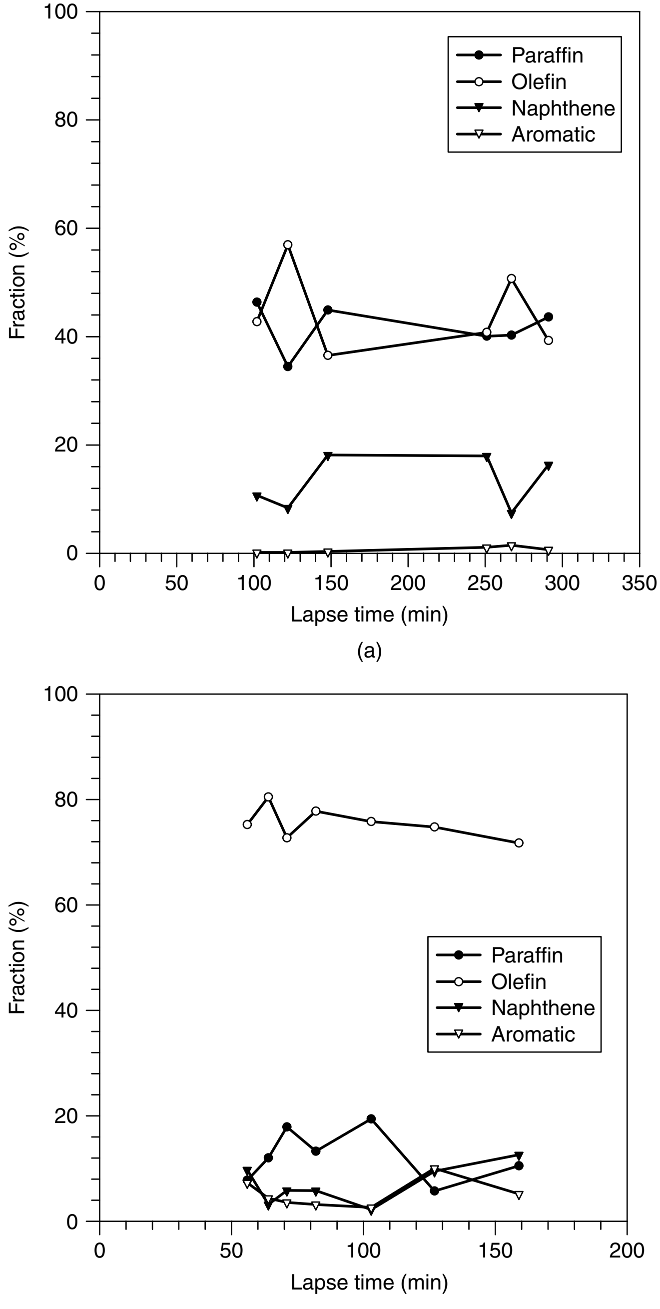


Figure 5.10 Cumulative yield of liquid products obtained from thermal and catalytic degradation of waste HDPE using spent FCC catalyst (solid line: catalytic degradation; dotted line: thermal degradation, for reaction temperature; circles: 430°C; squares: 400°C)



(a)

(b)

Figure 5.11 Fractions of paraffin, olefin, naphthene and aromatic products for thermal (a) and catalytic (b) degradation of waste HDPE at 430°C of reaction time. On the other hand, the catalytic degradation using spent FCC catalyst showed about 80% olefin products as the main product. Also, the paraffin products were decreased, whereas aromatic compounds were increased, compared with those of thermal degradation. Spent FCC catalyst improved the fraction of liquid olefin and aromatic components with comparatively high octane number. Molecular weight distribution of liquid product obtained at a similar reaction time is compared over thermal and catalytic degradation of waste HDPE in Figure 5.12. In the case of thermal degradation, both paraffin and olefin as a main liquid product were distributed in a wide molecular weight range, between 80 and 400, whereas naphthene products with cyclic structure showed a narrow molecular weight distribution. On the other hand, the catalytic degradation produced mainly light olefin products in the range of gasoline with molecular weight below 200.

Walendziewski and Steininger [8] have described thermal and catalytic conversion of waste polyethylene and polystyrene into oil recovery, in a small autoclave reactor. The optimum thermal cracking temperature of waste polyolefins is 410–430°C, while that of catalytic degradation is 390°C. Also, the yield of gas and liquid fraction with b.p. $<360^{\circ}$C was attained more than 90%. In the range of 0.3–1 wt% catalyst content, the catalyst amount is small influenced on polyolefin conversion and product composition. The thermal and catalytic degradation of PE, PP, PS and their mixture using alkaline catalyst was investigated by Walendziewski [1]. In two cases, the yield of liquid and gas fuel was over 95%. The application of cracking catalyst results in lowering of degradation temperature, boiling temperature range in liquid product and density of liquid products, and also the increase of gas product yield. Moreover, the products obtained in the cracking of polymers are highly unsaturated components, containing olefins and diolefins that can be hydrogenated over a bifunctional catalyst.

Aguado *et al.* [15] reported the thermal and catalytic degradation of low-density polyethylene using a continuous two-screw kiln reactor. Compared with thermal degradation, catalytic degradation is considerably faster and shows a completely different product distribution. It was stated that thermal degradation gives rise to a broad product distribution in liquid product, whereas the catalytic degradation over Al-MCM-41 leads mainly to the gasoline range hydrocarbons (C_5–C_{12}) with selectivities up to 80%, in spite of low degradation temperature, as shown in Figure 5.13. *n*-paraffins, iso-paraffins, olefins, naphthenes and aromatics (PIONA) analyses of gasoline fractions obtained in the LDPE catalytic degradation indicate that the main components are olefins (50%) and isoparaffins (20%), whereas the aromatic content is below 6%.

7 VARIOUS CATALYSTS

The thermal degradation of waste HDPE can be improved by using suitable catalysts in order to obtain valuable products. However, this method suffers from several drawbacks. The catalysts are deactivated by the deposition of carbonaceous residues and Cl, N compounds present in the raw waste stream. Furthermore, the inorganic material contained in the waste plastics tends to remain with the catalysts, which hinders their reuse. These reasons necessitate a relatively high purity of waste plastics, containing very low concentrations of a contaminant. Thus, various pretreatments are required to remove all the components that may negatively affect the catalyst.

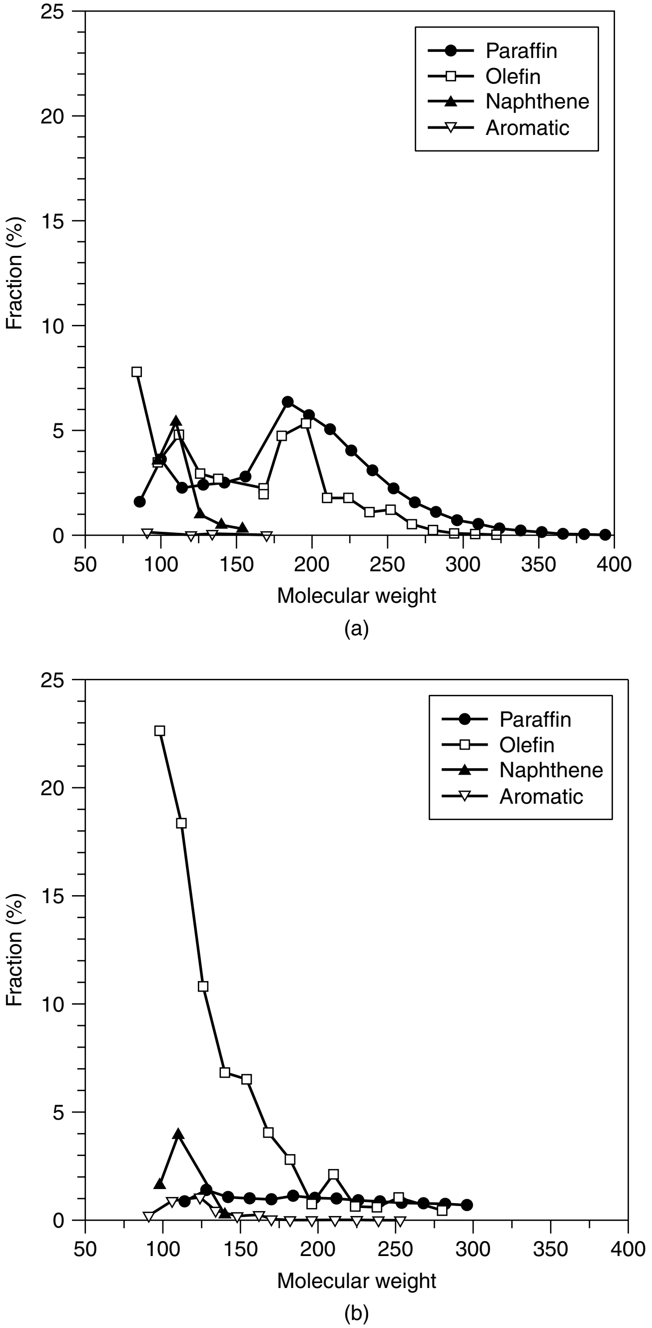


Figure 5.12 PONA distributions of liquid products for thermal (a) and catalytic (b) degradation of waste HDPE at 430°C

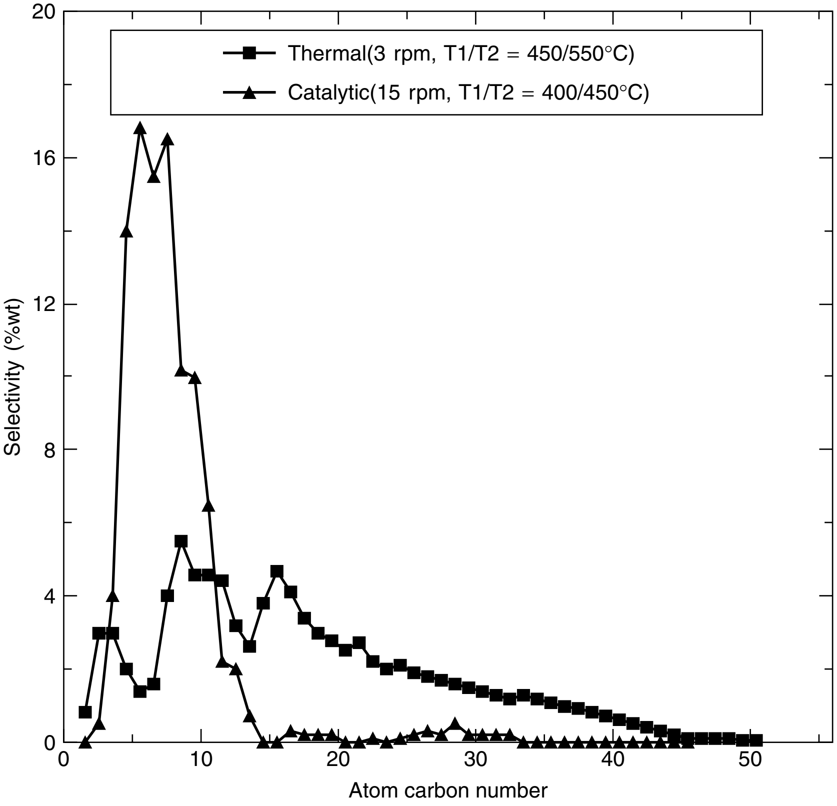


Figure 5.13 The selectivity of carbon atom number obtained in the thermal and catalytic degradation of LDPE in two-screw kiln reactor. (Reproduced with permission from Elsevier)

The pyrolysis process of waste plastics is classified into either liquid-phase contact or vapor-phase contact of catalyst in the continuous flow reactor. In the liquid phase reaction, the catalyst is a fine powder type with high external surface area which is contacted with melted plastics, which are degraded into light products from polymer chain on the active sites of catalyst. This process uses a large amount of catalyst, which becomes a high portion in total cost. Thus, the catalyst must be of low price and reused after regeneration, if possible. In the vapor-phase reaction, the polymer is first degraded into the hydrocarbon vapor in the thermal degradation process, aimed at reducing the viscosity of melted plastics and enabling the separation of undesired components. The cracked products are then contacted with the catalyst packed in the flow reactor, which plays a reforming role over the products formed by thermal degradation of polymers.

Various catalysts used in the two processes have been described as follows; zeolite, alumina, silica–alumina, FCC catalyst, reforming catalyst, and others. The most common catalysts used in the cracking of heavy hydrocarbons are acidic catalysts; alumina and silica–alumina with mesopores, and also zeolite with micropores, etc. They are typically used in the commercial petroleum process. For the chemical properties of catalyst, the catalysts consist of Lewis and Brönsted acid sites, which is an important factor in determining the catalytic activity and product selectivity. This is because Brönsted acid sites play a proton addition role and Lewis acid sites involve hydride abstraction, which leads to different reaction pathways in the cracking of hydrocarbons. Also, these acid sites are generated by Al species in the catalyst consisting of silica and alumina. Thus, Al content per unit cell or Si/Al ratio of catalyst is very related to the acid site density, which also has a masked influence on the cracking reaction. High acid site density favors the cracking reaction of hydrocarbons, but promotes undesired reactions such as coke formation. Thus, in order to design the catalysts with a high activity and also high selectivity of desired product, the acid site density of the catalyst is controlled by preparation methods and various pretreatment methods such as steam or acid/base solution treatment, etc.

In addition to the chemical properties of the catalyst, the physical properties are also very important in determining the catalytic activity and product selectivity. These parameters are the surface area, pore size, pore volume, pore size distribution, pore structure, etc. As an example, the zeolite has a micropore crystalline structure with pore size below 1.0 nm, whereas alumina and amorphous silica–alumina are mesoporous materials with a wide distribution of large pore size. Various natural or synthetic zeolites have relatively high surface area, but small pore size and also small pore volume. The narrow distribution of zeolite having a pore size below 1.0 nm allows different molecules to control a limited diffusion inside the pores, known as shape selectivity, which is selectively reacted on active sites within pores. Also, other advantages of zeolites are high acid strength, high stability and low coke formation, etc. Accordingly, zeolites such as zeolite Y and ZSM-5 have been extensively used for catalytic cracking of heavy hydrocarbons in many commercial processes. However, the catalytic degradation of waste plastics using zeolite may be a difficult problem due to a limited diffusion of big molecules into zeolite pores, which can be overcome with small crystal size and also high external surface area due to the use of a fine powder. Also, activated carbon impregnated with transition metals is a micropore material with a high surface area, which promotes hydrogen transfer reactions during decomposition of hydrocarbons like the reforming catalyst.

On the contrary, alumina and amorphous silica–alumina have relatively low surface area, but big pore size and large pore volume, due to their mesopore structure. They have low acid strength compared with zeolites. However, they have a sufficient diffusion of heavy hydrocarbon having large kinetic diameter through the pores, without control of different molecules. A similar catalyst is MCM-41, although it has high surface area, has a uniform mesopore structure. The utility of its high surface area and uniform mesopore in catalytic degradation of polyolefin has recently studied by several researchers [16–19]. Also, sulfated zirconia known as a superacid solid can be used as a catalyst in catalytic reaction of hydrocarbons [20, 21]. FCC catalyst has been developed for the cracking of heavy hydrocarbon molecules into gasoline range hydrocarbons. The catalyst consists of silica–alumina with a mesopore structure and zeolite with a micropore structure, which can be well cracked by step-by-step diffusion of heavy molecules in the catalyst of different pore structure. FCC catalyst has been found to have a significant effect in the pyrolysis of thermoplastics [22. 23].

Seo *et al.* [24] have described the catalytic degradation of polyethylene using various acidic catalysts at 450°C. The yields of gas, liquid and residue are illustrated in Table 5.3 and the PONA distribution in liquid products is shown in Table 5.4. Catalytic degradation

Table 5.3 Yields of liquid, gas and coke produced from thermal and catalytic degradation of HDPE with various catalysts at 450°C

Yields of products	Liquid (wt%)	Gas (wt%)	Coke (wt%)	Liquid[a] (wt%)		
				C_6–C_{12}	C_{13}–C_{23}	$\geq C_{24}$
Thermal cracking only	84.00	13.00	3.00	56.55	37.79	5.66
ZSM-5 (powder)	35.00	63.50	1.50	99.92	0.08	0
Zeolite Y (powder)	71.50	27.00	1.50	96.99	3.01	0
Zeolite Y (pellet)	81.00	17.50	1.50	86.07	11.59	2.34
Mordenite (pellet)	78.50	18.50	3.00	71.06	28.67	0.27
Silica-alumina(powder)	78.00	21.00	1.00	91.31	8.69	0
Alumina(powder)	82.00	15.90	2.10	53.02	43.27	3.71

[a] Determined by GC/MS

Table 5.4 PONA distribution in oil products from thermal and catalytic degradation of HDPE with various catalysts at 450°C

Catalyst	Total paraffin	(Total paraffin)		Total olefin	Naphthene	Aromatics	Others[a]
		n-paraffin	i-paraffin				
Thermal cracking	40.75	40.47	0.28	39.93	18.50	0.68	0.14
ZSM-5 (powder)	1.63	1.51	0.12	16.08	23.55	58.75	0.01
Zeolite Y(powder)	5.39	0.00	5.39	79.92	7.68	7.01	0.00
Zeolite Y (pellet)	25.10	20.68	4.42	49.28	12.05	8.43	5.14
Mordenite (pellet)	31.07	30.89	0.18	57.07	11.51	0.13	0.22
Silica–alumina (powder)	0.20	0.20	0.00	91.62	5.62	0.39	2.17
Alumina (powder)	32.57	32.57	0.00	50.19	14.99	1.14	1.11

[a] Others = hydrocarbons containing oxygen or unidentified organic compounds

of HDPE with zeolite Y, mordenite and silica–alumina gave 71–81 wt% oil yields, which mostly consist of C_6–C_{12} hydrocarbons in the gasoline range, whereas thermal degradation of HDPE produced 84 wt% oil yield with a much longer hydrocarbons like wax. In catalytic degradation, pellet zeolite Y that possesses less external surface area showed more oil yield and less gas yield than powder zeolite Y. Both all zeolites and silica-alumina increased olefin content in oil product. Particularly ZSM-5 and zeolite Y enhanced the formation of both aromatics and branched hydrocarbons having a high octane number. ZSM-5 among zeolites showed the greatest catalytic activity in cracking of heavy hydrocarbons to small gaseous hydrocarbons and formation of aromatics, which was related to the restricted channel of this zeolite that favors oligomerization reactions of olefins to form small alkyl aromatics, whereas mordenite produced the greatest amount of coke, due to its unidimensional straight-channel structure. Amorphous silica–alumina showed high yield of lighter olefins due to its strong acidity, but no activity in the formation of aromatics and branched hydrocarbons because of its amorphous structure.

Audiso *et al.* [25] has studied the catalytic degradation of polypropylene using silica, alumina and silica–alumina and zeolite catalysts in the range 200–600°C. The main products in oil production using more efficient catalyst were C_5–C_{12} olefins. Also the highest oil yields were obtained around 400°C. In catalysts, silica–alumina catalyst in comparison with alumina and silica only was much more reactive.

The liquid-phase catalytic degradation of HDPE over BEA, FAU, MWW, MOR and MFI zeolites with different pores in a batch reactor at 380 or 410°C has recently been studied by Park *et al.* [26]. Among zeolites, high activity was obtained with BEA and MFI zeolites, because of their bent pore structure suppressing carbon deposit, whereas MOR zeolite showed low activity, due to the rapid blocking of the linear pore structure even by a small amount of carbon deposit. Large three-dimensional pores of FAU enhanced mass transfer, resulting in a high yield of liquid product and also the slow diffusion of cracked product in MWW zeolite brought about much more cracking into small hydrocarbons. Accordingly, the pore shape of the zeolites was very important in determining the activity and product distribution in the degradation of polymers.

The catalytic degradation of HDPE and LDPE with MCM-41, ZSM-5 and silica–alumina in a batch reactor at 400°C was investigated by Aguado *et al.* [27]. The activity order in the catalytic degradation of HDPE and LDPE was ZSM-5>MCM-41>silica–alumina. The higher activity obtained over ZSM-5 was related to its stronger acid properties, whereas the high activity of MCM-41 compared with silica–alumina was influenced by the large surface area of MCM-41 with above 1000 m^2/g. The cracking of polyolefin over zeolite leads to a high proportion of gaseous hydrocarbons consisting of high olefin content and a liquid product in the range of gasoline with a high aromatic content. On the other hand, MCM-41 generated less olefinic gas products and, in addition to the gasoline fraction, the middle distillates in the range $C_{13}–C_{22}$ are produced. These activities and product distributions are highly related to the acidic and pore properties of the catalysts.

The activated carbon impregnated with different transition metals (Pt, Fe, Mo, Zn, Co, Ni and Cu) as a catalyst for PE conversion in a fixed-bed reactor has been studied by Uemichi *et al.* [28]. This catalyst plays a bifunctional role, with cracking and dehydrogenation/hydrogenation activity. The major effect of the metal impregnated on activated carbon was to increase the selectivity of aromatics with high octane number and to decrease the formation of *n*-alkanes. The aromatic yield was the most effective in Pt, Fe, Mo among various metals and also depended strongly on the support, which was much more efficient on activated carbon than on silica–alumina and alumina. It is proposed that two active sites with different function are to take part in the dehydrocyclization step involved in the degradation reaction. The abstraction of hydrogen atoms from polymer occurred predominantly on the acitivated carbon sites and the resulting hydrogen atoms migrate to the metal sites, while the metal sites catalyzed the desorption of hydrogen atoms.

8 EFFECT OF ADDITION OF OTHER THERMOPLASTICS

Lee *et al.* [29] reported the effect of PS addition in the catalytic degradation of waste HDPE and PS mixture using spent FCC catalyst at 400°C. Figure 5.14 shows the cumulative amount distributions of liquid products as a function of reaction time for the catalytic degradation of waste HDPE and PS mixture in different proportions. The increase of PS content in HDPE and PS mixture showed much high initial degradation rate and high

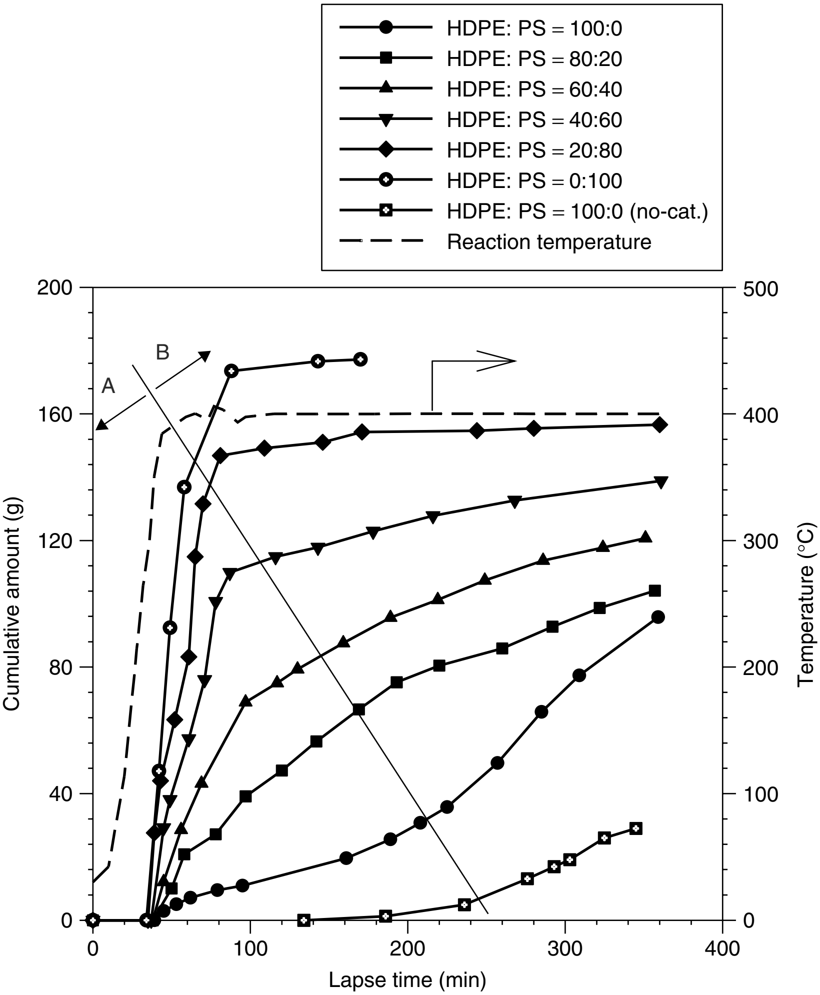


Figure 5.14 Cumulative amount distributions of liquid products for catalytic degradation of waste HDPE and PS mixture using spent FCC catalyst at 400°C. (A initial degradation region; B final degradation region). (Reproduced with permission from Elsevier)

liquid product yield, whereas that of HDPE showed high final degradation rate after a sufficient lapse in the reaction time.

According to the increase of PS content in HDPE and PS mixture, in Figure 5.15 the fraction of gasoline components in the liquid products was increased from about 85 wt% (pure HDPE) to about 98 wt% (pure PS) and the rest was kerosene + disel (C_{13}–C_{24}). No heavy oil ($>C_{24}$) was detected. In the catalytic degradation of pure HDPE without PS, the major product was olefin components whereas the paraffin products as well as the aromatic and naphthene products with a cyclic structure were minor products. According as PS content in the reactant increased from 0 to 20 wt%, the fraction of paraffin

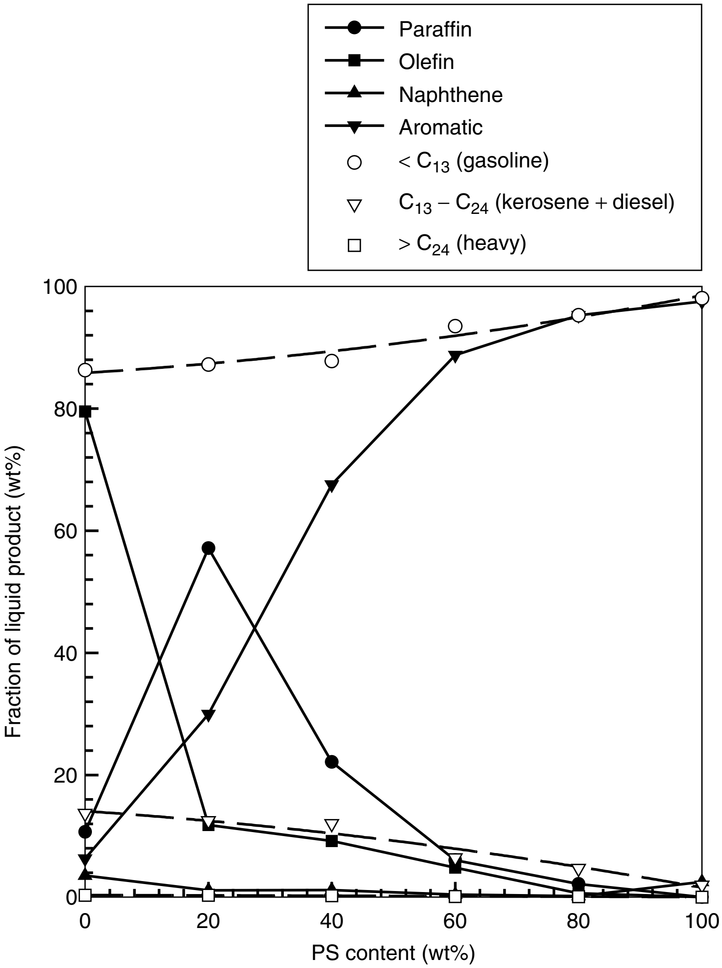


Figure 5.15 PONA and carbon number distributions of liquid products as a function of PS content for catalytic degradation of waste HDPE and PS mixture using spent FCC catalyst at 400°C. (Reproduced with permission from Elsevier)

products was sharply increased whereas that of olefin products were decreased, because of the increase of paraffin products by the availability of hydrogen in the carbenium ion from PS degradation to olefinic intermediates [30, 31]. However, in the range of PS content 20 wt% or above, the fraction of aromatic products as a function of PS content was sharply increased whereas that of paraffin products was sharply decreased. The PONA distribution of liquid products was influenced by the interaction of the degraded intermediates from HDPE and PS degradation. Furthermore, the aromatic product was accelerated with the cyclization of paraffinic and olefinic intermediates from HDPE degradation as well as the aromatic fragments from PS degradation. In aromatic products, as shown in Figure 5.16, the increase of PS content in the mixture was linearly increased the styrene product fraction, but decreased the ethylbenzene product fraction. Styrene product was

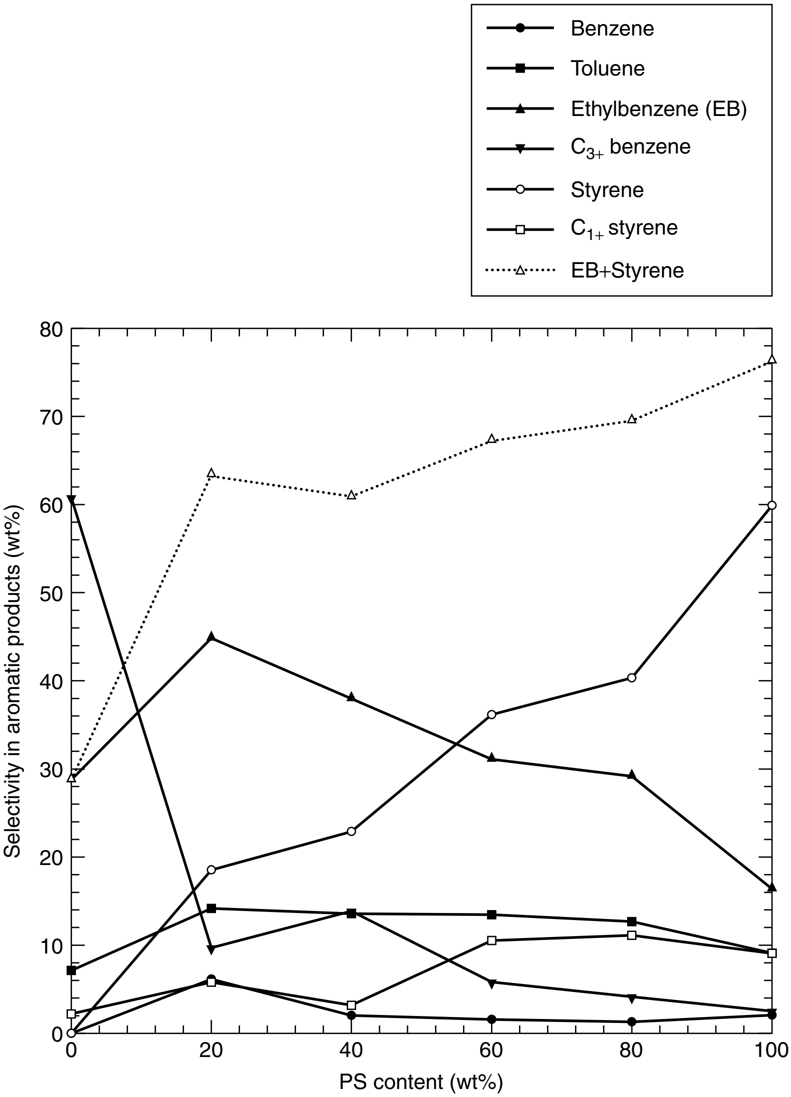


Figure 5.16 Selectivity in aromatic products as a function of PS content for catalytic degradation of waste HDPE and PS mixture using spent FCC catalyst at 400°C. (Reproduced with permission from Elsevier)

mainly produced from the degradation of PS while ethylbenzene product was influenced by HDPE content, due to the cyclization of the olefinic and paraffinic intermediates obtained by the first catalytic degradation of HDPE. Also their fraction with two carbon numbers in the side group showed the highest selectivity of 60 wt% or above. The addition of PS in the catalytic degradation of HDPE using spent FCC catalyst accelerated the production of ethylbenzene and styrene in pores of spent FCC catalyst as shape selectivity.

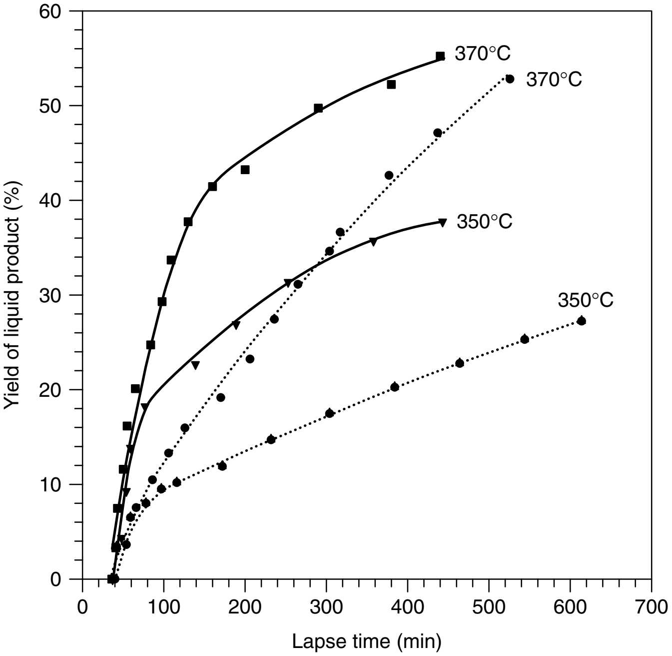


Figure 5.17 Yield of liquid product as a function of lapse time for catalytic degradation of waste HDPE and mixed plastics (HDPE:LDPE:PP:PS = 33%:22%:33%:11%) using spent FCC catalyst at 350°C and 370°C (solid line: mixed plastic; dotted line: HDPE)

Walendziewski [1] was reported the thermal and catalytic degradation of PE, PP, PS and their mixture using alkaline catalyst. The catalytic degradation of PE + PS, compared with that of PE, showed high aromatic content and low boiling temperature, and also high density, high RON and MON values in the gasoline fraction.

According to the type of plastics, the characteristics of oil product in thermoplastics was clearly differed. Figure 5.17 shows the cumulative yield distributions of liquid product as a function of reaction time for catalytic degradation of pure waste HDPE and mixed plastic (HDPE:LDPE:PP:PS = 33%:22%:33%:11%) at 350 and 370°C, respectively. Here the ratio in the mixed plastic was the average weight ratio of general thermoplastics generated in Korea. The mixed plastic showed much higher initial rate of liquid product yield than that of pure HDPE. Also, the catalytic degradation of mixed plastic occurred at lower reaction temperature (by about 20°C) than that of pure HDPE plastic, because it was included the plastics with low degradation temperature in the mixed plastic.

9 FRACTIONAL DISTILLATION OF PRODUCTS

Reactor effluent that is composed of oils with various boiling temperatures is fed into the base of the fractional distillation tower where it is fractionated into selected product streams. Various product streams in the distillation tower are fractionated from

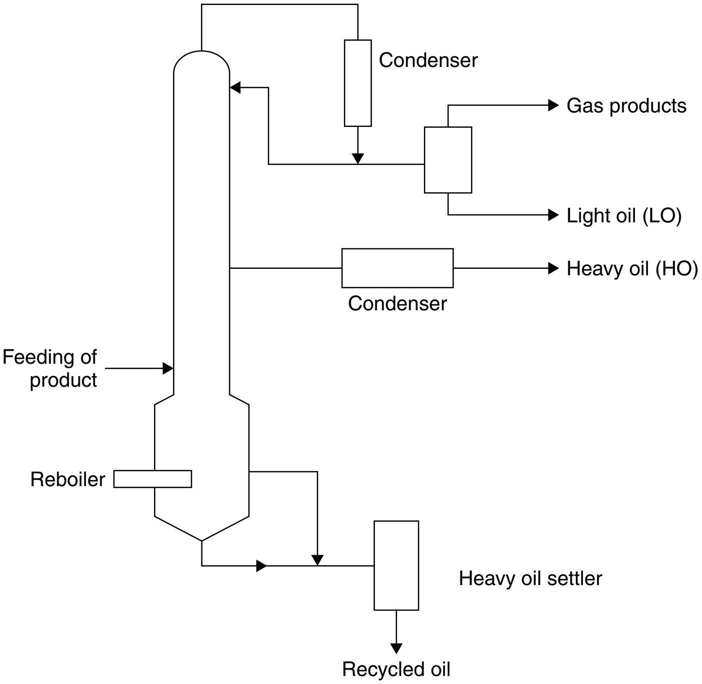


Figure 5.18 Flow diagram of distillation tower

reactor effluent due to their different boiling temperatures. The control variables are the temperature gradient in distillation tower, temperature of reboiler located at the main column, reflux ratio of product oil and pressure (vacuum or atmospheric pressure). Figure 5.18 shows two streams produced from the main column, including light product and heavy oil (HO). However, these product streams can be changed by regulation of the tower structure. Light products are taken overhead to the accumulator of light product after it is cooled in condenser, and are separated into both gas products and light oil (LO). The condensation of the product streams in the condenser may be cooled by a water stream. Gas products consisting of C_5 and below, with mainly alkane components may be used as fuel gas in the pyrolysis process or sent to a gas plant, the quality of which can be continuously monitored by an on-line analyzer.

Light oil is mainly obtained in the gasoline range and has a partial reflux stream by control of the reflux ratio that controls the temperature gradient in the distillation tower and also the product quality. HO consists mainly of kerosene and diesel range compounds, which is the desired product as fuel oil with high calorific value. The boiling range of LO and HO depend on the current desired product specifications, which are obtained by control of experimental variables in the distillation tower. A portion of the main column bottom passes to the heavy oil settler, which receives the overflowing heavy oil with high viscosity generated from the main column bottom. They are returned to the melting reactor or cracking reactor, in order to crack the heavy oil again into the light oil. In many cases, the oils produced by this method are marketed without any additional processing.

10 PROPERTIES OF LIQUID PRODUCT [32]

The need for various grades of the product oils separated in the distillation tower is evident. In order to keep the various grades on a uniform basis, the authorities in each country have standardized on a few grades by the properties of the oil produced.

It is necessary to compare reliable properties of the oil produced, as a comparison with those of commercial gasoline, kerosene and diesel. It is essential to determine the physical measurements such as those listed for a variety of the oils, as shown in Table 5.5. Based on these values, the oil produced in the process plant is tested, to determine whether it can be put on the market.

As the density of the oil produced is decreased, the heat value per volume decreases, but the heat value per mass will increase. If the oil is usually purchased and sold on a volume basis, heavy oil is more efficient. Also, if it is necessary to choose the most important specific of the oil produced, viscosity will be selected. Viscosity can aid combustion and can also be the cause of the greatest trouble. For proper and efficient combustion an oil should have a reasonable viscosity at the burner. In the case of too high viscosity, difficulty in pumping in the process and trouble at the burner are encountered and also carbon residue is high due to poor combustion. However, in case of too light oil, incomplete combustion occurs and there will be a loss of economy.

Further sources of trouble with the oil produced is water and sediment present in the oil, when it is used as a fuel oil. Water causes sparking, spitting and flashback of the flame, which result in loss of heat as a result of improper combustion. Sediments such as sand and carbon, etc. cause the erosion of burner tips, pump parts and sensitive control valves, etc. Also, some chemical compounds present in an oil will absorb oxygen from air or water, to form new compounds. Unfortunately, some of these chemical compounds are insoluble in the oil, with the result that they will either remain suspended in the oil or will drop to the bottom of the tank. They must not reach the suction lines in a storage tank.

When discussing the oil produced, the subject of carbon becomes an issue. Carbon is formed during cracking of hydrocarbons at high temperature and pressure. This carbon is present in heavy oil and will be suspended within the oil. However, oil containing a small amount of carbon is easily combustible without any trouble. The carbon content is

Table 5.5 Properties of the oil product

Items	LO (in KIER)[a]	Gasoline	HO (in KIER)[b]	Kerosene	Diesel
Ignition point (°C)			74	>40	>40
Pour point (°C)	<−50		−12.5	<−15	<−15
Copper corrosion (100°C, 3 h)	<1	<1	1	<1	<1
10%carbon residue (wt%)			0.01	0.21	<0.15
Ash (wt%)	0.001		0.003	<0.02	<0.02
Kinematic viscosity (40°C)	<1.0		6.5	1.4–3.0	1.9–5.5
Density (kg/m^3,15°C)	757		831		815–855
Distillation (T90)	232	<175	430	285–325	<360
Heat of combustion (kcal/kg)		11,180	10,983	11,020	10,800
Water & sediment (vol%)		<0.01	<0.005		<0.02

[a] Light oil produced in KIER process

[b] Heavy oil produced in KIER process

measured by the Conradson carbon test, as a relative value of coke formation. This is the amount of carbon remaining after evaporating all the volatile materials in a certain type of apparatus. It is representative of the tendency of the oil to form coke, in many practical uses such as household and industry, etc. But the light oil is very thin and does not have much carbon residue. This oil is distilled until 90% of the sample has been vaporized. The remaining 10%, the heaviest of the entire sample, is used to run the carbon test as 10% carbon residue value measured. For an example, the values for commercial kerosene and diesel would be below about 0.2.

There are certain impurities present in most fuel oils. These organic and inorganic substances are noncombustible and after combustion of the fuel oil they will form a residue called ash. The greatest percentage of ash found in various oils is directly related with the crude oils from which they are refined. The crude oil is usually mixed with water, mud and sand, etc. Most of these contaminants are removed from the crude oil, but very small amounts will still remain suspended in the crude oil. Moreover, the ash-producing materials found in crude oil are concentrated in the heaviest oils such as the residuals. In order to determine the ash amount, the oil in the presence of air is burned. The remaining materials are noncombustible ash, which is computed as the total percentage of ash in the sample. The ash amount measured for kerosene and diesel is below 0.2 wt%, but the oil of two types produced in KIER process is very low.

As the oil is heated, the oil vapors and air will ignite without the application of an external flame or spark at a certain temperature, which is called the ignition point of the oil. Generally the spontaneous ignition temperature reduces with increase in carbon number and is high for the aromatic hydrocarbons, due to the inherent structural stability of the benzene ring [33]. The ignition point of kerosene and diesel is required to be above 40°C. Thus, the oil produced in the pyrolysis process must be blended with a component of high ignition point, which should be watched with great care.

The temperature at which an oil will just flow under standardized conditions is known as the pour point. This test has particular significance in connection with oils that may require heating to liquefy them and also to enable them to be pumped. If an oil of low pour point begins to solidify in the storage tank in cold weather, some other means will be needed to prevent the mass from solidifying completely. For example, when the plant is shut down in cold weather, the oil in the line and tank, etc. will solidify and thus the oil is too viscous to be pumped. So the pour point of the oil produced must be checked during cold weather.

Sulfur is one of most important elements present in an oil, although the sulfur content may be very low. It is usually in combination with carbon, hydrogen, oxygen and nitrogen, forming many different compounds. They have mainly a high boiling point and are therefore concentrated in the residual oils. In the petroleum refinery industry, they break down during the refining processes such as the hydrodesulfurization process, which can lead to low-sulfur residuals. This process brings the residual oil into contact with hydrogen gas and a catalyst. The residual oil is split into low-sulfur oil and hydrogen sulfide gas. The most important trouble for oil containing sulfur is corrosion by its combustion products such as sulfur dioxide and sulfur trioxide. Moreover, the corrosiveness of these sulfur compounds is increased by moisture. But the sulfur has little effect on the handling and storage of the oil and also industrial instruments such as pump and mechanical parts.

Chemical compounds will boil at a certain temperatures. Thus, oil consisting of various compounds is made up of a series of fractions, defining the distillation range of the oil. Distillation range is the difference in degrees between the initial boiling point (IBP) and the end point (EP). Thus distillation range will vary according to the type of oil. The initial boiling point is the temperature at which the first drop of condensed vapor appears in a distillation test. The next temperature point is the 10% boiling point, which is the temperature that 10% of total volume of oil will distill off. The spread between the IBP and the 10% point should be small so that the oil will continue to burn in case of ignition. If the spread is too large, ignition and starting will be difficult. Also, the 90% point and the end point must be watched. If the spread between the 90% point and end point is very great, the oil has been blended or contaminated. This can cause poor combustion. If the end point is high, the 90% point will also be high, these high values may be difficult to burn and can cause carbon trouble. For efficient combustion, the distillation curve should be smooth. A fluctuating distillation curve implies an oil that may give irregular operation due to unstable conditions. Therefore, the distillation test is one of the best methods for detecting the quality of the oil produced such as light or heavy oil fractions.

As an example, the distillation curves of LO and HO obtained in KIER process was compared with those of commercial gasoline, kerosene and diesel are shown in Figure 5.19. The distillation curve of LO product was distributed between commercial

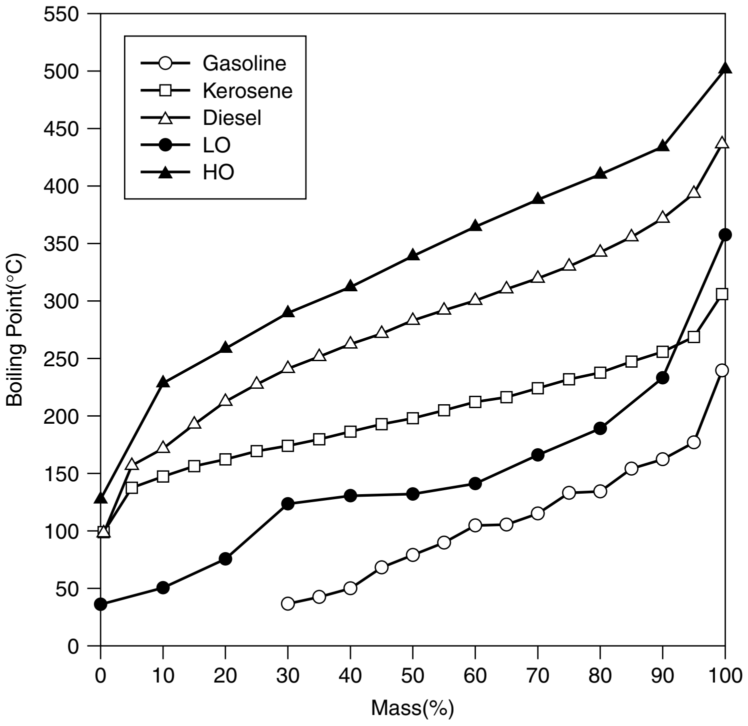


Figure 5.19 Boiling point distribution of commercial gasoline, kerosene and diesel, and LO and HO products obtained in the KIER process

gasoline and kerosene. For LO product, the spread between the 90% point and end point is big, because of the mixing of heavy oil. On the other hand, HO product has a higher boiling point distribution than commercial diesel. Their distillation curves can be changed by experimental variables in the distillation tower, such as temperature gradient, pressure, reflux ratio and reboiler temperature, etc.

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6

Development of a Process for the Continuous Conversion of Waste Plastics Mixtures to Fuel

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1 INTRODUCTION

The amount of waste plastics discarded each year is constantly increasing and is causing serious pollution-related problems worldwide. Chemically recycling such waste might provide cheap and abundant sources of useful chemicals and energy. Among a number of potential approaches to recycling, chemical approaches, which convert waste plastics to useful hydrocarbons, have been recognized as being of particular promise.

Presently, about half of the waste generated in Japan is derived from factories as specific plastics, such as polyolefins, polystyrene (PS) [1–4], poly(ethylene terephthalate) (PET) [5–6], and polyvinylchloride (PVC) [2, 3, 7–11]. To date, several studies have focused on the individual degradation of these waste plastics. The remaining half of the waste plastics in Japan is generated from households in the form of plastic mixtures and waste-containing kitchen refuse. PVCs can be removed from such waste mixtures by utilizing PVCs with a higher density than that of other plastics. However, there remain certain unresolved issues, such as the lack of an efficient continuous chemical recycling process for application to a mixture of remaining waste plastics. Specifically, it remains problematic that each type of plastics has different pyrolytic properties, as is the fact that large amount of sublimate materials, such as terephthalic acid (sublimation point ∼300°C), are produced from the degradation of some plastics, such as PET. Terephthalic acid is precipitated as a hard, solid body around valves and pipelines, i.e. at locations where the temperature is below 300°C.

Waste plastics are primarily generated by small-to-medium-size enterprises and households. Therefore, it is preferable to build chemical plants for the recycling of waste

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plastics locally, i.e. in each self-governing region or prefecture. However, in this respect, it should be noted that it is costly to use nitrogen or hydrogen as the carrier gas. Because steam is cheaper and easy to handle, it is a potential candidate carrier gas in such plants.

The chemical recycling of waste plastics consists of two processes: the first is the degradation of waste plastics for the production of heavy oils, and the second is a catalytic cracking process that converts the heavy oils into useful hydrocarbons. To achieve these recycling goals, it remains necessary to develop efficient chemical recycling processes that can operate in a steam atmosphere.

In this chapter, a chemical recycling method for the mixtures of waste plastics is described. First, a number of possibilities are examined that would realize the formation of pyrolytic properties with a uniform reaction rate among oxygen-containing plastics; furthermore, it would be advantageous to achieve the degradation of such plastics with the production of a minimal carbonaceous residue [5–6]. To this end, a new pyrolytic reactor [12] has been proposed that has been shown to achieve high hold-up, a high level of heat transfer, and good contact between melted plastics and steam, thus accelerating hydrolysis. Using this reactor, a mixture of waste plastics can be degraded and further decomposed over an FeOOH catalyst in a steam atmosphere. Second, chemical processes are described here that can achieve a catalytic cracking of the heavy oil, achieved by the pyrolysis and hydrolysis of the waste plastics, and producing useful fuels [13–15]. The catalyst used in the recycling process must exhibit high and stable activity during the catalytic cracking of the heavy oil in a steam atmosphere [16]. Finally, the rationale for and usefulness of the proposed chemical recycling method are both validated by the experimental results obtained in a pilot-scale plant.

2 RECOVERY OF HEAVY OIL FROM WASTE PLASTIC

The waste plastics generated from households are in the form of plastic mixtures; among such mixtures, the amount of PET generated as a household waste has rapidly increased as the production of PET bottles has increased. PET is formed by the ester bonding of terephthalic acid and ethylene glycol. When PET is heated above 380°C, pyrolysis suddenly starts, yielding oxygen-containing hydrocarbons and a significant amount of carbonaceous residue [17–19]. Accordingly, in order to develop a recycling process for the conversion of waste plastics into useful liquid hydrocarbons, a method for the degradation of a mixture of waste plastics without the production of such a carbonaceous residue is required.

2.1 DEGRADATION OF VARIOUS PLASTICS

The relationship between the rate of PET degradation and the molar fraction of steam in the carrier gas was investigated using a thermogravimetric apparatus equipped with a thermobalance. Figure 6.1 shows the remarkable change in the fraction of unreacted PET as the molar fraction of steam in the carrier gas was varied. When a pure nitrogen stream (steam molar fraction = 0%) was used, the degradation of PET was initiated

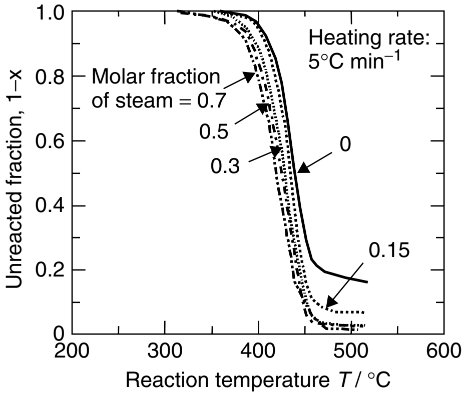


Figure 6.1 Change in the fraction of unreacted PET in a steam atmosphere. Heating rate: 5°C min^{-1}. (Reproduced with permission from Elsevier)

at about 380°C and was terminated at about 530°C, leaving about 16% carbonaceous residue. When the carrier gas contained steam, the fraction of carbonaceous residue was drastically reduced from 16% (100% nitrogen) to below 2% (70 mol% steam). Furthermore, the initiation temperature for pyrolysis decreased by about 30°C. Figure 6.2 shows the relationship between the molar fraction of steam in the carrier gas and the amount of carbonaceous residue remaining at 520°C. The circles, triangles, and squares represent the results obtained at heating rates of 2.5, 5.0, and 10°C min^{-1}, respectively. All data lie on a single curve, suggesting that the amount of carbonaceous residue depends only on the partial pressure of steam, and not on the rate of increasing temperature. The amount of residue thus decreases with increases in the partial pressure of steam. Less than 1% residue was found to remain under 100% steam carrier gas conditions.

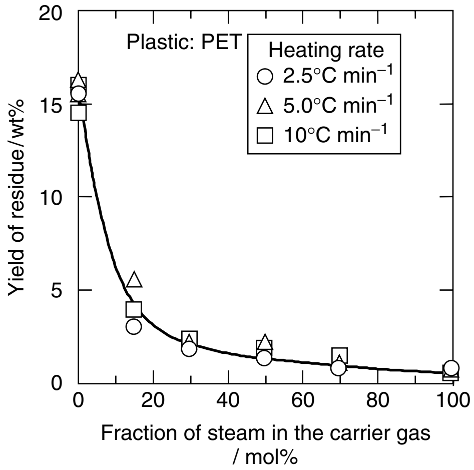


Figure 6.2 Relationship between the molar fraction of steam in the carrier gas and the yield of residue at 520°C. (Reproduced with permission from Elsevier)

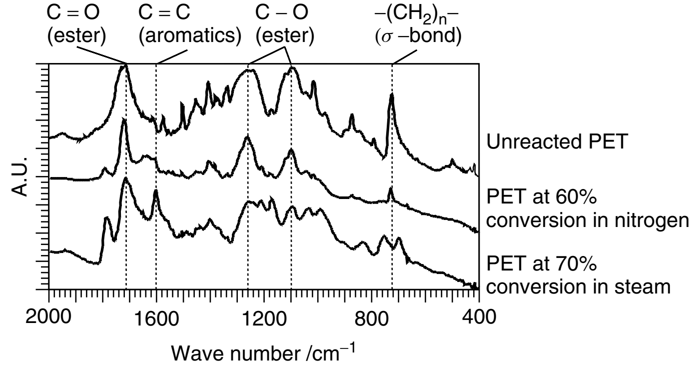


Figure 6.3 FTIR spectra of unreacted PET and of residues obtained from PET at 60% conversion in both nitrogen and steam (70 mol%) atmospheres. (Reproduced with permission from Elsevier)

Figure 6.3 shows the FT-IR spectra of residues obtained in nitrogen at a PET conversion of 60%, and in a steam atmosphere at a conversion of 70%. This figure also shows the spectrum for unreacted PET. PET is formed by the ester bonding of terephthalic acid and ethylene glycol. In the case of thermal pyrolysis in nitrogen, the dehydration of the chemical bonds and the random scission of the main chain of PET occurred, resulting in a reduction in the peak strengths corresponding to bonds involving the oxygen atom (C–O, C=O) and σ-bonds, leaving a hydrogen-poor residue. On the other hand, when the degradation of PET was conducted in the presence of steam, the C–O bond and σ-bond were preferentially weakened, and a peak corresponding to free aromatics (C=C) appeared. These aromatics were considered to be terephthalic acids at the ends of the main chain of PET. Hence, steam was found to accelerate the hydrolysis of PET, producing monomers of PET such as terephthalic acid.

Figure 6.4(a, b) shows the thermogravimetric curves (TG-curves) for plastics at a heating rate of 5°C min^{-1} in nitrogen and in steam, respectively. Seven types of plastics were used in this series: polyethylene (PE), polypropylene (PP), polycarbonate (PC), polybutyleneterephthalate (PBT), polystyrene (PS), nylon-6 (N6) and nylon-6,6 (N6,6). The curves for the degradation of PET are also shown in the figure for comparison. The TG curves were remarkably different among the plastics in a nitrogen stream, due to differences in the main chains of the plastics. Furthermore, polyester resins, such as PC, PBT, and PET, yielded large amounts of carbonaceous residue at 527°C, due to dehydration during the degradation in nitrogen. In contrast, in a steam atmosphere, the TG curves of PC, PBT, and PET were remarkably altered by shifts to lower temperature regions and by reducing the amount of carbonaceous residue, as compared with those in a nitrogen atmosphere. Accordingly, it was concluded that the dominant mechanism of degradation of polyester resins changed from thermal pyrolysis to hydrolysis by introducing steam as the carrier gas.

Under the nitrogen steam conditions, PC showed the lowest degradation rate. On the other hand, the plastic resin with the lowest degradation rate was PE in a steam atmosphere. Therefore, the size of a degradation reactor could be designed by considering the degradation rate of PE alone.

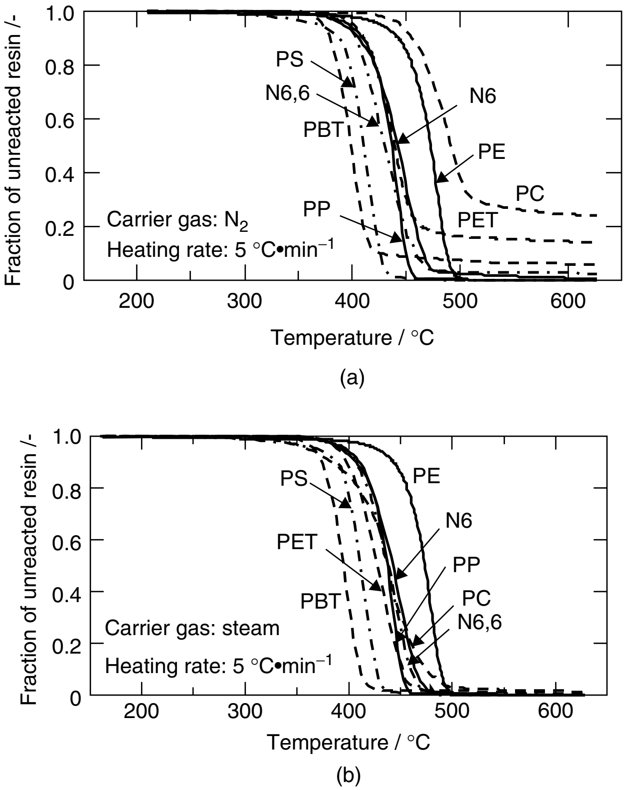


Figure 6.4 Change in the fraction of unreacted plastics used in this study at a heating rate of 5°C min^{-1}: (a) in nitrogen; (b) in steam. (Reproduced with permission from Elsevier)

2.2 CATALYTIC CRACKING OF WASTE PLASTICS WITHOUT RESIDUE

The degradation of PET in a steam atmosphere is effective at reducing carbonaceous residue, and this type of degradation produces terephthalic acid and oxygen-containing compounds. However, terephthalic acid is precipitated as a hard solid body around valves and pipelines, because this compound is a sublimate material (sublimation point ~300°C). Therefore, in this case, sublimate materials such as terephthalic acid should be converted into liquid hydrocarbons. In order to convert this produced terephthalic acid, a catalyst for cracking carbonyl groups of terephthalic acid is required. For this reason, transition metal oxides, which easily form carbonyl complexes, were considered to be suitable catalyst materials. Moreover, the transition metal oxides such as iron oxide and nickel oxide are inexpensive. In this section, a method for the decomposition of terephthalic acid into useful liquid hydrocarbons is described. The screening of potential catalysts was conducted using transition metal oxide catalysts.

The catalytic cracking of PET was carried out using a fixed-bed type of reactor in a steam atmosphere. The reactor was heated to the desired temperature in a mixture of steam and nitrogen as the carrier gas. After feeding PET particles into the reactor, the particles were heated to the reaction temperature, and then underwent the hydrolysis in a steam atmosphere to be decomposed to terephthalic acid and lighter hydrocarbons. These molecules were cracked through the catalyst bed. The liquid products were condensed in two condensers cooled with ice and water. Lighter hydrocarbons were collected in a gas pack. The amount of carbonaceous residue was calculated from the difference between the mass of the catalyst before and after the experiment. The reaction was conducted at the temperatures ranging from 450 to 530 K.

Figure 6.5 shows the yields ([wt%]) of the reaction of PET using several transition metal oxide catalysts under the following conditions: a temperature of 500°C, a time factor (the ratio of the mass of the catalyst *W*, to the PET feed rate *F*) of 0.317 h, and a particle size of 0.21–0.25 mm. Fe_2O_3 did not show activity, hence these results have been omitted. With respect to the reduction of terephthalic acid, FeOOH, nickel hydroxide and nickel oxide showed the decomposition activity of terephthalic acid. However, a large amount of benzoic acid, which is also a sublimate material (sublimation point ~100°C), was produced over nickel hydroxide and nickel oxide. Because these nickel compounds are more expensive than FeOOH, FeOOH was considered to be a suitable catalyst for the decomposition of terephthalic acid.

Figure 6.6 shows the change in product yield with increase in the time factor W/F. The amount of sublimate materials (terephthalic acid and benzoic acid) decreased remarkably with increase in the time factor, and no sublimate materials were observed after approximately 0.5 h. Moreover, carbon dioxide was produced, and the yield of the carbon dioxide

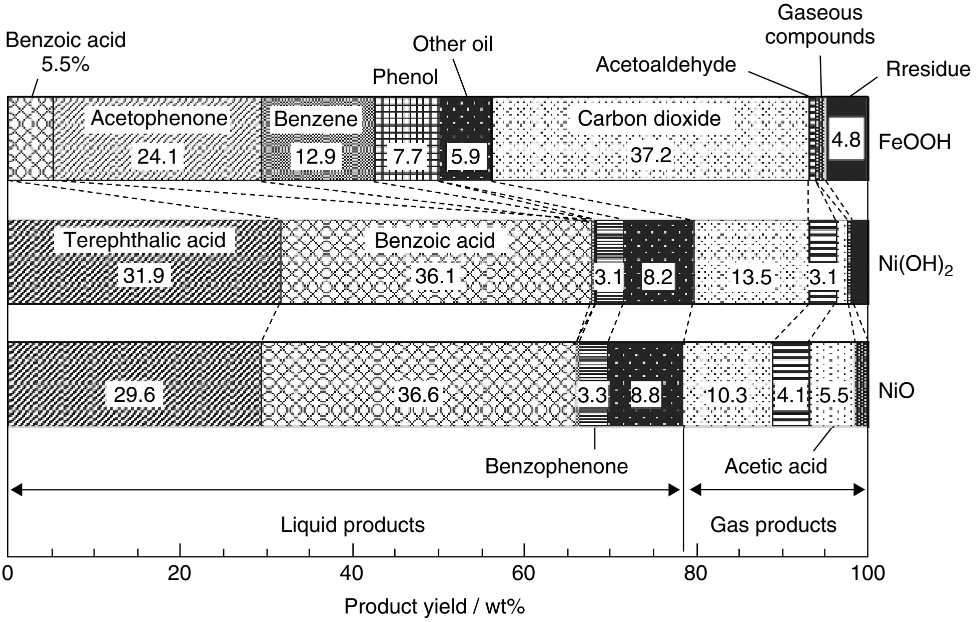


Figure 6.5 Production yields of the reaction of PET over transition metal catalysts. $T = 500°C$, $W/F = 0.32\ h^{-1}$, particle size = 0.21–0.25 mm, molar fraction of steam = 0.94%. (Reproduced with permission from Elsevier)

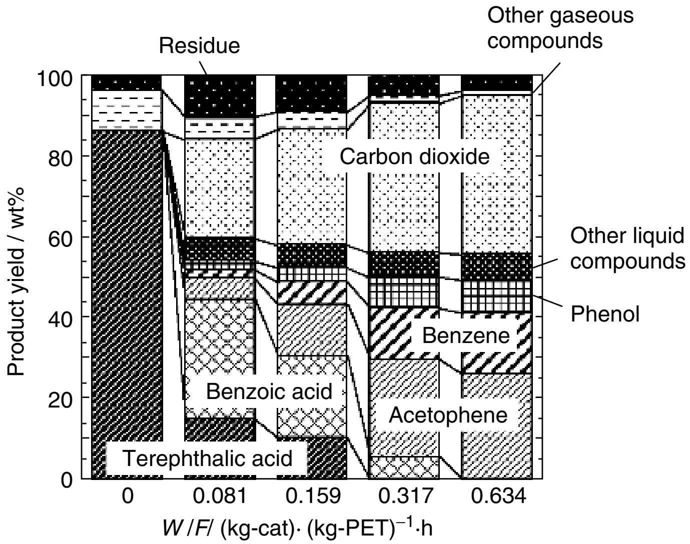


Figure 6.6 (a) Change in product yield with an increase in the time factor, W/F. $T = 500°C$, particle size = 0.21–0.25 mm, molar fraction of steam = 0.94%. (Reproduced with permission from Elsevier); (b) Change in product yield with an increase in the time factor. The solid curves represent the calculated results

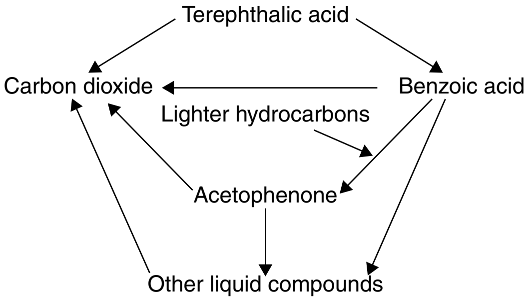


Figure 6.7 Reaction pathway proposed for the reaction of terephthalic acid produced by the hydrolysis of PET. (Reproduced with permission from Elsevier)

increased with decrease in the yield of the sublimate materials. Figure 6.7 shows the putative reaction mechanisms [5], i.e. the carbonyl groups of terephthalic acid are decomposed to yield carbon dioxide and benzoic acid, and benzoic acid undergoes further reactions to produce acetophenone and carbon dioxide. Some of the acetophenone was converted to benzene and phenol, which are components classified under *other liquid compounds*. Two reaction pathways, from acetophenone and other liquid compounds to carbon dioxide, are negligibly small. In the reaction path from terephthalic acid to benzoic acid, benzene and phenol were also produced. As a result, since sublimate materials such as terephthalic acid and benzoic acid were successfully decomposed using an FeOOH catalyst, serious pipe blocking at source plants could be avoided.

The structure and morphology of FeOOH treated at 500°C in a steam atmosphere was analyzed by X-ray diffraction and transmission electron microscopy, respectively. The X-ray diffraction analysis showed that FeOOH was transformed to Fe_2O_3 during the treatment in the steam atmosphere. In contrast, the TEM observation revealed micropores of 1 nm diameter in the untreated FeOOH, which was not observed with commercial Fe_2O_3. Moreover, the pores increased in diameter to approximately 5–100 nm after the steam treatment. This morphology was thought to be the result of the dehydration of FeOOH. It is possible that many active sites were generated on the surface of the pores, resulting in the observation that treated FeOOH showed high activity, even though its crystal structure is the same as that of Fe_2O_3 [6, 20].

Terephthalic acid is a useful source material of PET, as well as benzoic acid and benzoates. However, in order to recycle the terephthalic acid, produced further purification is required, because other organic compounds are also produced as impurities in the degradation process of waste plastic mixtures, e.g. PE and PET mixtures described in Section 2.3.

2.3 CONTINUOUS DEGRADATION OF WASTE PLASTICS MIXTURES FOR THE RECOVERY OF HEAVY OIL

The dominant mechanisms of polyester resin degradation (such as polycarbonate, polybutyleneterephthalate and polyethyleneterephthalate) changes from thermal pyrolysis to hydrolysis by the introduction of steam as the carrier gas. PET was successfully degraded by hydrolysis in a steam atmosphere, yielding an amount of pure terephthalic acid that could be predicted from the chemical formula of PET, and leaving carbonaceous residue of less than 1%. From economic and energetic viewpoints, it is both inexpensive and easy to employ steam as the carrier gas in chemical recycling plants. Furthermore, the temperature required to initiate was found to decrease approximately 70°C when polyester resins were degraded by hydrolysis in a steam atmosphere [12].

When the mixture of waste plastics was degraded by accelerating the hydrolysis of the plastics with steam and by decomposing the generated sublimate materials over FeOOH catalyst, the following reaction conditions are needed:

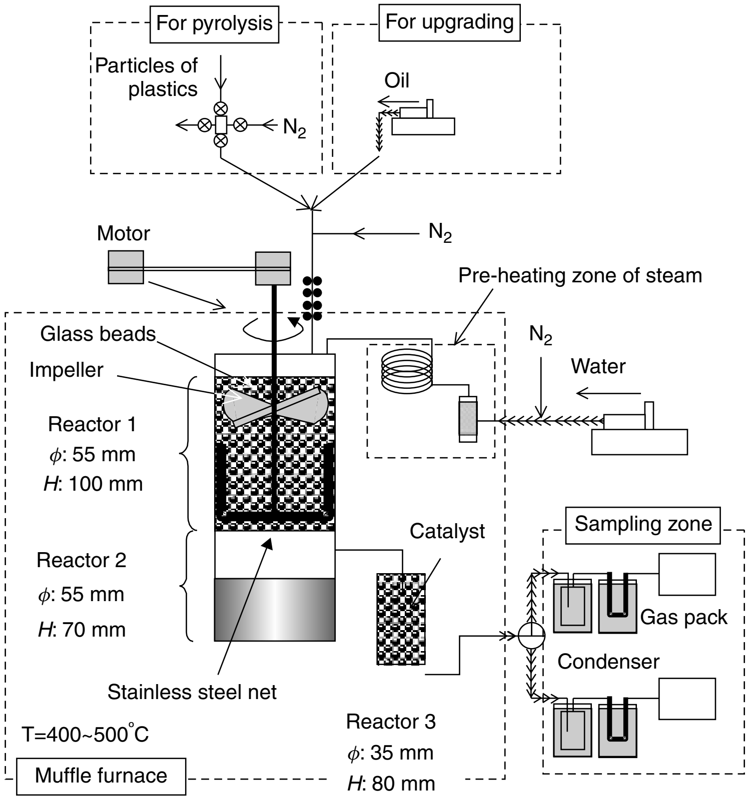
1. A good contact of melted plastics with steam to accelerate the hydrolysis of plastics.
2. Large rate of the heat transfer to heat plastics up to a desired temperature.
3. High hold-up of plastics in a reactor to achieve an enough reaction time for degrading plastics.
4. Contact of vapor of sublimate materials with FeOOH catalyst to decompose the materials.

Bockhorn *et al.* [2, 3] proposed circulated-spheres reactor for the pyrolysis of waste plastics. This reactor enabled one to remove gaseous products from the reaction zone and to achieve high heat transfer rates, namely condition (2) described above. The concept of this circulated-spheres reactor has the possibility to attain conditions (1) and (3) by improving the reactor.

Based the discussions above, a new pyrolytic reactor can be proposed that would be capable of achieving a high hold-up, high heat transfer, and good contact between melted plastics and steam for the acceleration of hydrolysis. Using this novel reactor system, a mixture of waste plastics was degraded, and further decomposition over an FeOOH catalyst was also achieved.

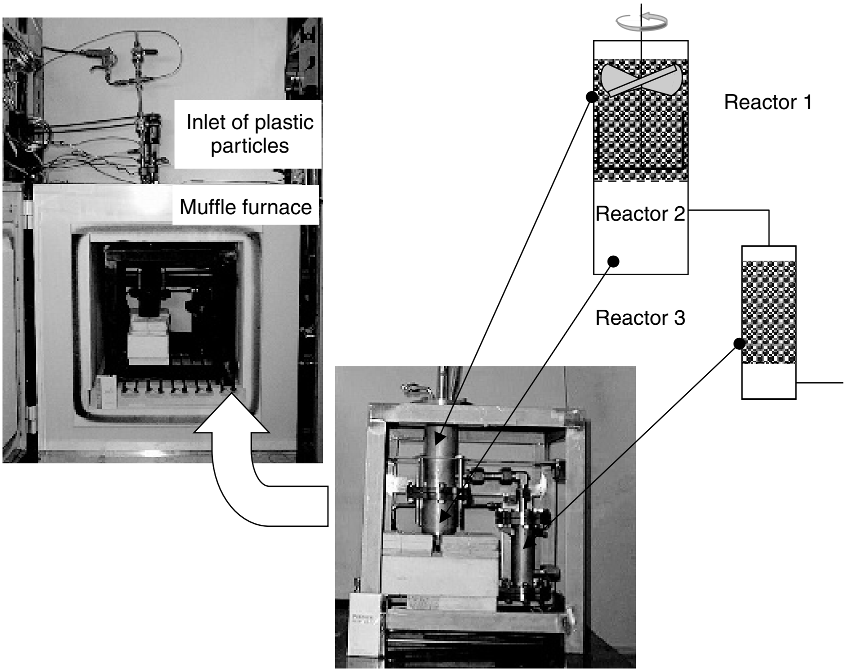
This novel reactor is a pyrolytic reactor system using stirred heat-medium-particles (Figure 6.8). This pyrolytic reactor system is composed of a series of three types of reactor. The first reactor uses stirred heat-medium-particles (reactor 1), the second is a tank reactor (reactor 2), and the remaining reactor is a fixed-bed reactor (reactor 3). Reactor 2 is located under reactor 1, and is separated from reactor 1 by a stainless steel net. The seizes of these reactors are described in the figure. The expected reaction behavior is described below.

In reactor 1, plastic particles are fed into the top of a bed of glass beads as the heat-medium-particles, and the particles are then melted and adhered to the beads. The glass beads are stirred slowly by two equipped impellers, one of which is the propeller-type of impeller, and the other is an anchor-type of impeller located at the bottom of the bed of glass beads. The propeller-type of impeller is turned to lift the particles. In this manner, the glass beads at the top layer of the bed of glass beads are replaced continuously by



(a)

Figure 6.8 (a) Schematic view of the proposed reactor system for the chemical recycling of plastics; (b) photograph of the proposed reactor system. (Reproduced with permission from Elsevier)



(b)

Figure 6.8 (*continued*)

other beads lying beneath the top layer. These stirred beads increase the rate of heat transfer. Following the string of the glass beads, the melted plastics are transported over the bed of glass beads, resulting in a high hold-up of plastics in the reactor and good contact with the steam, which functions as the carrier gas. The melted plastics on the glass beads are decomposed by hydrolysis with steam and the random scission of C–C bonds. Some of the melted plastics on the glass beads are carried to the bottom of the bed of glass beads, and are dripped onto reactor 2 (tank reactor). In reactor 2, the unreacted plastics undergo further decomposition, yielding various gaseous compounds. Reactor 3 is filled with an FeOOH catalyst. Gaseous compounds, including the vapors of sublimate materials, are passed through the FeOOH catalyst bed, where they undergo the catalytic degradation.

A mixture of PE and PET was used as a model waste plastic mixture. The ratio of PE/PET was 15:2, which is the ratio of the amounts of the two plastics discarded in Kyoto, Japan. After continuous degradation with and without stirring of the glass beads, the glass beads were collected from reactor 1 (Figure 6.8). When the glass beads were not stirred, which corresponded to a trickle-bed type of reactor, a massive carbonaceous residue remained with the glass beads on the top of the bed of glass beads. For this reason, the heat transfer rate was low and the melted plastics did not make good contact with the steam. On the other hand, there was not a massive amount of residue and glass beads slightly colored yellow, when the glass beads were stirred by rotating the impellers at rates exceeding 8 rpm. Furthermore, no residue nor oil was in reactor 2, the tank reactor,

(Figure 6.8). These results indicate that the proposed reactor system is useful for the continuous degradation of plastics.

Figure 6.9 shows the dependency of the product yields, based on data collected at the outlet of reactor 3 (see Figure 6.8), on the ratio of the catalyst mass W to the feed rate of the plastics F and the time factor W/F increased from 0 to 1.5 h. Reactions were conducted under temperature conditions ranging from 500°C, at a catalyst weight W of about 2.0×10^{-2} kg. When the FeOOH catalyst was not loaded into reactor 3, a large amount of yellow wax was obtained. When the FeOOH catalyst was loaded into reactor 3, oil and carbon dioxide were produced. The amount of carbon dioxide and that of gaseous hydrocarbons increased, and the yield of oil decreased, as the amount of FeOOH catalyst loaded increased. This suggests that the FeOOH catalyst is capable of catalysis, leading to the decomposition of a wax via oxidation by oxygen atoms from the lattice of FeOOH and/or from H_2O.

When a wax is decomposed via oxidation by the oxygen atoms from the lattice of FeOOH catalyst, the catalytic activity of an FeOOH catalyst will decrease. Therefore, the gaseous product yields of the reaction were measured by sampling at different intervals at a temperature of 500°C and the time factor of 1 h. The main gaseous products were carbon dioxide (~3 wt% for 140 min), n-C_4H_{10} (2 wt%), n-C_3H_8 (2 wt%), C_2H_6 (0.5 wt%), C_2H_4 (1.5 wt%), and CH_4 (0.5 wt%). Except for at the beginning of the reaction, there were only negligible changes in the product yields. The amount of oxygen required for producing carbon dioxide during a reaction time of 140 min was evaluated, and was found to be larger than that generated through the phase change of iron from Fe_2O_3 to Fe_3O_4. These results suggest that the wax was decomposed by reaction with H_2O over the FeOOH catalyst, and the catalytic activity of the FeOOH catalyst remained stable in the steam atmosphere.

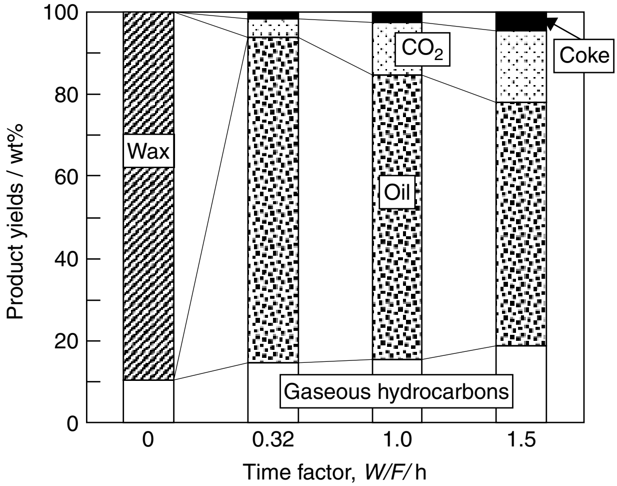


Figure 6.9 Effect of an FeOOH catalyst loaded in reactor 3 (see Figure 6.8) on product yield; temperature = 500°C, carrier gas: steam. (Reproduced with permission from Elsevier)

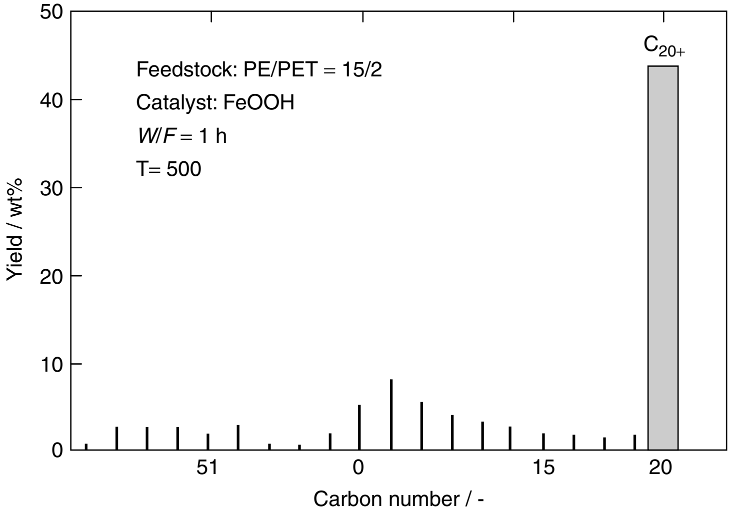


Figure 6.10 Carbon number distribution of heavy oil produced by degradation of a mixture of polyethylene (PE) and poly(ethylene terephthalate) (PET), at a weight ratio of PE/PET = 15/2, temperature = 500°C, time factor $W/F = 1$ h, carrier gas: steam. (Reproduced with permission from Elsevier)

Figure 6.10 shows the carbon number distribution of the products obtained when the temperature was 500°C and the time factor was 1 h. The oil produced was considered to correspond to heavy oil, as based on the carbon number distribution. Therefore, it would be necessary to upgrade this oil for practical applications.

3 UPGRADING OF WASTE-PLASTICS-DERIVED HEAVY OIL OVER CATALYSTS

In the series described thus far, it was found that the degradation of waste plastics proceeds efficiently by both thermal pyrolysis and hydrolysis in a steam atmosphere. A wax and carbonaceous residue produced by the hydrolysis of PET are decomposed by reaction with steam over an FeOOH catalyst, the activity of which remains stable in a steam atmosphere. However, the liquid product from generated from the process mentioned above contains a large amount of heavy oil, as shown in Figure 6.10. Both catalysts and chemical processes are required for efficiently upgrading the quality of the heavy oil.

3.1 CATALYTIC CRACKING OF HEAVY OIL OVER SOLID-ACID CATALYSTS

The most widely used conventional chemical methods are pyrolysis [21–25] and catalytic cracking [13, 26–30]. The latter yields products with a smaller range of carbon numbers and of a higher quality than products generated by the former method. Several types of solid acid catalysts, which are known to be effective for catalytic cracking (e.g. HZSM-5, HY and rare earth metal-exchanged Y-type (REY) zeolite and silica–alumina (SA)) were evaluated by catalyst screening tests and are listed in Table 6.1. The acidic

Table 6.1 Properties of the catalysts. (Reproduced with permission from Elsevier)

Properties	Catalyst				
	REY	HY	Silica–alumina (SA)	HZSM-5 (65)	HZSM-5 (1000)
Si/Al	4.8	4.8	13% alumina	65	1000
Pore size (A)	7.4	7.4	60–100	5.3×5.6	5.3×5.6
Amount of total acid sites[b] [mol · kg-cat^{-1}]	1.048	1.207	0.560	0.235	0.067
Amount of strong acid sites[c] [mol · kg-cat^{-1}]	0.375	0.441	0.187	0.122	0.031
Supercage	Yes (11.8A)	Yes (11.8A)	No	No	No

[a] Measured by conventional TPD experiment

[b] Based on the total amount of ammonia desorbed in the TPD experiment

[c] Based on the amount of ammonia desorbed above 300°C in the TPD experiment

properties of the catalysts were measured from the temperature-programmed desorption spectra of ammonia (NH_3-TPD) method. The feed oil was obtained by the pyrolysis of solid polyethylene plastics at 450°C. To ensure homogeneity and to remove the lighter hydrocarbons, the oil was distilled at 473 K. Table 6.2 shows the results of the elementary analysis of the oil, which was used as a feed oil in the catalytic reforming reaction. A continuous-flow, fixed-bed reactor was utilized for the catalytic reforming of the oil. The reaction was carried out at 400°C under a nitrogen stream. The oil was fed at a constant weight hourly space velocity (WHSV) of 1.0 kg-oil·kg-cat^{-1}·h^{-1} for all catalysts.

Figure 6.11 shows the product yields for each catalyst. The products are classified into four lumps, i.e. gas (carbon number 1–4), gasoline (5–11), heavy oil (above 12), and a carbonaceous residue referred to as coke. In the figure, PE oil represents the feed oil and contains a 34% gasoline fraction. The feed oil was effectively cracked by solid acid catalysts. The gasoline yield was highest with REY zeolite. HZSM-5(65) yielded the

Table 6.2 Analysis of the feed oil. (Reproduced by permission of the American Chemical Society)

	wt%	mol%
Heavy oil ($\geq C_{12}$)	95	
Gasoline (C_5–C_{11})	5	
Elemental analysis		
H	13.7	66.0
C	82.0	32.9
N	0.0	0.0
O	4.3	1.1
H/C		2.00

RON of liquid [−] 4.5.

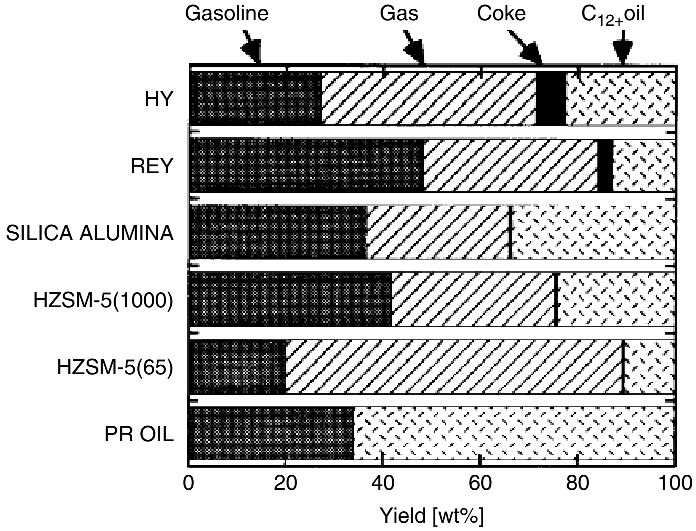


Figure 6.11 Distribution of product yields under nitrogen. WHSV = 1, $T = 400°C$ and $t = 3$ h. (Reproduced with permission from Elsevier)

largest quantity of gaseous compounds and the lowest amount of gasoline, which was even lower than the gasoline fraction in the feed oil. While coke loading was highest with HY zeolite, both HZSM-5 zeolites generated a negligibly small amount of coke deposition. As the amount of coke deposition increased, the catalytic activity decreased.

Table 6.3 summarizes the yield of gaseous products according to the carbon number. In this table, $C_2 =$ to $C_5 =$ indicate olefins corresponding to their respective carbon numbers.

Table 6.3 Yield of each gaseous product according to carbon number. The values in brackets refer to the corresponding olefins. (Reproduced with permission from Elsevier)

	Catalyst				
Carbon Number	REY	HY	Silica–alumina (SA)	HZSM-5 (65)	HZSM-5 (1000)
C1	0.09	0.20	0.07	0.12	0.01
C2	0.76	1.39	0.23	6.32	0.43
(C2=)	(0.69)	(1.39)	(0.17)	(6.01)	(0.40)
C3	7.71	9.85	7.99	30.92	11.00
(C3=)	(5.85)	(3.25)	(6.91)	(29.90)	(11.00)
C4	16.28	20.50	17.35	23.80	14.21
(C4=)	(12.22)	(15.51)	(11.24)	(13.78)	(8.27)
C5	6.60	9.23	3.51	3.84	5.62
(C5=)	(0.0)	(0.0)	(2.30)	(1.80)	(1.52)
C6	2.81	1.55	0.06	1.48	1.09
C7	1.23	1.02	0.0	0.62	0.41
C8	0.40	0.46	0.0	0.14	0.75
Total yield, (wt%)	35.88	44.20	29.20	69.04	33.52

A significant amount of C_3–C_5 gaseous compounds were produced. With the exception of ZSM-5(65) zeolite which favored the production of the C_3 fraction, the other catalysts yielded C_4 as the main component.

HZSM-5 zeolite has channels within its crystals. The size of the channel is nearly equal to that of benzene and is too small for easy penetration by oil molecules. Hence, the ends of only certain molecules can penetrate the channels and undergo cracking. This leads to a higher yield of gaseous products and a lower gasoline yield, indicating that HZSM-5 zeolite is not suitable for the cracking reaction of heavy oil. In contrast, the HY and REY zeolites have larger pores. Therefore, the oil molecules can penetrate into the pores and undergo cracking. Moreover, the existence of rare earth metals in REY zeolite results in a decrease in the amount of stronger acid sites (see Table 6.1). This in turn leads to a reduction in the deactivation rate and the amount of coke loading in comparison with that obtained with HY zeolite. Accordingly, REY zeolite has the proper acidic properties and pore size, and is suitable for the reaction with heavy oil.

3.2 PRODUCTION OF HIGH-QUALITY GASOLINE OVER REY ZEOLITES

The effects of the reaction conditions and the catalytic properties of REY zeolites on reaction product yields and on the quality of the gasoline can now be examined.

Four types of REY zeolite (Si/Al = 4.8) with different crystal sizes and acidic properties were used. The physical and chemical properties of the fresh zeolites are given in Table 6.4. Polyethylene plastics-derived heavy oil, shown in Table 6.2, was used as the feed oil. The cracking reaction was conducted in a tubular reactor filled with catalyst particles under the following conditions: time factor $W/F = 0.2$–3.0 kg-cat kg oil^{-1} h^{-1} and reaction temperature = 300–450°C. The lumping of reaction products were gas (carbon number 1–4), gasoline (5–11), heavy oil (above 12), and a carbonaceous residue referred to as coke. The index of the gasoline quality used was the research octane number (RON), which was calculated from Equation 6.1 [31].

$$\mathrm{RON} = -1.0729Y_{\mathrm{NP2}} + 0.7875Y_{\mathrm{IP1}} + 0.0978Y_{\mathrm{IP2}} + 0.3395Y_{\mathrm{CP}} + 0.4049Y_{\mathrm{AR}} + 69.0306 \tag{6.1}$$

Table 6.4 Physical and chemical properties of the fresh REY zeolites. (Reproduced by permission of the American Chemical Society)

	Catalyst			
Property	REY-1	REY-2	REY-3	REY-4
Si/Al	4.8	4.8	4.8	4.8
Crystal size (μm)	0.1	1.0	0.1	0.1
Amount of total acid sites[a] (mol kg cat^{-1})	2.91	2.44	2.99	2.78
Amount of strong acid sites[b] (mol kg cat^{-1})	0.79	0.57	0.66	0.70

[a] Based on the total amount of ammonia desorbed in the TPD experiment

[b] Based on the amount of ammonia desorbed above 300°C in the TPD experiment

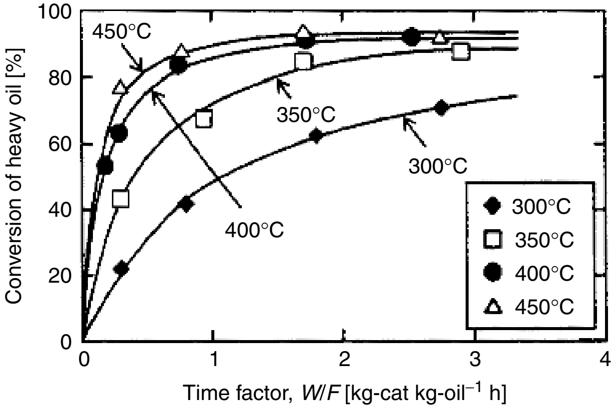


Figure 6.12 Dependence associated with the reaction temperature and the time factor, *W/F*, on the conversion of heavy oil: zeolite crystal size = 0.1 μm. (Reproduced by permission of the American Chemical Society)

where Y_i is the weight fraction of the ith component in the gasoline fraction. The subscript NP2 denotes the *n*-paraffins without C_5, IP1 the total isoparaffins from C_5 to C_7, IP2 the total isoparaffins without C_5–C_7, CP the total cycloparaffins, and AR the total aromatics.

The relationship between the conversion of heavy oil and the time factor, W/F, at different reaction temperatures is shown in Figure 6.12. Conversion was defined as the mass fraction of heavy oil (components above C_{12}) converted to gasoline, gas, and coke. This value was calculated from the following equation:

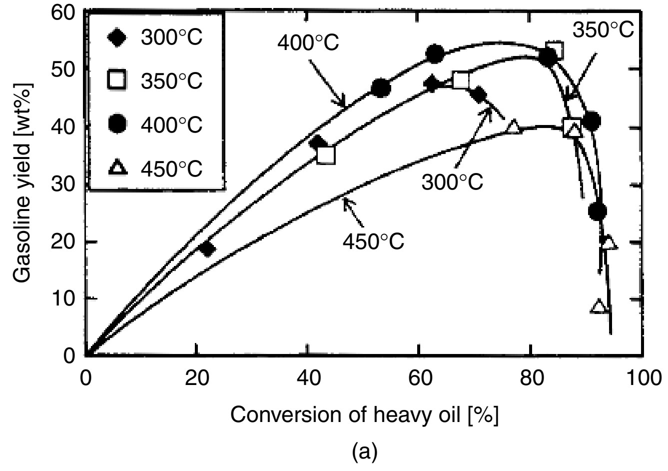
$$\text{conversion} = 1 - \frac{\text{mass of heavy oil at the outlet}}{\text{mass of heavy oil at the inlet}} \tag{6.2}$$

As the reaction temperature increased, the reaction proceeded. Although conversion was greater as the temperature increased, there was no significant difference between the conversions at 400 and 450°C. The effects of temperature on the respective yields of the reaction products are shown in Table 6.5. As the temperature increased, the amount of unreacted heavy oil decreased, and the yields of both gas and coke increased. The gasoline yield reached a maximum value at 400°C, and then decreased with further increases in temperature.

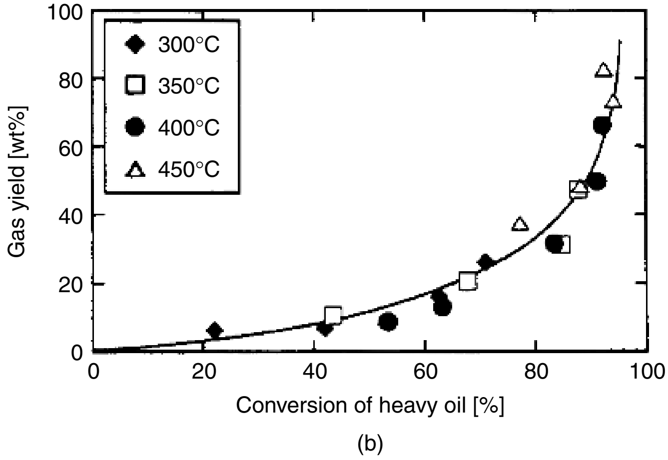
Table 6.5 Effect of temperature on product yield at $W/F = 0.75$ kg-cat kg oil^{-1}h. (Reproduced by permission of the American Chemical Society)

Temperature (°C)	Heavy oil (wt%)	Gasoline (wt%)	Gas (wt%)	Coke (wt%)
300	55.45	37.22	6.96	0.37
350	30.77	48.04	20.76	0.43
400	15.84	51.93	31.71	0.52
450	11.43	39.61	48.42	0.54

Figure 6.13(a) shows the effect of the reaction temperature on the relationship between gasoline yield and the conversion of heavy oil. The gasoline yield increased with increasing conversion to the maximum value, and then decreased significantly. This suggests that the gasoline formed by the cracking of heavy oil subsequently undergoes further cracking, which in turn yields gaseous products and coke. Thus, gasoline is an intermediate product. The maximum gasoline yield, which is related to the rates of gasoline formation and cracking, was observed at about 400°C. The same optimum temperature has been found for the catalytic cracking of gas oil [32]. Figure 6.13(b) shows the relationship between the gas yield and the conversion of heavy oil at various reaction temperatures. Because almost all of the data lie on a single curve, the reaction temperature had no significant effect on the gas yield at a constant conversion level. The yield of gas products increased



(a)



(b)

Figure 6.13 Effect of the reaction temperature on the relationship between product yield and the conversion of heavy oil (zeolite crystal size = 0.1 μm): (a) gasoline yield; (b) gas yield; (c) coke yield. (Reproduced by permission of the American Chemical Society)

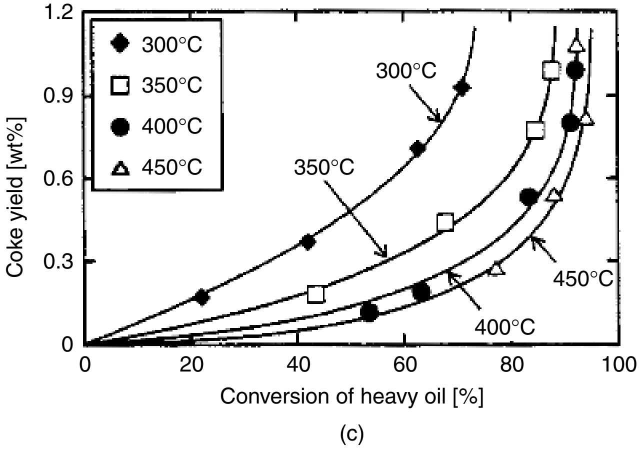


Figure 6.13 (*continued*)

as the reaction progressed. Figure 6.13(c) shows the effect of different reaction temperatures and conversion levels of heavy oil on the coke yield. At the same conversion level, high temperatures reduced coke formation. The difference between the coke yields at 400 and 450°C was small. Similar findings have been reported for the catalytic cracking reaction of gas oil, in which coke formation proceeded well at reaction temperatures below 400°C [32].

The effect of reaction temperature on gasoline quality and its main components are shown in Figure 6.14. Below 400°C, the RON value increased with temperature due to an acceleration of the formation rate of the IP1 fraction and the cracking rate of the NP2 fraction. Above 400°C, however, the cracking of IP1 proceeded (i.e. a reduction in the yield of IP1), leading to a decrease in the RON value. On the basis of the gasoline, coke,

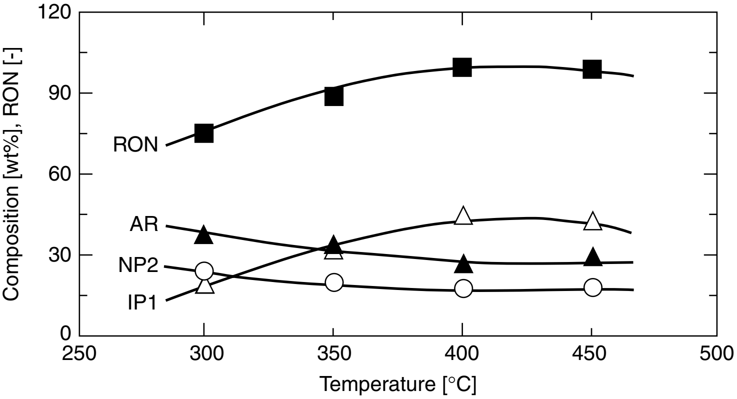


Figure 6.14 Effect of the reaction temperature on the RON value of the gasoline and main components (zeolite crystal size = 0.1 μm, $W/F = 0.75$ kg-cat kg-oil^{-1}h): NP2 = *n*-paraffins without C_5, IP1 = C_5–C_7 isoparaffins, AR = aromatics. (Reproduced by permission of the American Chemical Society)

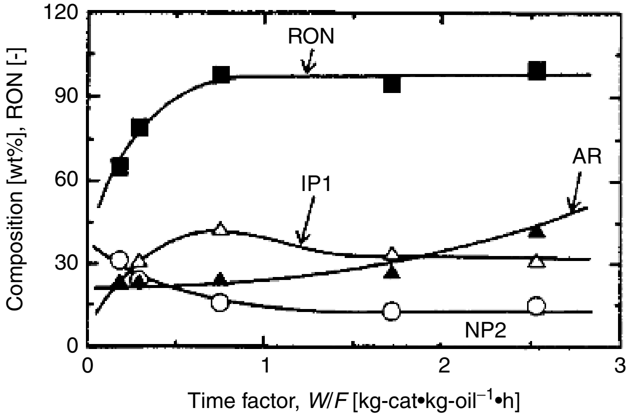


Figure 6.15 Effect of the time factor, W/F, on the RON value of the gasoline and the main components (zeolite crystal size = 0.1 μm, reaction temperature = 400°C): NP2 = *n*-paraffins without C_5, IP1 = C_5–C_7 isoparaffins, AR = aromatics. (Reproduced by permission of the American Chemical Society)

Table 6.6 Comparison of commercial gasoline and the gasoline obtained from heavy oil derived from waste plastics. (Reproduced by permission of the American Chemical Society)

Component	Gasoline obtained (optimized)	Regular gasoline	High-octane gasoline
IP1 (wt%)	40.44	29.47	36.78
AR (wt%)	29.03	33.23	50.53
NP2 (wt%)	12.36	15.41	9.96
RON (–)	100.92	90.44	108.01

and gas yields, as well as the RON value, the most favorable reaction temperature was determined to be approximately 400°C.

The effect of the time factor, W/F, on gasoline quality and its main components obtained at 673 K is shown in Figure 6.15. Below a W/F value of 0.75 kg-cat kg-oil^{-1} h, the increase in the RON value was due to the significant increase in the IP1 fraction and the large reduction in the NP2 fraction. Above a W/F value of 1 kg-cat kg-oil^{-1} h, only the reaction of IP1 to AR took place, producing a slight decrease in the RON value. These results suggest that the optimum W/F value for the production of gasoline of the highest quality is in the range 0.75–1 kg-cat kg-oil^{-1} h.

Table 6.6 compares the contents of the main components of regular and high-octane gasoline with those of gasoline obtained under the optimal conditions, namely, temperature = 673 K, time factor = 0.75 – 1 kg cat kg oil^{-1} h, crystal size of the REY zeolite catalyst = 0.1 μm, and the number of strong acid sites on the used catalyst = 0.28 mol kg^{-1}. The gasoline obtained under the optimum contained a larger amount of IP1 and a smaller amount of AR than the corresponding amounts in commercial gasoline. The amount of NP2 in the gasoline obtained in this study was between that of regular and high-octane gasoline.

3.3 KINETICS OF THE CATALYTIC CRACKING OF HEAVY OIL OVER REY ZEOLITES

A rare earth metal-exchanged Y-type (REY) zeolite catalyst was found to be an effective catalyst for the catalytic cracking of heavy oil. The influence of the reaction conditions and the catalytic properties of REY zeolite on the product yield and on gasoline quality have been described above. In this section, a reaction pathway is proposed for the catalytic cracking reaction of heavy oil, and a kinetic model for the cracking reaction is developed [14,33].

Figure 6.16 shows the typical relationship between product distribution and the time factor, *W*/*F*, at different temperatures [13]. The experimental conditions are described in Section 3.2. As the *W*/*F* value increased, heavy oil was cracked to produce gasoline and gaseous products. Moreover, the gasoline product subsequently underwent further cracking to yield gaseous products. Hence, the gasoline yield was shown to have a maximum value

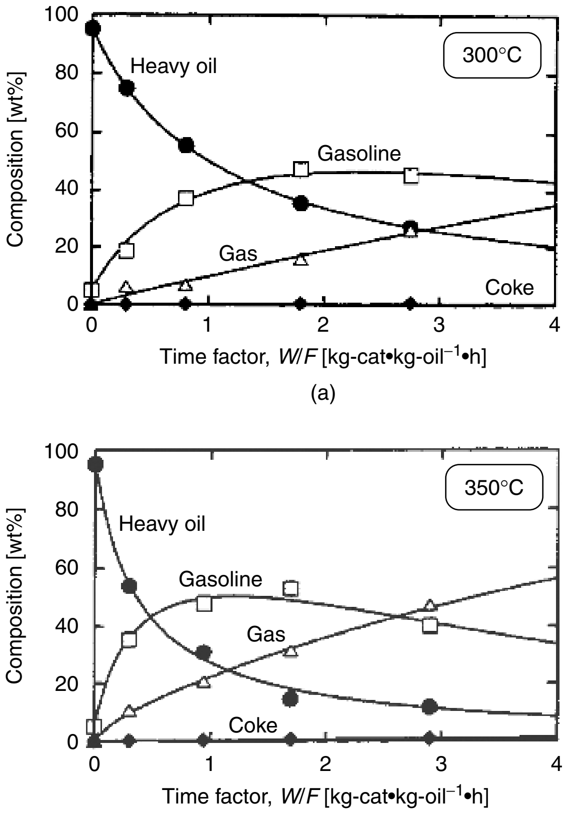
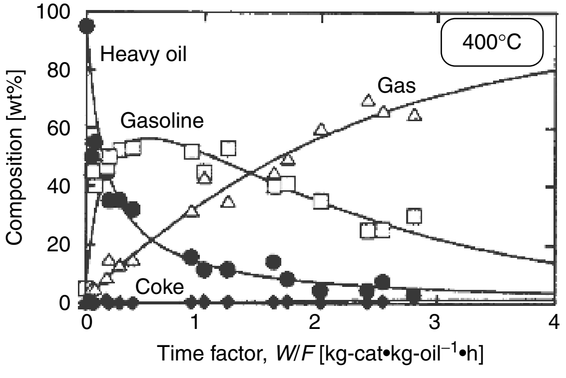
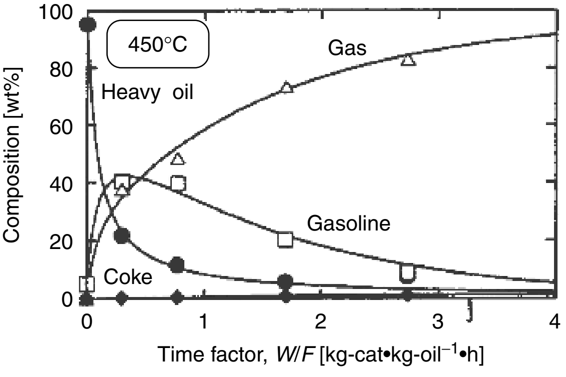


Figure 6.16 Kinetic runs performed using a catalyst with a crystal size of 0.1 μm: (a) 300°C; (b) 350°C; (c) 400°C; (d) 450°C. (Reproduced by permission of the American Chemical Society)



(c)



(d)

Figure 6.16 (*continued*)

that appeared at a low W/F value and a high reaction temperature. The yield of coke gradually increased and was considered to be the product of gasoline and heavy oil.

Figure 6.17 illustrates a possible reaction pathway that could account for the product distributions shown in Figure 6.16. The proposed reaction pathway separately takes into account the heavy oil, gasoline, gas, and coke lumps and is considered to represent the product distribution.

The experimental conditions were set up to ensure that both the heat and mass transport limitations across the film would be negligible. Moreover, limitations due to intraparticle diffusion were assumed to be insignificant. The mass balance equation of the ith component can be written as follows:

$$\frac{\mathrm{d}F_i}{\mathrm{d}W} = r_i \quad (i = \mathrm{A, B, C, D}) \tag{6.3}$$

where F_i is the mass flow rate of the ith lump (kg h^{-1}); W is the mass of catalyst (kg); r_i is the production rate of the ith lump per unit mass of catalyst (kg (kg cat)$^{-1}$ h^{-1}); and suffixes A, B, C and D refer to heavy oil, gasoline, gas, and coke lumps, respectively.

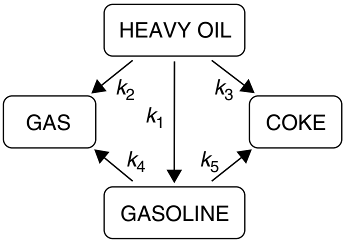


Figure 6.17 Reaction pathway proposed in this study. (Reproduced by permission of the American Chemical Society)

Figure 6.18 shows the Arrhenius plots using the evaluated kinetic parameters. The data were found to lie on a straight line for each parameter. The slopes of these straight lines gave the activation energies, which are listed in Table 6.7. The activation energy for the reaction of gas formation from heavy oil k_2 is 75.5 kJ mol^{-1} and is comparable with other data for gasification reactions: 58.6 kJ mol^{-1} in the case of a CaX catalyst (Ca ion-exchanged X-type zeolite catalyst) [34], and 61.5 kJ mol^{-1} in the case of the silica alumina [35] for the gasification of a polymer waste, and 75 kJ mol^{-1} for the reaction of gas oil [36]. The difference in the activation energies between gaseous formation k_2

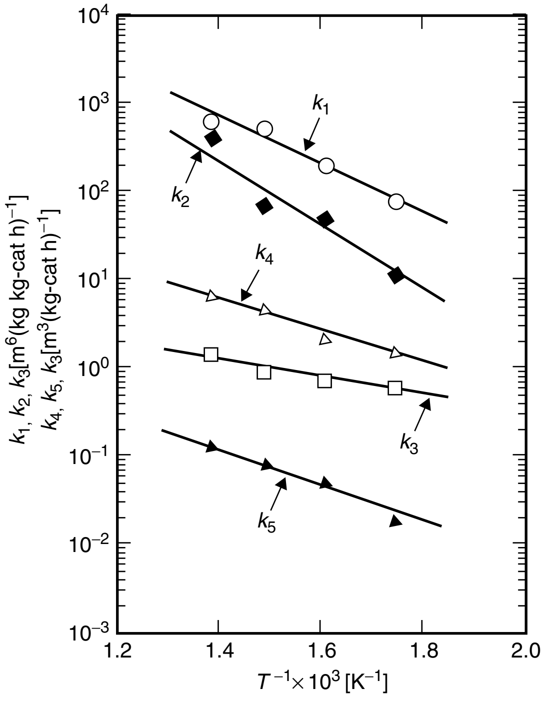


Figure 6.18 Arrhenius plots of the kinetic parameters. (Reproduced by permission of the American Chemical Society)

Table 6.7 Activation energies using a catalyst with a crystal size of 0.1 μm. (Reproduced by permission of the American Chemical Society)

Rate constants	E_a (kJ mol)	Rate constants	E_a (kJ mol)
k_1	50.7	k_4	35.1
k_2	75.5	k_5	42.1
k_3	18.5		

and gasoline formation k_1 accounts for the fact that the selectivity of gaseous products increases, while that of gasoline decreases with increases in temperature, especially at temperatures above 400°C.

3.4 USAGE OF STEAM AS A CARRIER GAS

As it is both inexpensive and easy to handle, steam is a potential candidate carrier gas for waste plastic recycling in chemical plants. Furthermore, as mentioned in Section 2.1, the degradation temperatures for polyester resins are remarkably shifted to low-temperature regions, and the amount of carbonaceous residue produced in the degradation process is reduced in a steam atmosphere, as compared with that in a nitrogen atmosphere. Accordingly, the preparation of a catalyst that could demonstrate both stable activity for the catalytic cracking of PE-derived heavy oil, but that would also remain stable in a steam atmosphere, was examined [16].

Nickel is a well-known catalyst component and is thought to play an important role in the transformation of the hydrogen of steam to hydrocarbons. Hence, a part of the rare earth metal in REY is exchanged with Ni to become prepared Ni and the rare earth metal-exchanged Y-type zeolite catalyst (Ni–REY) [14, 15]. The physical and chemical properties of the catalysts are listed in Table 6.8. The polyethylene plastics-derived heavy oil shown in Table 6.2 was used as the feed oil.

A continuous-flow, fixed-bed reactor was utilized for the catalytic cracking of the heavy oil. Reactions were conducted under temperature conditions ranging from 300 to 600°C, at a catalyst weight W of about 1.0×10^{-3} kg and a feed oil mass flow rate F of about 1.0×10^{-3} kg h^{-1}. In order to examine the catalysis of Ni in Ni–REY for hydrogenation, experiments using hydrogen as the carrier gas were also conducted.

Table 6.8 Physical and chemical properties of the catalyst samples. (Reproduced with permission from Elsevier)

		Ni–REY				
	REY	Ni content 0.5 wt%	1.0 wt%	3.0 wt%	HY	MFI
SiO_2/Al_2O_3	4.8	4.8	4.8	4.8	4.8	65
Crystal size (mm)	0.1	0.1	0.1	0.1	0.1	1.1
Number of strong acid sites (mol kg^{-1})	0.375				0.441	0.122

The selectivity of the products of the reaction in nitrogen and hydrogen stream at 400°C was compared among the catalysts used at a feed oil conversion of about 80%. Hydrocarbons with carbon numbers ranging from 1 to 4 were regarded as gaseous compounds, and those with carbon numbers from 5 to 11 were regarded as gasoline fractions. MFI-type zeolite (ZSM-5) yielded the largest quantity of gaseous compounds (selectivity: 64%) and the lowest amount of gasoline (35%) because its pores are too small for the penetration of heavy oil, and reactions such as dewaxing are likely to proceed inside. As HY-type zeolite had a large umber of strong acid sites, and excessive cracking occurred, a low yield of gasoline was obtained (46%). The usage of REY, on which the number of strong acid sites is lower than that on the HY-type zeolite, gave a higher yield of gasoline (57%) as compared with that of HY. On the other hand, when the reaction was conducted using the Ni–REY catalyst in hydrogen stream, the selectivity towards gasoline was found to be the highest at 64%, at the same temperature and conversion of the feed oil.

The reactions over HY, MFI, and REY zeolite catalysts in nitrogen proceed over their acid sites. During the reactions, paraffins are first decomposed to yield lighter olefins and paraffins. The produced olefins are preferentially adsorbed on acid sites and undergo further reaction, yielding gaseous compounds and aromatics. When a Ni–REY catalyst is employed in a hydrogen atmosphere, the decomposition of hydrogen to hydrogen atoms also proceeds over Ni in the catalyst. These hydrogen atoms diffuse on the pore surface (e.g. the spillover phenomenon) and when they make contact with the olefins adsorbed on the acid sites, the hydrogenation of the olefins occurs. The paraffins formed in this manner easily desorb from the acid sites without undergoing any further reactions. Therefore, the reactions using Ni–REY in this series showed the highest selectivity towards gasoline.

In order to optimize the Ni content of Ni–REY, the compositions of the obtained gasoline fraction were measured and were divided into lumps as shown in Figure 6.19. Figure 6.20 shows the RON value calculated from the data in Fig. 6.19 using Equation (6.1). The results obtained with commercial regular-grade and high-RON-grade gasoline are also shown in these figures for comparison. Commercial gasoline with a high RON value contains large amounts of isoparaffins (IP1), aromatics (AR), and cycloparaffins (CP), as well as a small amount of *n*-paraffins (NP2). For the complete combustion of gasoline, the AR content must be low. Therefore, high-quality gasoline must contain large amounts of IP1 and CP and small amounts of NP2 and AR. Using Ni–REY with a 0.5 wt% Ni content, gasoline with larger amounts of CP and IP1 and smaller amounts of AR and NP2 was obtained, as compared with a commercial high-RON-grade gasoline. Furthermore, the RON value of the gasoline produced over Ni–REY (0.5 wt%) was larger than that of commercial gasoline. As the content of Ni increased, the number of strong acid sites decreased, resulting in a reduction in cracking. This explains why the amount of IP1 decreased and that of NP2 increased with the increase in the Ni content (from 0.5 to 3.0 wt%), leading to the reduction of the RON value of the gasoline produced in this manner. Based on the above information, it was concluded that Ni–REY with a Ni content of 0.5 wt% could be used for the following experiments.

The effects of reaction temperature on the conversion of the heavy oil and the gasoline yield are shown in Figure 6.21 for reactions using Ni–REY in steam and hydrogen streams. At temperatures below 400°C, both the conversion and the gasoline yield increased as temperature increased. However, at temperatures above 400°C, excessive

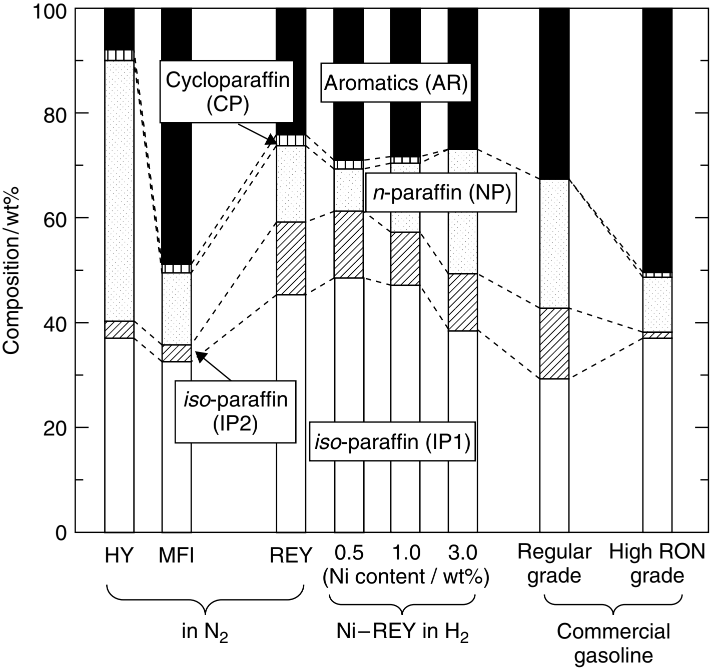


Figure 6.19 Comparison of gasoline fractions produced by catalytic cracking over the various catalysts used ($T = 400°C$, $W/F =$ 1 h). (Reproduced by permission from Elsevier)

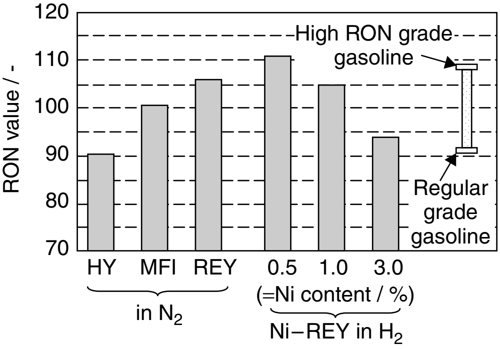


Figure 6.20 Research octane umber (RON value) of the gasoline fraction produced with the catalysts used. (Reproduced by permission from Elsevier)

cracking proceeded, followed by coke formation, leading to a decrease in both conversion and gasoline yield. This tendency was clearly observed in the case of hydrogen stream. Strong acid sites, on which coke formation proceeds and is accelerated at higher temperatures, are partially covered by water molecules in a steam atmosphere. Therefore, the catalyst is able to maintain activity above 400°C in a steam atmosphere.

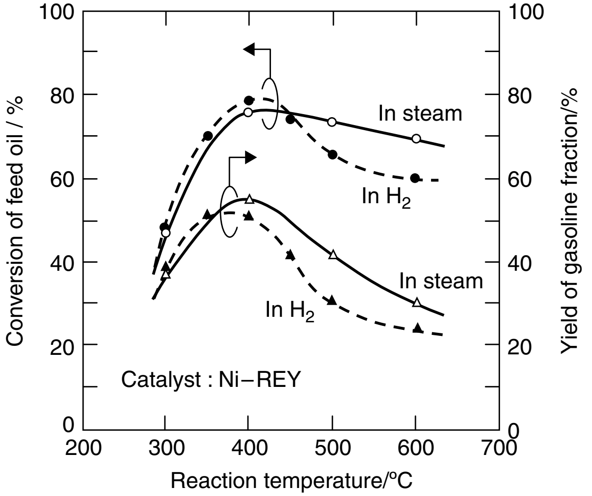


Figure 6.21 Dependence of both conversion and gasoline yield on reaction temperature ($W/F = 1$ h)

Figure 6.22 shows the typical carbon number distribution of products obtained using Ni–REY in steam at 400°C and with a time factor W/F of 1 h. The results obtained with MFI-type (ZSM-5) and REY zeolites in N_2 are also shown for comparison. Although steam was used as a carrier gas, Ni–REY gave the largest amount of fuel, e.g. gasoline, kerosene, and gas oil, thus suggesting the potential use of steam as a carrier gas.

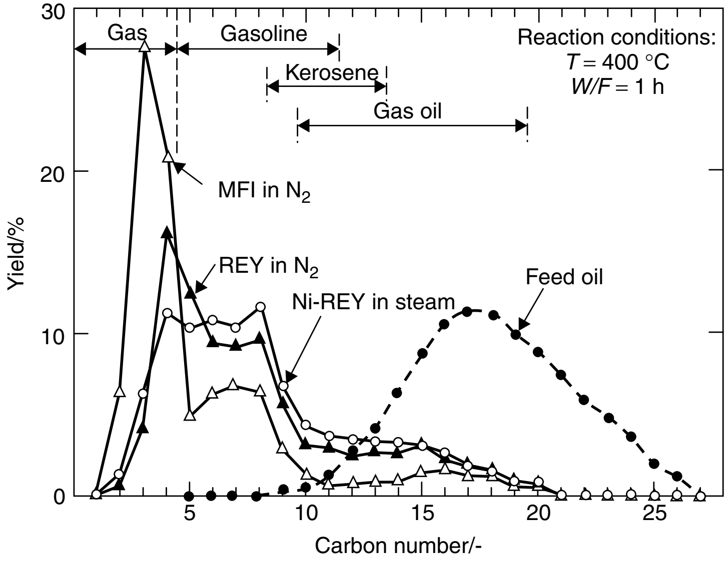


Figure 6.22 Carbon number distribution of products of the catalytic cracking of oil obtained by the pyrolysis of PE. (Reproduced with permission from Elsevier)

From the results discussed above, the combination of Ni–REY as the catalyst and steam as the carrier gas was considered preferable for achieving a realistic recycling process. In order to confirm the long-term stability of Ni–REY, repeated sequences of reaction and regeneration were conducted. Reaction and regeneration were conducted at 400°C for 3 h in a steam atmosphere, and at 500°C for 3 h in an air stream, respectively. This experiment was also conducted using an MFI-type zeolite catalyst for comparison by exchanging the carrier gas in the reaction from steam to nitrogen. Figure 6.23 shows changes in the conversion of the feed oil and the selectivity towards gasoline for REY and Ni–REY catalysts during the sequences of reaction and regeneration. The carrier gas in the reaction was steam for the REY and Ni–REY catalysts. Both the activity and the selectivity remained almost constant for REY and Ni–REY, indicating that both catalysts are stable in a steam atmosphere. The stable activity observed with REY and Ni–REY could be ascribed to the stability of the acid sites on the REY and Ni–REY catalysts [37]. Furthermore, Ni–REY showed higher selectivity towards gasoline (78%). A small amount of hydrogen was detected in the exit gas of the reactor. This finding suggested that Ni plays an important role in the hydrogen transportation from steam to hydrocarbons, resulting in a high selectivity towards gasoline. The above findings thus confirmed that PE-derived heavy oil can be efficiently upgraded to useful fuels when it is reacted over Ni–REY in a steam atmosphere.

In order to verify the high efficiency of Ni–REY in an actual system, the catalytic cracking of the oil derived from a mixture of PE and PET was conducted in a bench-scale reactor (see Figure 6.8). The Ni–REY catalyst was placed in reactor 3, shown in Figure 6.7. Figure 6.24 represents the carbon number distribution of the feed oil and the product of the reaction over Ni–REY in a steam atmosphere. The fraction of aliphatic heavy oil was completely converted to gasoline and kerosene, indicating that the Ni–REY catalyst can be used for the upgrading of oil derived from a mixture of PE and PET. The

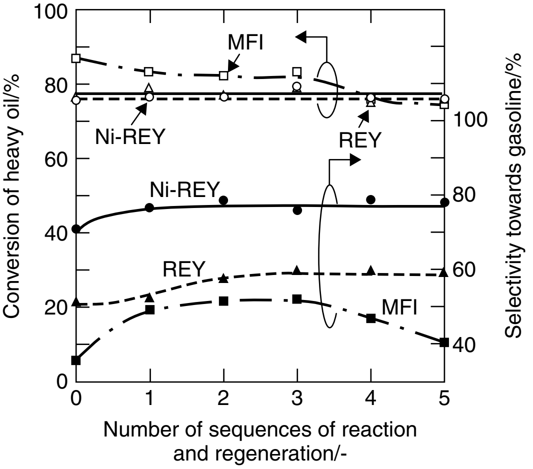


Figure 6.23 Changes in the catalytic activity of the MFI-type zeolite, Ni–REY, and REY catalysts during the repetition of a sequence of reaction and regeneration ($T = 400°C$, $W/F = 1$ h), carrier gas in the reaction: nitrogen for MFI, steam for REY and Ni–REY. (Reproduced with permission from Elsevier)

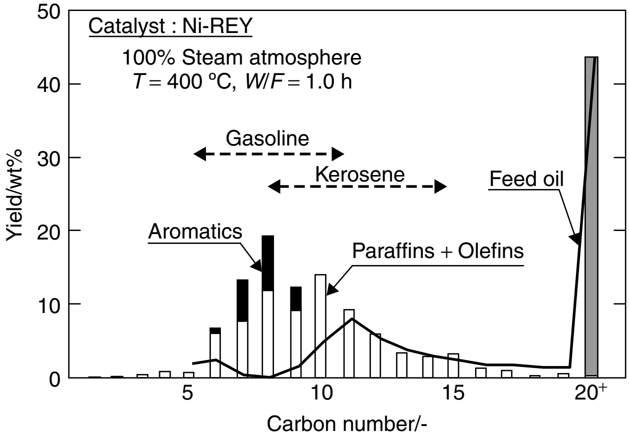


Figure 6.24 Carbon number distribution of products obtained by the catalytic cracking of oil derived from a mixture of PE and PET (reaction conditions: $T = 400°C$, $W/F = 1$ h). (Reproduced with permission from Elsevier)

products with carbon numbers from C_5 to C_{11} (i.e. the gasoline fraction) contained about 30% aromatics, almost the same result observed in the case of the products obtained from the reaction over Ni–REY in H_2 (see Figure 6.19). This finding suggests that cracking, followed by hydrogenation, proceeds in a steam atmosphere due to the existence of Ni in the catalyst.

4 CONTINUOUS PRODUCTION OF FUELS FROM WASTE PLASTICS

4.1 CONTINUOUS PRODUCTION OF FUELS

First, by decomposing waste plastics in a steam stream, it was shown that waste plastics could be degraded without producing a carbonaceous residue. Furthermore, it was found that the decomposition of oxygen-containing plastics can proceed at a uniform reaction rate. Second, a new reactor was proposed to achieve high hold-up, high heat transfer, and good contact between melted plastics with steam in order to accelerate hydrolysis. Using this reactor, a mixture of waste plastics can be degraded, and further decomposition over an FeOOH catalyst can also be achieved. Finally, the oil obtained was upgraded to a variety of fuels, indicating gasoline and kerosene, over a Ni–REY catalyst in a steam atmosphere. On the basis of these laboratory-scale experimental results, a pilot-scale plant was built and the validity of the proposed chemical recycling process was examined.

Figure 6.25(a) shows a novel process for the continuous production of fuels from waste plastics. The proposed process consists primarily of three reactors. A mixture of waste plastics is fed into a pyrolytic reactor with heat-medium-particles stirred by a helical impeller (Figure 6.25(b)), where melted plastics are hydrothermally decomposed with steam and the random scission of C–C bonds. The produced mixture of a heavy oil containing wax and sublimate material is carried by steam stream to the next reactor, which is filled with an FeOOH catalyst (i.e. a catalytic hydrolysis reactor). The gaseous compounds, including the vapors of the wax and sublimate materials, are passed through an FeOOH catalyst bed, and the oxidative decomposition over the FeOOH catalyst with steam proceeds. The quality of the oil thus obtained is further upgraded over Ni–REY zeolite catalysts in the catalytic cracking reactor, and fuels, such as gasoline, kerosene, and gas oil are produced. The weights of the FeOOH catalyst and the Ni–REY zeolite catalyst were 45 and 20 kg, respectively. The feed rate of the waste plastics, F, was 45 kg/h (the time factor in the pyrolytic reactor, $W/F = 1.0$ h).

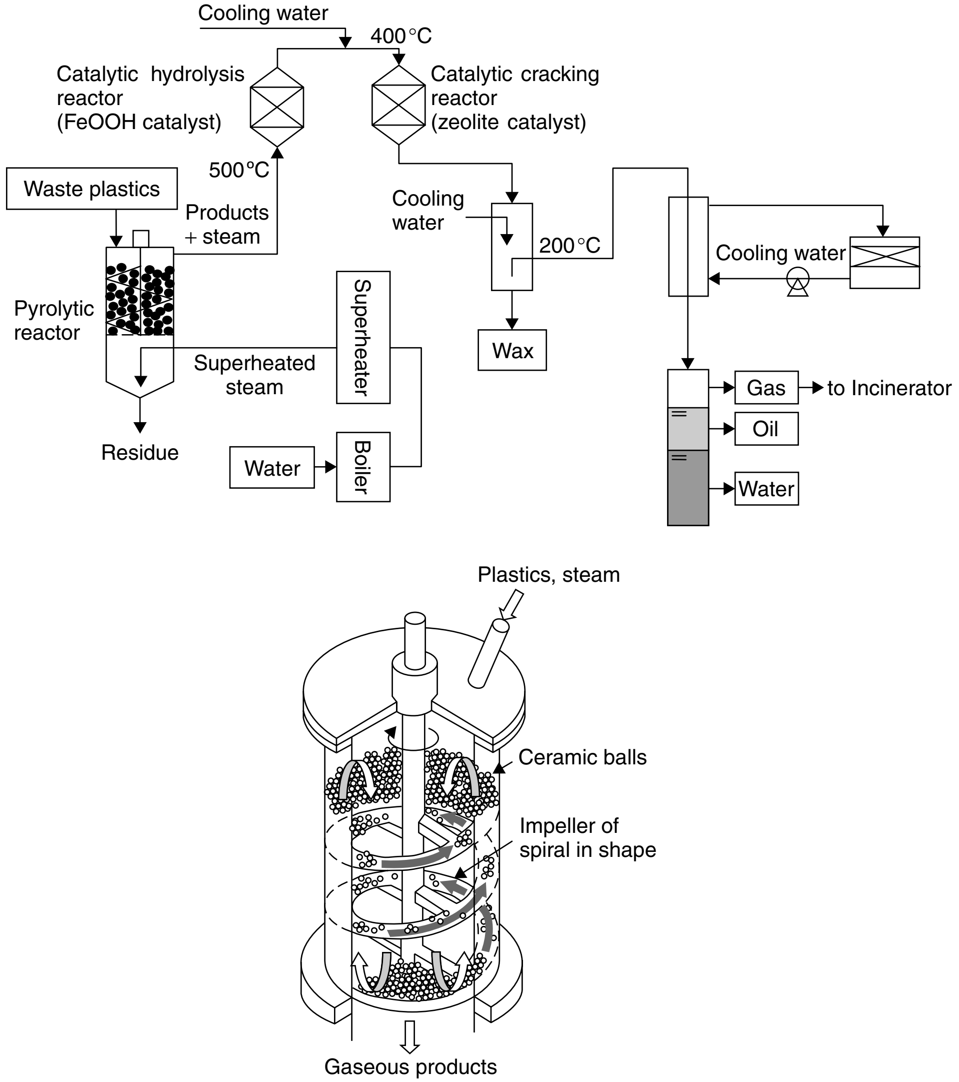


Figure 6.25 (a) Flow scheme of the continuous production of fuels from waste plastics; (b) schematic diagram of the pyrolytic reactor used in the pilot plant. (Reproduced with permission from Elsevier)

Table 6.9 Product yield at the outlet of the catalytic hydrolysis reactor and the catalytic cracking reactor in the pilot-scale plant

	Gas (C_1–C_4) (wt%)	Fuel (C_5–C_{19}) (wt%)	Heavy oil (C_{20+}) (wt%)	Others (wt%)
Outlet of reactor with FeOOH	2.1	46.7	50.3	0.9
Outlet of reactor with zeolite	13.5	52.4	33.9	0.2

The product yields at the outlet of the catalytic hydrolysis reactor and at the catalytic cracking reactor are listed in Table 6.9. The product yields of liquid fuel (gasoline-kerosene) and heavy oil reached to 46.7 and 50.3 wt%, respectively, even at the outlet of the catalytic hydrolysis reactor. The catalytic cracking reactor yielded 13.5 wt% gaseous fuel, 52.4 wt% liquid fuels, and 33.9 wt% heavy oil, indicating that the heavy oil obtained at the outlet of the catalytic hydrolysis reactor efficiently upgraded the quality of the fuel oil. Using this method, the storage of carbonaceous residue and sublimate materials in reactors, valves, and pipelines can be avoided. Moreover, recycling heavy oil at the outlet of the catalytic cracking reactor into the pyrolytic reactor can enable an improvement in the yield of liquid fuel to 72.4 wt%. Accordingly, the validity of the proposed process for the continuous conversion of waste plastic mixtures to various fuels was demonstrated on the basis of this pilot-scale plant.

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7

Catalytic Degradation of Plastic Waste to Fuel over Microporous Materials

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1 INTRODUCTION

The dramatic growth of living standards in the second half of the twentieth century was accompanied by a drastic increase in plastic product use. This unavoidably had a huge impact on the environment, as it caused a rapid increase in plastic waste that does not degrade and remains in municipal refuse tips for decades. Consequently plastic waste is a large strain on existing disposal methods, landfill and incineration. Landfill space is becoming scarce and expensive, a problem exacerbated by the fact that plastic waste is more voluminous than other waste type. On the other hand, incineration to recover energy, produces toxic gaseous products, which only shifts a solid waste problem to an air pollution one. Polymer recycling becomes an increasingly better alternative to those methods. Polymer recycling has become a necessity.

Apart from providing a solution to a disposal problem, we can look at polymer recycling as turning waste into valuable products, namely chemicals and fuel. We should consider plastic waste as a cheap source of raw materials in times of accelerated depletion of natural resources.

Ideally we would like to reuse plastic waste to form directly new plastic products, but mechanical reprocessing of used plastics into new products has so far limited application. It is restricted to the treatment of relatively pure and well-defined waste, mainly from polymer processing factories. Mechanical reprocessing of municipal plastic waste results in new products of quality inferior to their virgin plastic ones. Separation of waste to streams of the same polymer type on the other hand is still very expensive. This fact restricts the applicability of mechanical reprocessing in polymer waste that is homogeneous in type and properties.

Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels Edited by J. Scheirs and W. Kaminsky © 2006 John Wiley & Sons, Ltd ISBN: 0-470-02152-7

Thermal and/or catalytic degradation of plastic waste to gas and liquid products, which can be utilized as fuels or chemicals, seem to be the most promising methods to be developed into a cost-effective commercial polymer recycling process to solve the acute environmental problem of plastic waste disposal. These methods solve an environmental problem, producing valuable products. Comparing pure thermal degradation in the absence of a catalyst with a catalytic one, the first one demands relatively high temperatures and its products require further processing for their quality to be upgraded. Hence this recycling method is restricted to areas of existing oil refineries to whose processes the wax-type products of the thermal degradation need to be fed for their quality to improve. Catalytic degradation of plastic waste offers considerable advantages. It occurs at considerably lower temperatures and forms hydrocarbons in the motor fuel range, eliminating the necessity of further processing.

In such a recycling process, we consider the liquid fuel as the most valuable product. Although gaseous products are useful too, as their burning can contribute to the energy demand of an endothermic polymer cracking process, excess gas production is not desirable. Gaseous products are considered of low value because of their transportation costs. Consequently, the target of a commercially viable recycling process should be an increase of the liquid product yield.

Generally the whole polymer recycling policy has to consider the problem in a holistic way. A combination of recycling methods has to be considered and polymer recycling has to be viewed in conjunction with recycling of other waste type. Issues such as sorting of waste into various waste types as well as separation issues have still to be tested.

In this chapter an overview of the characteristics of plastic catalytic degradation is presented, focusing mainly on our own work. We will focus on polyolefins that constitute by far the majority of municipal plastic waste [1]. Polystyrene is another polymer type with considerable percentages in the municipal polymer waste stream and we will refer to results of other studies trying to identify main differences from polyolefins. PVC causes problems in recycling technologies based on degradation because of the HCl formed, which has to be removed. In catalytic degradation formed HCl affects negatively the catalyst stability. However we do not consider as priority to study the catalytic degradation of PVC as it is more and more removed from food packaging and its fraction in municipal plastic waste is decreasing steadily. PVC is now mainly used in construction, such as PVC window frames. The life of PVC construction products is considerably higher than packaging material, reducing the acuteness of the waste problem. On the other side PVC products are replaced by specialized technical personnel who can ensure that PVC waste is collected separately and is not mixed with other plastic-type waste. That gives the opportunity for more efficient PVC-specific recycling technology to be developed.

2 OPERATION MODES

In the following a brief selective overview, rather a personal account, is presented, in order to highlight variations in polymer catalytic pyrolysis scheme regarding modes of operations and reactor types. Prompted by the oil crises of the mid 1970s and early 1980s, the first research projects trying to convert plastic waste to fuel go back to the second half of the 1980s [2,3]. It was logical to extend earlier work on thermal noncatalytic conversion of plastic waste [4], as its products needed further upgrading in order to be utilized. The first attempts were carried out almost exclusively in autoclaves which were opened after the reaction was carried out and the liquid and gaseous components formed were collected and analysed. The first catalyst systems used in those works were well-established industrial acidic catalysts such as silica–alumina and zeolites, mainly Y-type. In the 1990s numerous studies have been carried out using as catalysts silica–alumina [5–7], zeolites [6–11], zeolite-based commercial cracking catalysts [12–14], MCM mesoporous materials [15] or clays and pillared clays [16, 17]

Besides the direct catalytic conversion of plastic, the subsequent *in situ* catalytic conversion of products of noncatalytic thermal degradation was also researched [18, 19]. These studies have confirmed the superior quality of the hydrocarbon mixtures produced and highlighted the potential of catalytic degradation. The majority of the studies have been carried out in batch/semi-batch systems where polymer and catalyst particles have been both introduced into the reactor together, followed by heating up and reaction, making this reactor operation batch wise regarding raw material and catalyst. In semi-batch systems there is continuous flow of a carrier gas that removes formed products out of the reactor, minimizing their further reaction. Besides batch reactor studies, a specially designed continuous screw kiln reactor was also used for the direct catalytic conversion of polymers [20–21] reducing overcracking compared to batch systems.

Although the more advanced version of a thermal noncatalytic process, developed by Kaminsky's group to pilot plant scale, is the Hamburg process [22–24] that uses a sand fluidized-bed reactor, there are no studies involving a continuous fluidized-bed catalytic degradation reactor, apart from tests carried out by the same group [25]. When they replaced sand with a commercial cracking catalyst, the product spectrum shifted drastically from waxes to gases and low-boiling aliphatic oils.

The few other catalytic studies involving a fluidized bed [10, 11, 26] operated in a batch mode, confirming a superior heat transfer efficiency. In respect to fluidized beds one issue that has to be researched further and solved is defluidization.

Furthermore, a study of the behaviour of a fluidized-bed reactor is very important as one of the options for a possible commercialization of such a pyrolysis recycle process is to co-feed plastic waste into the FCC cracker unit of an oil refinery. Studies of plastic being a fraction of the feed of a cracking process have been carried out by Ng *et al.* [7] and Arandes *et al.* [12, 27, 28]. They not only showed the applicability of the method, but discovered a synergetic effect on the cracking of the oil decreasing the amount of aromatics.

3 ZEOLITES

The decomposition of a polymer chain, being a hydrocarbon cracking reaction, is catalysed by acidic catalysts. The main category of solid cracking catalysts, as well as the more widely used in industry, are zeolites, as they constitute the main ingredient of catalysts used in the FCC process in refineries. Zeolites are crystalline aluminosilicates with a well-defined microporous structure with cages and channels of dimensions comparable to the size of common simple organic molecules. Zeolites have SiO_4 and AlO_4 tetrahedra as the primary structure units that link together through shared oxygen atoms in a three-dimensional structure. The AlO_4 tetrahedra carry a negative charge that is counter-balanced by cations inside the zeolite pore structure, usually Na^+, K^+ or Ca^{++}. When these cations are exchanged by protons, zeolitic acid sites are formed. Zeolite acidity can be either of Brönsted type, proton donors, or Lewis type, electron pair acceptors. Each acidity type leads to different reaction mechanisms, as hydrocarbon reactions are catalysed by proton addition over Brönsted sites rather than by hydride abstraction over Lewis sites. Another important characteristic of acidity is its strength that is usually measured by temperature-programmed desorption (TPD) of base components, usually NH_3. The catalyst sample is saturated with the base molecule first, with the physisorbed amount removed afterwards, and then the sample temperature increases, usually with a linear temperature programme. During the temperature programme stage the desorbed amount is monitored using a detector, such as a TCD (thermal conductivity detector). Obviously, the stronger the acid sites the higher is the temperature needed for the desorption of the base molecules from these sites. Stronger acid sites favour cracking reactions.

There is a plethora of natural or synthetic zeolite structures, each one existing in a wide range of relative compositions of Si or Al atoms, characterized by the Si/Al ratio [29]. Two examples of widely used zeolites types are ZSM-5 and Y-zeolite. The first structure consists of two sets of channels connected to each other; straight channels of 0.54 × 0.56 nm size and zig-zag 0.51 × 0.55 nm size. Y-zeolite consists of cages of 1.18 nm connected through 0.74 nm windows, placed in a tetrahedral arrangement, into a three-dimensional pore structure [29, 30]. The Si/Al ratio ranges between around 10 to infinite (pure siliceous structure named silicalite) for ZSM-5 and 1.5–3 for Y-zeolite. Ultrastable Y-zeolite (US-Y), the active ingredient of FCC catalysts, is a special case of Y-zeolite formed through the following process in order for the stability of the zeolitic structure to enhance. Under the harsh high-temperature conditions of an FCC regenerator the steam present extracts Al from the highly aluminous zeolite framework, forming holes and causing collapse of the structure. In order to avoid this, Y-zeolite undergoes a dealumination treatment in a similar, but controlled environment. Steam flows through a zeolite bed at high temperature in a controlled manner. During this treatment Al is extracted from the zeolite framework, the Si-O-Al network, but it remains inside the zeolite pore structure as extra framework Al (EFAL) in the form of cations, e.g. $Al(OH)_2{}^+$, AlO^+. It is believed that the interaction of EFAL with the acid sites increases their strength [29]. Through dealumination the framework Si/Al ratio decreases, while the bulk stays the same as that of the original Y-zeolite. Dealumination of Y-zeolite to form US-Y can take place through other processes, for example through reaction with reagents such as $SiCl_4$.

Chemical reactions carried over zeolites show shape selectivity, since they are able to discriminate between reactants, products and/or transition states compared to the size of their channels [29].

4 POLYMER-TO-CATALYST RATIO

An important aspect in a future catalytic process for degradation of plastic waste is the amount of catalyst used in such a process. In a batch system, which is the most broadly used so far to test the performance of various catalytic systems, the amount of catalyst is characterized by the polymer-to catalyst mass ratio. Results from initial experiments carried out on a TGA equipment Figure 7.1 [9] using high-density polyethylene (HDPE) as raw material at different polymer to catalyst mass ratios showed the existence of a limit below which the addition of more catalyst does not change the degradation pattern. In the absence of catalyst, the polymer (HDPE) degradation pattern showed a very steep decrease at about 773 K. The degradation set up very late at quite high temperature, but it progressed very rapidly after initiation. In the presence of catalyst, the polymer degradation occurred at much lower temperatures and more gradually. Even with the smallest catalyst amount (polymer: catalyst = 9 : 1) the degradation commenced at much lower temperature than in the absence of catalyst. As more catalyst was added the reaction proceeded at enhanced rates. At polymer-to-catalyst mass ratios 1:2, 1:1 and 2:1 the polymer degradation curves were very similar.

These results have been confirmed by estimating the activation energies at various ratios by a series of experiments with different heating rates [31]. The activation energy of pure thermal degradation of HDPE in the absence of catalyst was considerably higher (61 kcal/mol) than even the one with only 10% of zeolite USY (HDPE: US-Y = 9:1), 47 kcal/mol. However at HDPE:US-Y ratios 2:1, 1:1, 1:2 the difference of the activation energy was minimal, 25, 24 and 22 kcal/mol respectively.

All the above results indicated the possible existence of a limiting step over the whole reaction process. It is reasonable to assume that large macromolecules had to react on the external surface of the zeolite catalyst first, which could be the limiting reaction step.

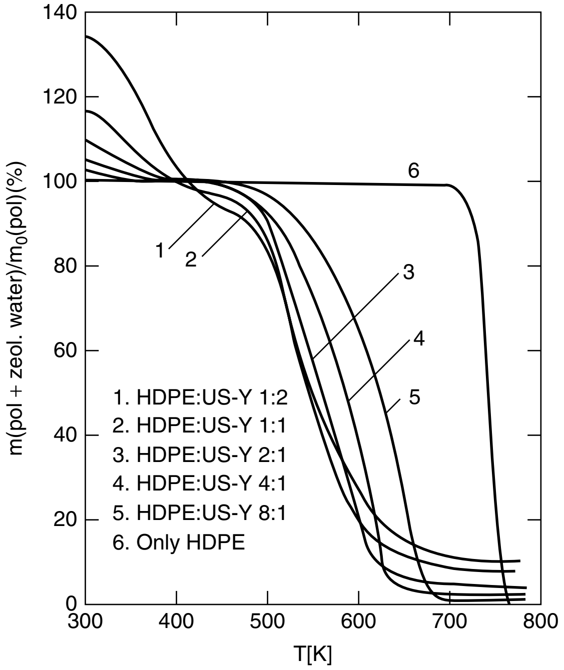

Figure 7.1 TGA graphs of HDPE at various polymer-to-US-Y zeolite ratios. Heating rate, 5 K/min; nitrogen flow, 50 mL$_N$/min. (From [8]. Reproduced by permission of the American Chemical Society)

Smaller cracked fragments diffused subsequently into the zeolite pores and underwent further reactions. It seemed that the addition of more zeolite above a specific quantity, corresponding to a polymer-to-catalyst ratio between 1:1 and 2:1, did not increase the overall degradation rate.

The melted polymer resided in the voids of the zeolitic bed. When the amount of polymer was high (high polymer-to-catalyst ratio), polymer filled these voids fully with the excessive polymer mass not being in contact with zeolite. The more zeolite was added, the more polymer was in contact with it and more polymer participated in the initial degradation step. This was true to a point when the added zeolite was no longer in contact with plastic. In the last case the excessive zeolite did not contribute to the initial degradation step of the large macromolecules.

TGA experiments however do not reveal the whole picture. They show only the overall change of the polymer mass without any indication of product distribution. Therefore further experiments were carried out with linear low-density polyethylene (LLDPE), this time using a laboratory semi-batch reactor with quantities at gram levels rather than milligrams. In these experiments various liquid fractions were collected at different stages. Surprisingly, no difference in the liquid yield, neither conversion nor liquid selectivity, was observed in an even wider range of USY-to-polymer ratio (Figure 7.2).

However this figure shows only part of the truth. If the results are plotted for all three stages of the temperature programme used (Figure 7.3), the systems with the most zeolite (US-Y), i.e. zeolite-to-polymer ratio of 1:1 and 1:2, form more liquid (indicative here of higher conversion) than the other two systems at the first stage, i.e. lower temperature ($T = 573$ K).

However this is compensated by the temperature increase. At the second stage ($T = 633$ K) the two systems with the lowest zeolite amounts, i.e. zeolite-to-polymer ratio of 1:3 and 1:4, form the highest liquid fraction amount. At the third stage ($T = 673$ K) the degradation had been already completed for all systems. Minimal liquid amounts were formed.

In order to confirm these results, a linear heating programme has been applied where the relatively mild final temperature was reached only at the end of the experiment, not leaving further time at the top temperature to react. The presence of more catalyst has indeed formed more liquid products (Figure 7.4), confirming the above findings.

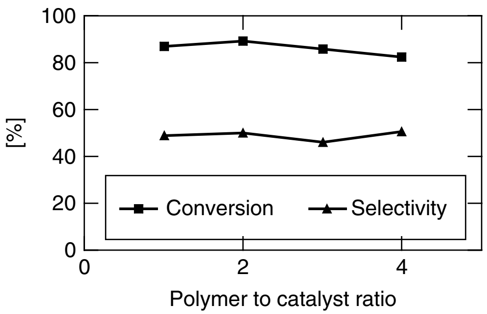

Figure 7.2 Conversion and liquid selectivity during degradation of LLDPE over US-Y zeolite at different ratios and a step temperature programme (0–5 min:573 K, 5–10 min: 633 K, 10–15 min:673 K)

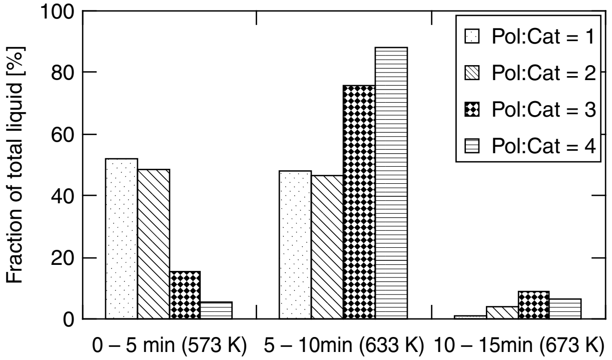

Figure 7.3 Liquid formation during degradation of LLDPE over US-Y zeolite at different ratios

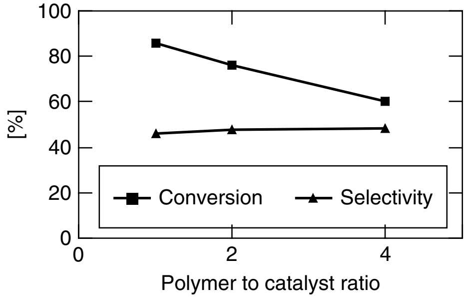

Figure 7.4 Conversion and liquid selectivity during degradation of LLDPE over US-Y zeolite at different ratios and a linear temperature programme (16 K/min to 633 K)

5 INITIAL DEGRADATION MECHANISM

TGA is an excellent technique for a fast evaluation of the polymer degradation. However it does not reveal anything about solid state reactions taking place during degradation. TGA experiments showed that in the absence of catalyst, HDPE was decomposed very rapidly at around 773 K, without any weight loss at lower temperatures, indicating that no volatile products were formed until then. TGA experiments were not conclusive on the existence of any solid state reaction that would have changed the polymer structure, as they would not necessarily lead to mass change and would be undetectable by the TGA equipment. This question of solid state reactions is an important one, as homogeneous solid state reactions could be the initial step in the heterogeneously catalysed process. To clarify the mechanism of the first degradation step, homogeneous or heterogeneous, a series of experiments were carried out at relatively mild temperatures in the semi-batch reactor. Each polymer sample was recovered at the end of these experiments and its molar mass distribution has been determined by gel permeation chromatography (Figure 7.5) [9].

Curve number 1 shows the molar mass distribution of the original hdPE sample. Curves number 2 and 3 show the molar mass distribution of samples heated in the absence of catalyst over 4 h at 413–423 K (curve number 2) and 6 h at maximum temperature

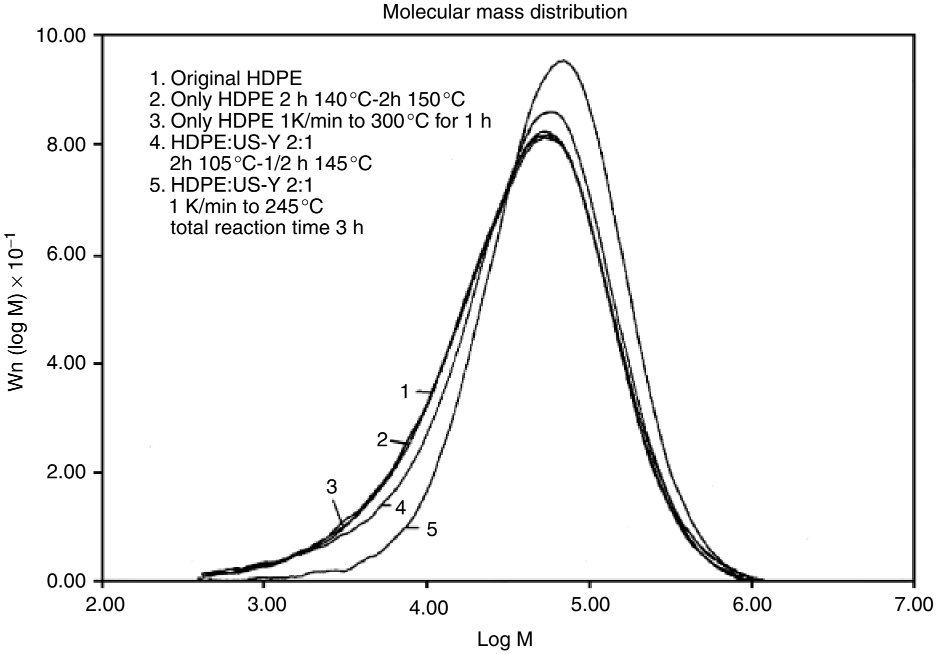

Figure 7.5 Molar mass distribution of fresh HDPE and heated HDPE in the absence and presence of US-Y zeolite. (From [9]. Reproduced by permission of the American Chemical Society)

573 K (curve number 3). The molar mass distribution curves of the samples exposed at higher temperatures in the absence of catalyst were identical to the curve of the original polymer sample.

This implied that the polymer structure has not been changed, indicating that no solid state reactions took place. These experiments did not yield even trace amounts of volatile products.

However all the samples heated in the presence of US-Y catalyst (polymer-to-catalyst mass ratio 2:1) showed a deviation from the original polymer molar mass distribution in the region of lower molar masses. In the first experiment, the polymer/US-Y-zeolite sample was exposed at a temperature of 378 K, which is below its melting point, for 120 min and then for 30 min at 418 K. No volatile products were initially observed, but traces of isobutane and isopentane were detected when the temperature was raised to 418 K. Although these conditions were much milder than in the equivalent experiment with pure polymer (curve number 2), the molar mass distribution, curve number 5 in Figure 7.5, was different from that of the original polymer.

In the second experiment the mixture of hdPE and US-Y was exposed at significantly higher temperatures. From ambient temperature to 443 K with 5 K/min, then to 518 K with 1 K/min. The experiment was stopped when the final temperature was reached and the total experiment duration was 3 h. The sample of this experiment showed much larger deviation in the molar mass distribution, although the conditions were again milder than those at which the pure polymer was exposed (curve number 3). In this experiment the first liquid drops of hydrocarbon products (~5 mg) were collected when the reactor temperature was 478 K.

These experiments concluded that no reaction occurred in the absence of catalyst. The presence of catalyst was necessary to initiate solid state reactions that changed the polymer structure, mainly by breaking of chains of low molar mass to smaller chains. In the catalytic process the first gaseous products, even if only in traces, were formed at about 413 K and the first liquid products slightly above 473 K. Differential thermal analysis (DTA) runs had revealed that 413 K was the melting point of the polymer sample.

Current studies are focused on clarifying some further mechanistic aspects, namely the question if indeed the initial decomposition step occurs on the external catalyst surface or chain ends and/or branches intrude into the pore catalyst structure and decompose on internal acidic sites. In order to investigate this aspect, we use selective poisoning of the external catalytic sites using large molecules that do not enter the zeolite structure.

6 PRODUCT DISTRIBUTION

The original polymer mass in the presence of a catalyst is generally converted into volatile products while a residue is left unconverted. This residue consists of a polymer solid residue of genuinely unconverted plastic, although usually not of the same composition and molar mass distribution as the original, and coke formed on the catalyst surface. From these two residue components, the first one can be eliminated by changing the reaction conditions; most obviously by increasing the polymer reaction temperature and time. The second one, coke, can not be avoided. The raw polymer material, being of hydrocarbon nature, undergoes coking reactions on acidic catalytic surfaces [29]. However, the coke amount can be minimized depending upon process conditions and characteristics, most importantly catalyst type.

The volatile (at reaction temperature) products can be grouped into liquids and gases, depending upon the state they are at ambient conditions. However, for practical reasons in all our experimental studies we used an ice bath ($T = 273$ K) to collect the liquid products. This way we avoided possible condensation problems of the collected gases as well as variations due to seasonal room temperature fluctuations. A diagrammatic overview of the process mass balance is shown in Figure 7.6.

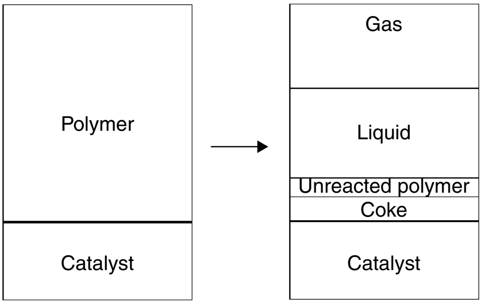

Figure 7.6 Diagrammatic overview of the transformations during catalytic polymer degradation

In the following the characteristics of product distribution over various microporous solid acidic catalysts are discussed. The catalysts tested were zeolites, commercial cracking catalysts, clays and their pillared analogues.

Zeolites are widely used in acidic processes and they are an obvious catalyst choice. The suitability of commercial cracking catalysts to degrade polymer waste is vital as one of the options of commercializing this polymer recycling method is to co-feed polymer waste to existing refinery crackers [13]. Furthermore, in the search for cheaper catalysts, clays and their pillared analogues are also introduced in the polymer catalytic degradation [16, 17].

6.1 CONVERSION, LIQUID YIELD, COKE CONTENT

First, the behaviour of these catalysts on the overall conversion, liquid selectivity/yield and coke formation is discussed. Overall conversion is the fraction of the original polymer mass that is converted into volatile products, liquids and gases. Liquid selectivity is the fraction of the volatile products that are in liquid form, while liquid yield is the fraction of the original polymer mass that is converted into liquid. Coke yield is the fraction of the original polymer mass that is converted to coke on the solid catalyst. As at most conditions applied, no unreacted solid polymer remnants were left, the sum of coke yield and conversion is equal to 1 (100%). Therefore overall conversion is not a good measure of the activity of the catalyst. It rather reflects coking tendency over the specific catalyst. Overall conversion levels over zeolites are lower than clay-based catalysts as more coke is formed over zeolites due to their stronger acidity. The same trend is followed by commercial FCC catalysts, where the lower amount of the active zeolitic ingredient leads to lower density of acid sites. Compared with levels of coke yield above 10% on USY, on commercial cracking catalysts coke yield is around 5% and well below that on clays/pillared clays [13].

An exception is ZSM-5 which has a coke-forming resistance due to its shape selectivity properties. The channels of ZSM-5 have a size comparable to that of many organic molecules. This small pore size hinders the formation of bulky coke precursors and coke molecules, decreasing the coke formation. Indeed, in polymer catalytic degradation experiments less than 1% coke is formed over ZSM-5, most probably on the external catalytic surface of the catalyst, compared with more than 10% over the large-pore and strongly acidic US-Y. Another characteristic of zeolite catalysts regarding coke formation and hence conversion is that over zeolites with cage and supercage structure, such as Y and USY, more coke was formed than over channel structure zeolites of similar acidity, such as β-zeolite, resulting in lower overall conversion [8].

Generally over clays and pillared clays higher liquid yield values are reached than over zeolites [13, 16, 17]. Over US-Y zeolite values around 45% are achieved compared with values around 70% over clay-based catalysts. The strong zeolitic acidity leads to overcracking forming products that are collected mainly in the gaseous fraction. Over clay based catalysts of weaker and/or lower acidity higher temperatures are needed for the polymer degradation to occur, but much less overcracking takes place leading to significantly higher liquid yields of above 70%.

6.2 CHARACTERIZATION OF GASEOUS/LIQUID PRODUCTS

The volatile products of catalytic degradation of polyolefins over zeolites, estimated using gas chromatography coupled with a mass spectrometer (GC/MS), lie in the range C_3–C_{15} with distinctive patterns among various zeolitic structures [8]. Over large-pore zeolites, ultrastable Y, Y and β-alkanes are the main products with less alkenes and aromatics and only very small amounts of cycloalkanes and cycloalkenes. Over medium-pore zeolites, ZSM-5 and mordenite, lighter hydrocarbons are formed and significantly more olefins than over large-pore zeolites [8]. Both characteristics, length of the hydrocarbon chain formed and chemical character of the hydrocarbons formed, seem to depend upon the catalyst structure as well as strength/density of the catalytic acid sites. Over commercial cracking catalysts containing only a fraction of US-Y zeolite as well as clays/pillared clays with significantly weaker and less acid sites, significantly lower amounts of alkanes are formed than alkenes [6, 13, 17]. Alkenes as the primary products of a cracking process undergo secondary reactions the extent of which increases with the acidity. Furthermore secondary reactions, being bimolecular, are sterically hindered in the constrained internal structure of medium-pore zeolites [8].

For estimation of the relative amount of paraffins/olefins in order to avoid the laborious GC/MS method we also used solution H NMR. GC/MS needs painstaking search as the number of candidate molecules for a mass spectrum and their similarities increase steeply with the molecule chain length. GC/MS provides of course a full picture of the chemical identity of the components of a mixture. However, if specific information is looked for, other specific methods can shorten the analysis time. In H NMR, olefinic hydrogen atoms show separate distinctive peaks from paraffinic hydrogens. While over US-Y zeolite the ratio of olefinic hydrogens to aliphatic (olefinic plus paraffinic) hydrogens is below 1.5% over commercial cracking catalysts it is between 4.5 and 5.5% and over pillared clays above 10% [13]. Due to the milder acidity of pillared clays, secondary reactions have been limited with the result of a much higher presence of primary products alkenes in the sample. Cracking catalysts produced intermediate figures. Due to the presence of US-Y, secondary reactions occurred, but did not progress to the same degree as with pure US-Y. It should be emphasized that the ratio of olefinic hydrogens to aliphatic hydrogens is much lower than the actual molar ratio of alkenes to the sum of alkanes and alkenes, as only hydrogens of the double bond contribute to the olefinic NMR peak, not all hydrogen atoms of the alkene molecule, while the rest hydrogens do contribute to the paraffinic peak.

The chemical character of liquid products usually coincides with that of gaseous ones. The gaseous products over clay catalysts are predominantly alkenes compared with alkanes over US-Y [16, 17]. Similarly over ZSM-5 gaseous products are predominantly alkenes, although more aromatics are formed too [8].

6.3 BOILING POINT DISTRIBUTION OF LIQUID FRACTION

Liquid hydrocarbons are considered to be the most valuable products of a potential recycling process as they can be used as blends for motor engine fuels. In such a process short-chain hydrocarbons in the gas phase are also produced and they are crucial to provide the heat needed for an endothermic reaction such as polymer cracking, but their value is considered low due to their transportation cost.

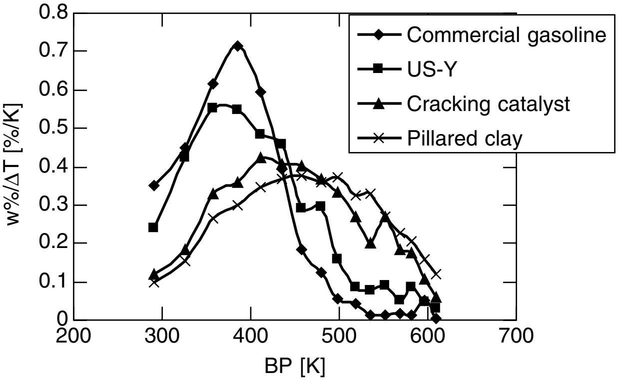

Figure 7.7 Boiling point distribution of liquid fuel formed over US-Y zeolite, a commercial cracking catalyst, a pillared clay (polymer-to-catalyst ratio 2:1) and comparison with a commercial gasoline sample

To characterize the quality of liquid fuel we use the boiling point distribution, which we estimate chromatographically using a 100 m nonpolar column that separates the components of a mixture according to their volatility/boiling point. Employing a calibration mixture consisting of normal alkanes, boiling points are allocated to retention times under the same chromatographic conditions as the ones used in the GC analysis.

Figure 7.7 compares the boiling point distribution of liquid products formed over US-Y, a commercial cracking catalyst and a pillared clay. In the same figure is plotted the boiling point distribution of a commercial gasoline sample.

The liquid hydrocarbon fraction formed over US-Y is similar to the commercial gasoline sample regarding volatility. Commercial gasoline contains slightly higher amounts of volatiles, around the boiling point range of heptane/octane. A considerable shift towards heavier components is obvious from US-Y to cracking catalyst and even more to clay-based catalysts. Stronger catalyst acidity enhances the extent of cracking reactions, leading to more volatile, shorter-chain hydrocarbons. Clays and generally not strongly acidic catalysts enhance the yield to liquid hydrocarbons. However this is accompanied by shifting the fuel quality towards diesel rather than gasoline.

7 CONCLUDING REMARKS

The presence of acidic microporous catalysts speeds up the rate of polymer degradation, leading to lower reaction temperatures and shorter reaction times. The energy demands of a potential catalytic degradation process should therefore be much less than these of a pure thermal process. Furthermore the quality of the products of catalytic degradation are in the range of motor engine fuels, eliminating the necessity of any further upgrade.

More specifically, over microporous catalysts such as zeolites, cracking catalysts and clays, the lower the catalyst acidity:

- the more liquid fuel is formed, and
- the more the liquid fraction distribution is shifted towards heavier hydrocarbons.

Both effects are due to the lower extent that cracking reactions take place. Over strongly acidic catalysts overcracking leads to the formation of smaller molecules, increasing the volatility of the liquid fraction, but also increasing the amount collected in the gaseous fraction. Furthermore, stronger acidity leads to higher extent of secondary reactions and the formation of more saturated products, namely paraffins rather than olefins, which are the primary products of a hydrocarbon cracking process. Hence, mainly alkenes are formed over clay based catalysts, while over commercial cracking catalysts the amount of olefins is higher than their parent US-Y. On zeolites steric restriction of bimolecular secondary reactions inside the structure of medium-pore zeolites, such as ZSM-5, leads also to higher formation of primary cracking products, olefins.

On the way to an industrial polymer recycling process of catalytic pyrolysis of waste plastics into fuel, a lot of research has still to be carried out. However, it is not too early to think about the logistics of the whole operation. Although the polymer catalytic degradation research is only in the beginning and no specific optimized reactor design has emerged, it is important to have a holistic approach in the polymer recycling problem. Catalytic pyrolysis is only one of a combination of recycling methods applicable. Economic studies should assess the viability of each recycling method. Obviously the direct recycle of plastic refuse in a plastic processing factory makes much more sense than any other method. Only in cases where reprocessed goods do not comply with quality specifications, other alternatives should be considered.

In particular, as far as the plastic catalytic degradation is concerned, there are various possible scenarios. In large urban areas the best approach probably is to build a plastic waste pyrolysis plant in an acceptable near area at not to great distance, in order to minimize transport cost of the plastic waste. In that case, safety and environmental concerns of such a new plant should first be dealed with satisfactorily before the new plant can get the go-ahead. Near refineries however, the best approach might be to co-feed plastic waste with oil fractions into refinery crackers, or even have a unit of pure thermal pyrolysis first with the produced wax-type fraction to be upstaged in another reactive refinery process. In the first case of co-feeding, a lot of research has to be carried out, addressing aspects of defluidization mainly, before an alteration of a process of the scale of FCC units can go ahead.

In all scenarios one thing is clear already. The amount of fuel produced by a pyrolysis process is not large enough to enable the producing company to compete in the fuel market. Taking as basis a yearly polymer consumption of 100 kg/person [1] and assuming in the most optimistic case (though unrealistic, as fuel density is lower than 1 kg/L) that 100 L of motor engine fuel, gasoline or diesel, can be produced, it becomes obvious that this amount is a small (rather tiny) fraction of the fuel consumed per person per year in the developed world. There is no way that fuel produced from recycled polymer can dictate terms in a very competitive market. However as mentioned in the introduction, in times of depleted natural resources turning waste into useful products is too big an opportunity to leave it purely on free market terms. The suggested solution is in the framework of free market economies and has two aspects.

First, the fuel produced from recycled plastic waste needs to be exempted, at least partially, from tax and second, agreements with fuel commercial companies need to be reached in order for them to accept the produced fuel in their fuel pools, with the advantage of lower tax for this fraction.

We can not see any other way that such a process can become commercially viable. In the end, the right degree of competition is reached only if 'alternative competing technologies' are properly costed in a sustainable manner. Currently, the cost of landfill disposal does not recover all costs to make this disposal method sustainable and in that sense landfill disposal is heavily subsidized.

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8

Liquefaction of Municipal Waste Plastics over Acidic and Nonacidic Catalysts

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1 INTRODUCTION

Municipal waste plastics (MWP) are a significant part of municipal solid wastes which are collected as household waste. Municipal plastic wastes usually account for about 8% of the total municipal solid wastes (MSW) by weight and much more by volume [1]. Separation of the plastics from MSW is mainly by hand, either by the household prior to collection or at a materials recycling facility. An average weight composition of the separated plastic wastes is given in Table 8.1. According to an APME report, in 2003, the amount of MWP was 13671 million tonnes in the European Union, which was 66.3% of the total collectable plastic waste. Japan generates about 5280 million tonnes of MWP [2]. Although landfilling and incineration of solid wastes have been restricted by environmental law since 1995, these operations are still in demand due to their ease and low cost. Thus, large amounts of MWP are being treated by landfilling or incineration (without energy recovery). Since mechanical recycling is the preferred recovery route for homogeneous and relatively clean plastics waste streams, converting of MWP into liquid hydrocarbons is being considered as a promising recycling method.

Research in producing liquid fuels and chemicals from waste plastics has been a focus for about 20 years. Traditional thermal and catalytic–hydrocracking processes can be applied to transform plastic wastes into liquid hydrocarbons. Thermal cracking, of plastic waste has been investigated at the laboratory and pilot plant level, and technologies such as the Polymer Cracking Process, BASF Conversion Process, Hamburg/ABB, Amoco, etc. for liquefaction processing of plastic waste have been developed in Europe, Japan and the US. However, the products of thermal cracking are distributed over a wide range of carbon numbers and their commercial value is low. Because thermal cracking demands

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Table 8.1 Composition of MWP

	A	B
PE + PP + PS	81.3–86.7	79–90
PVC	4.3–9.4	3.8–1.2
PET	0.5–3.9	7.2–1.5
ABS, etc	2.1–3.6	2.0–1.3
Ash	3.7–6.8	4.0–1.9

A: collected from Nigaata city, Japan [2]
B: collected by the DSD system in Germany [3]

relatively high temperatures and its products require further processing to upgrade their quality, catalytic cracking of plastic waste offers considerable advantages. It occurs at considerably lower temperatures, and the composition and yield of the product can be controlled by the catalyst.

2 CATALYTIC LIQUEFACTION OF MWP

There are different methods for carrying out the catalytic liquefaction of plastic wastes.

- catalytic cracking of plastic wastes by direct contact with the catalyst (liquid phase contact);
- thermal cracking plus catalytic upgrading;
- hydrocracking;
- co-processing of plastic wastes in a refinery stream or with coal.

First of all, the dechlorination of waste plastics is necessary. This is because chlorine (e.g. from PVC) in MWP causes contamination of all product streams with chlorinated organics, as well as corrosion problems. Dechlorination of MWP can be carried out in a twin screw at around 300°C, at which temperature other plastics do not start to degrade; HCl gas envolved from degradation of PVC in MWP is recovered as a hydrochloric acid. Subsequently, the dechlorinated MWP in the melted form is liquefied using the above methods.

2.1 LIQUID PHASE CONTACT

The catalyst makes contact with melted MWP. Good contact between plastic particles and the catalyst is one of the key points for process development. Melted plastics can be degraded in a fluidized-bed reactor or a fixed-bed reactor. Since the usage of fixed beds leads to problems of blockage, scale-up to industrial size is not feasible. However the fluidized bed has a number of special advantages for catalytic degradation of plastics, because it is characterized by a good contact between catalyst and plastics as well as an excellent heat and mass transfer [4]. In addition to selection of a suitable reactor, the catalyst used is very important in the process.

Catalytic degradation involving liquid phase contact of common plastics, such as PE and PP has already been tested extensively [5–10]. The most commonly used catalysts in these studies were solid acids (amorphous silica–alumina, zeolites, zeolite-based FCC catalysts, MCM mesoporous materials and super acidic zirconia, etc.). Besides acidic catalysts, a few studies have been performed with activated carbon and nonacidic mesoporous silica catalyst (FSM) [11–15]. Acidic cracking catalysts are very useful for direct liquefaction of PE and PP. The catalytic effect of acidic catalysts in plastic pyrolysis has been explained by a carbonium ion theory. The catalytic mechanism over acidic catalysts has been reviewed by Bukens [16]. In brief, this mechanism involves: (1) an initiation step, involving chain carbonium ion formation by proton addition; (2) a depropagation step, chain cleavage yields an oligomer fraction by β-scission of chain-end carbonium ions leading to gas formation on the one hand, and a liquid fraction on the other; (3) an isomerization step, double bond isomerization of an olefin and isomerization of saturated hydrocarbons; (4) an aromatization step; aromatic formation following cyclization via an olefinic carbonium ion.

The problem relating to steric and/or internal diffusion hindrances in the cracking of bulky polymeric molecules can be solved using catalysts of larger pores or zeolites with smaller crystal size. Although suitable acidic catalysts can control the product range in catalytic cracking of polymers, they are easily deactivated by nitrogen, sulfur and impurities in MWP [17]. This type of catalysts can be regenerated by burning off the coke, but this can result in a loss of activity [18].

On the other hand, activated carbon may be considered as a catalyst in the cracking of waste plastics. This is because it is a neutral catalyst with a high surface area and, therefore, it might be more resistant to impurities and coke formation. It has been reported that Pt-, Fe- and Mo-supported activated carbon catalysts were effective for the pyrolysis of PE and PP [11, 14, 15]. Use of metal-supported activated carbon catalysts has enhanced the formation of aromatics via dehydrocyclization of straight- or branched-chain radicalic intermediates.

Although a large variety of catalysts have been used, even if performing well, many can be unrealistic for MWP. Thus, although the option based on cracking of plastic wastes by direct contact with catalyst seems the simplest way, the catalyst cost can affect the economics of the process considerably

2.2 THERMAL CRACKING PLUS CATALYTIC UPGRADING

The problems in catalytic cracking of MWP by direct contact with the catalyst can be overcome by two-step processing. This method involves an initial thermal cracking of waste plastics to produce low-quality hydrocarbons (vapors or liquid) that are treated afterwards in a catalytic reactor to obtain high-quality liquid fuels.

A full-scale pyrolysis–catalytic process in which the catalytic cracking zone is directly connected to the pyrolysis zone was developed in Japan (Fuji Process) [19]. In this process, after separation of PVC and impurities by wet techniques, waste plastics are thermally pretreated at 300°C for dechlorination and then introduced into the pyrolysis reactor and thermally cracked at 400°C. Subsequently, degradation products are fed directly to the fixed-bed reactor using a ZSM-5 catalyst.

Catalytic cracking yields the following products:

- oil, 80%;
- gas, 15%;
- residue, 5%.

Composition of the oil produced is:

- gasoline 60%;
- kerosene 20%;
- diesel 20%.

The main problem is the sensitivity of the zeolite catalyst towards impurities coming from the waste.

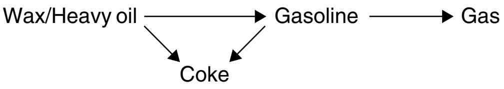
The pyrolysis–catalytic cracking reactor scheme poses the serious engineering and economic problems of a complicated reaction mechanism and high capital cost because of the infrastructure needed. Another possibility is to separate the thermal cracking from the catalytic cracking operation, in which first the waste plastics are cracked thermally in a pyrolysis plant and the wax/oil produced is catalytically treated in a conventional cracking or hydrocracking reactor to high yields of gasoline of improved octane rating.

A fluidized-bed pyrolysis reactor is the most suitable for thermal cracking of MWP to obtain liquid/waxy product. Key features of the fluidized-bed pyrolysis include [3, 20]:

- conducting pyrolysis at lower temperatures, an aliphatic heavy oil and/or wax can be obtained;
- by addition of lime into the reactor, HCl evolved from the PVC fraction in MWP is captured. The dechlorination step is not needed for MWP containing up to 2% chlorine;
- Solid impurities in MWP either accumulate in the bed or leave the reactor with the hot gas as fine particles which are collected in cyclones.

The liquid product obtained from thermal cracking can be either catalytically cracked/hydrocracked or co-processed with a refinery feed. Since the catalytic cracking of oil derived from MWP is more or less problematic, any cracking catalyst can be applied to oil derived from pyrolysis of plastics. But the yield and the quality of gasoline obtained from cracking step vary with the type of catalyst and the properties of the pyrolytic oil derivated from waste plastics.

The amount of strong acid sites of the catalyst used influences the product distribution from catalytic cracking in addition to the temperature. The reaction scheme below can be considered for the catalytic cracking.



The amount of gas product shows an increase with an increasing amount of strong acid sites on the catalyst. Because gasoline is an intermediate product, its yield gradually increases to a maximum value and then decreases with the increase in the amount of strong acid sites [21].

As an example, the results from catalytic cracking of three types of waxes from thermal cracking of PE are given in Table 8.2 [22]. The catalyst used, the equilibrium FCC catalyst,

Table 8.2 Properties of pyrolytic wax derived from PE pyrolysis

Pyrolytic wax	A	B	C
Fractions (vol%)			
Gasoline (IBP-216°C)	18.0	20.2	28.2
LCO (216–343°C)	25	29.3	37.8
HCO (>343°C)	57	50.5	34
GC analysis, wt%			
n-paraffins	76.8	38.6	36.2
α-olefins	18.1	34.5	42.8

Table 8.3 Some results from catalytic cracking of pyrolytic wax derived from PE pyrolysis

Feed	Wax A		Wax B		Wax C	
Temperature (°C)	470	510	470	470	470	470
Catalyst/oil (wt/wt)	0.43	3.99	0.47	4.15	0.48	4.20
WHSV (h^{-1})	333	20.0	300	19.3	298	19.0
Yields (wt%)						
Dry gas	1.22	1.81	0.62	0.95	0.18	0.59
LPG	10.61	22.39	6.31	17.4	3.46	14.6
Gasoline	45.9	63.0	39.2	67.7	40.9	64.0
LCO	22.8	8.80	27.3	10.7	33.0	10.8
HCO	17.3	1.3	25.1	1.3	21.9	6.9
Coke	1.8	2.4	1.4	1.9	0.5	3.2
Conversion (%)	59.9	89.9	47.7	88.0	45.1	82.4
Composition of C_4–C_{11} in gasoline, wt%						
n-paraffins	17.2	10.6	20.3	14.9	21.7	17.3
i-paraffins	12.6	31.2	12.2	47.7	10.2	46.1
Olefins	38.5	18.2	43.4	15.4	45.2	13.4
Naphthenes	14.4	15.6	12.8	11.3	14.3	12.0
Aromatics	17.3	24.5	11.3	10.6	8.6	11.2

KOB-627, is an octane-enhancing catalyst containing Y-type (US-Y) zeolite. Its matrix (about 50 μm) cracks primarily the large and bulky molecules prior to their secondary cracking in the small pores of the zeolite. The medium activity of this catalyst is reduced over cracking of gasoline. This catalyst produced high yields of gasoline with improved quality from pyrolytic waxy products, as shown in Table 8.3.

Similarly, it was observed that rare earth metal exchanged Y-type zeolite (REY) catalyst, having a moderate amount of strong acid sites, has a selectivity towards gasoline in the catalytic cracking of oils derived from plastics. HZSM-5, silica-alumina and Y-type zeolite (REY) were tested for catalytic reforming of heavy oil derived from PE pyrolysis. REY zeolite, which has a small crystal size and a low amount of strong acid sites, was found to be the most suitable catalyst to obtain the highest research octane number (RON) of 97.5 and a gasoline yield of 48 wt%. In contrast, HZSM-5 has the lowest RON value (23) and gasoline yield (18 wt%) [21, 23].

It is however necessary to remember that products from cracking of heavy oils are highly unsaturated and therefore they have to be further submitted to hydrofining.

Upgrading of heavy oils derived from waste plastics by catalytic hydrocracking is also one of the most promising processes for conversion of waste plastics. Dual-functional catalysts, having both cracking and hydrogenation–dehydrogenation functions, are used for this process. The cracking function is realized by an acidic support, while the hydrogenation component is usually a metal, oxide, or sulfide of group VIII and/or VIb [17]. Commercial catalysts usually adapt Ni, Mo, W, Co and their combinations as the active metal sulfide component, whereas silica–alumina and zeolites are used as acidic support.

Activity of these catalysts depends on the balance between the hydrogenation and acidic functions. For example, it was found that HZSM-5 was effective for the hydrocracking of HDPE and plastic waste [24]. But the liquid product contained much less *n*-paraffins and a greater amounts of aromatics (34%) and naphthenes (21.7%) because of a lack of sufficient hydrogenation function. The reaction mechanism over HZSM-5 can be considered as follows;

$$n\text{-Paraffins} \longrightarrow \text{Olefins} \longrightarrow \text{Naphthenes} \longrightarrow \text{Aromatics}$$

$$\underset{(C_2\text{-}C_4)}{\alpha\text{-Olefins}} \longrightarrow \text{Naphthenes} \longrightarrow \text{Aromatics}$$

However, in the case of hydrocracking over a dual functional catalyst, isoparaffins are the major compounds in the liquid product.

Although the hydrocracking process (Figure 8.1) has many advantages for the heavy oils containing heteroatoms, there are a few studies on the hydrocracking of heavy oils derived from plastics. The conversion of waste plastics to naphtha by thermal cracking followed by hydrocracking over an acidic catalysts was investigated in two post-consumer waste plastics, namely DSD and APC [25]. DSD was provided by the Duales System Deutschland. DSD (containing 1.126 wt% of Cl and 4.4 wt% of ash) and is considered as a real post-consumer plastic. However, APC provided by the American Plastic Council is a relatively clean waste plastic (containing 0.03 wt% of Cl and 0.45 wt% of ash). The catalytic effect on oil yields from hydrocracking was neglible for DSD and APC. Several catalyst had a significant effect on the boiling point distribution for the APC plastic, producing lighter products, but had little or no effect for the DSD plastic. Hydrocracking of heavy oil from DSD pyrolysis yielded 55–65% gasoline fraction, whereas the gasoline yield was more than 90% for heavy oil from APC. However, in these studies gasoline quality was not determined.

A more detailed investigation on the quality of gasoline from hydrocracking was carried out by Masuda *et al.* [26]. They examined the activity and selectivity of a Ni-REY catalysts with different nickel contents in the hydrocatalytic upgrading of heavy oils obtained from the waste PE and a mixture of PE and PET. The selectivity towards gasoline of Ni (0.5 wt%)-REY was 78% and the RON value of the produced gasoline was 110. Besides this, Ni-REY a showed constant activity during repetition of the sequence of reaction and regeneration.

Based on the above results, it can be mentioned that the catalyst having both hydrogenation and acidic functions can successfully convert heavy oil derived from plastic wastes (relatively clean) into environmentally acceptable transport fuels. However, for the heavy oils containing impurities, the dual functional hydrocracking catalysts still need to be improved. In the hydrocracking process over the acidic catalyst, nitrogen content in feed is limited because basic nitrogen compounds poison the acidic sites of the catalyst.

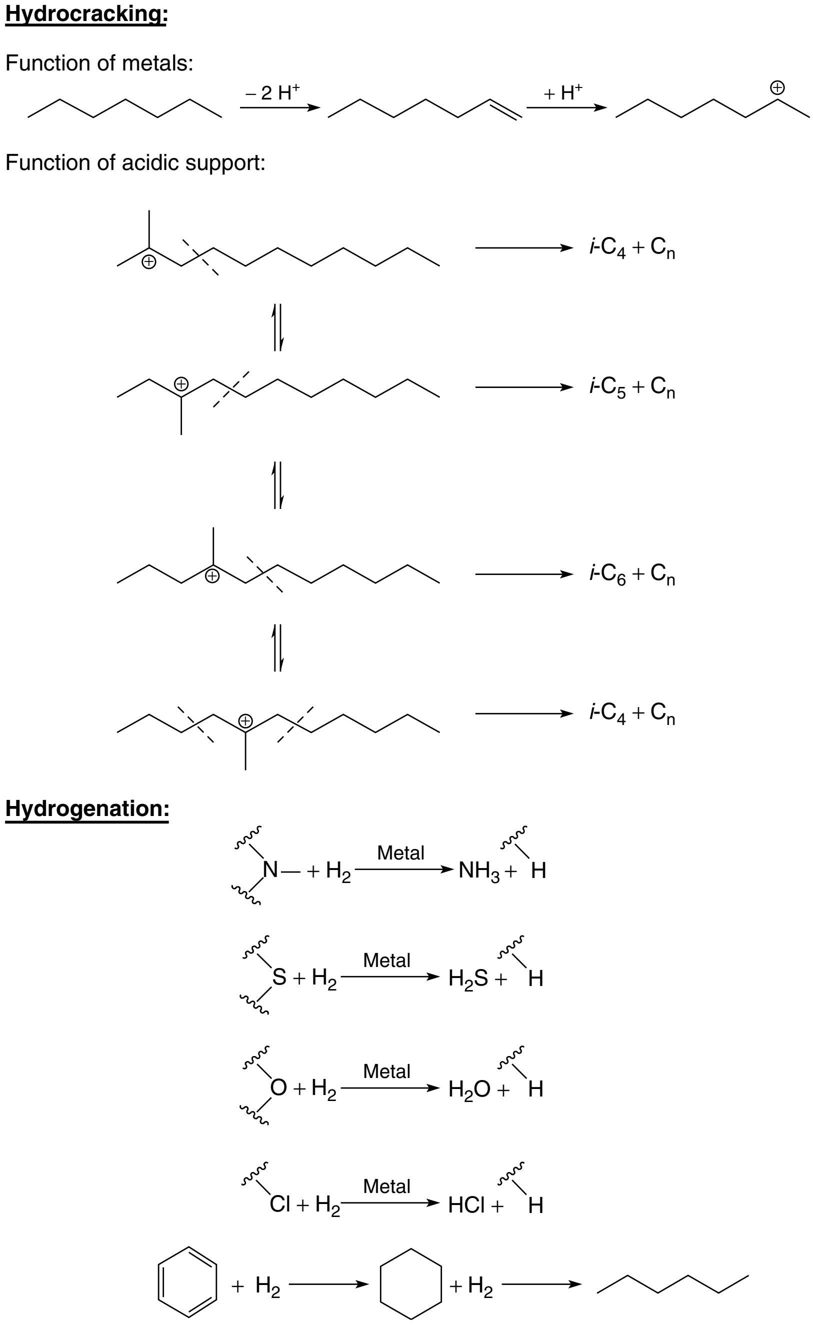


Figure 8.1 The hydrocracking and hydrogenation mechanism of metal-supported acidic catalyst

In addition, in order to prevent the deactivation of the catalyst caused by the deposited coke or coke precursor, the process needs to be operated at high hydrogen pressures and this leads to high hydrogen consumption and high construction cost of the reactor.

Activated carbon catalysts, which are neutral, can be considered as an alternative catalyst for hydrocracking of heavy oils derived from waste plastics. In recent years, carbon has received much attention as a support for hydrodesulfurization (HDS) catalysts as high HDS activities have been reported [27, 28], which may be due to more favorable support/catalytic species interactions. In addition, activated carbon catalysts have many other interesting features such as high surface areas with controlled pore volume and pore size, reduced coking activity and controllable surface functionality. The use of activated carbons as a catalyst support offers some advantages over the more traditional acidic oxide supports, such as stability in acidic and basic media, ease of recovery of precious metals supported on them, and the possibility of tailoring their properties to specific needs [29, 31]. It has been reported that metal-supported activated carbon (M-AC) catalysts have shown excellent cracking activity in addition to hydrogenation, on petroleum-derived heavy oils and some coal model compounds [32–38]. The catalytic effects of M-AC catalysts in hydrocracking of vacuum gas oil have been explained by a radical mechanism. Thus, activated carbons (AC) have the ability to abstract hydrogen from a hydrocarbon and free radicals are formed on AC. These free radicals initiate the cracking reactions. In the presence of H_2, hydrocarbon free radicals are hydrogenated by hydrogen atoms which are generated on M-AC from gaseous hydrogen to form stable hydrocarbon molecules and consequently to suppress overcracking. This hydrogen quenching reaction produces the higher middle distillate yield and lower gas and naphtha yield [37]. AC catalysts have also been found to have a better ability to restrict the coke formation and show high activity for the removal of such impurities as sulfur and heavy metals during hydrocracking of heavy oil [32]. Even though no data are available in the literature, it can be suggested that AC as the catalyst is well suited to upgrade the heavy oil derived from MWP:

In conclusion, it is certainly possible to develop commercial processes based on pyrolysis–hydrocracking/cracking. But it must be noted that the viability of this two-stage conversion technique depends on process economics and future regulatory considerations.

2.3 CO-PROCESSING OF MWP

Another approach in liquefaction of MWP is co-processing which has a special importance from the viewpoint of feedstock recycling. Most co-processing studies have involved the hydrothermal cracking of single plastics or waste plastics with coal using HZSM-5 and the bifunctional (hydrotreating and hydrocracking) acidic catalysts. The results have shown good conversion for autoclave liquefaction of plastic/coal mixtures. However, there were also conflicting reports of whether co-processing led to better or worse conversions. Coal rank and type of plastics emerges as a significant characteristic, affecting its synergy with the various reaction parameters. Co-processing of coal and waste plastics is difficult, as neither the reaction conditions nor the catalyst can be tailored simultaneously for both materials. Moreover, it must be noted that, co-liquefaction of waste plastics with coal may be a promising process to develop an economically feasible process for coal liquefaction, since the waste plastics play the role of hydrogen donor for coal liquefaction.

A more interesting approach for co-processing is the conventional treatment of plastic with a heavy petroleum fraction blend in a refinery unit. The main advantage of this coprocessing method is that it utilizes existing processes within a refinery complex, resulting in reduced capital costs. Little research has focused on the co-processing of plastics with a feedstock of a refinery unit. Studies have been carried out with different plastics and refinery feeds.

Ng [39] evaluated conversion of HDPE blended with vacuum gasoil (VGO) to transportation fuels by catalytic cracking over an acidic catalyst (KOB-627). It has been shown that addition of HDPE increased the gasoline yields significantly when more than 10% plastics were dissolved in the VGO. In cracking of light cycle oil (LCO, containing 66.9 wt% aromatics) over a neutral catalyst (mesoporous silica), the addition of polyolefins (PE, 10 wt% and PP, 5 wt%) to the LCO showed a synergistic effect on the cracking of LCO and led to a remarkable decrease in the content of aromatics in the gasoline fraction and an increase in the content of olefins, paraffins and isoparaffins. It was stated that this result was a consequence of the high reactivity of radical intermediate compounds from polyolefin cracking and of their global hydrogenating contribution [40].

On the other hand, studies on hydrocracking of blends containing HDPE, LDPE and PP in HVGO over acidic catalysts showed that the effect of polymer on the cracking of HVGO changed, depending on the type of catalysts [41–43]. The presence of polyethylenes affected the cracking properties in hydrocracking over DHC-8 (a commercial hydrocracking catalyst). Over DHC-8, the liquids from PE/HVGO blends were less and waxy compounds were more than from VGO alone. However, the yields were similar for both blend and HVGO alone over HZSM-5. Although HZSM-5 showed a high cracking activity, it gave liquid products containing the highest amount of aromatic species and sulfur content. The studies on liquefaction of polyolefines in HVGO showed that the type of polymer and catalyst had a great effect on the product distribution of cracking/hydrocracking.

The principal limitation to co-processing is the need for important refining liquid streams which are necessary taking into account the limited amount of plastics that can be mixed, and the restricted use of chlorine and other hetereoatoms contained in the plastics that can negatively affect the refinery unit and catalyst.

In the case of waste polymer mixture, it is expected that impurities in the waste plastic mixture, as well as polymer type, have an effect on the hydrocracking process. In addition, the degradation of single polymers might be different from that of mixtures of polymers.

In conventional refinery processes utilized for the conversion of MWP into fuel, the presence of PVC in MWP might cause some problems such as poisoning of the catalyst, evolution of corrosive gases and products containing chlorine. For these reasons, chlorine has to be eliminated from the feed before processing. Preheating plastic mixtures at lower temperatures (300–350°C) is the conventional way of elimination of chlorine because the thermal stability of PVC is much lower than that of other polymers. Dechlorination of MWP in a heavy petroleum fraction is more demanding than dechlorination of MWP alone. The heavy petroleum fraction acts a solvent during dechlorination, preventing the blockage of gas line and decreasing energy requirement with improving heat transfer. It might be expected that the dechlorination step is not only responsible for elimination of chlorine, but also effects the properties of the blend which will be cracked/hydrocracked.

Table 8.4 The composition of MWP (wt. %)

HDPE	LDPE	PP	PVC	PS	PET	inerts
12	21	56	2	2	1	6

Table 8.5 Product distribution of hydrocracking of MWP/HVGO blend and HVGO

Reaction products (wt%)	Dechlorinated MWP/HVGO				HVGO			
	None	DHC-8	Co-AC	HZSM-5	None	DHC-8	Co-AC	HZSM-5
Reaction temperature at 425°C								
Gas[a]			28.3	31.4	47.2	55.2	18.5	27.6
Liquid			27.1	32.4	40.5	40.4	61.2	60.1
Wax			32.9	28.3	11.2	4.4	18.6	12.3
Coke			5.4	7.2	1.1	0	1.7	0
Undegraded MWP[b]			31.6	3.4				
Reaction temperature at 435°C								
Gas[a]	30.8	28.1	39.3	51.9	62.3	57.1	22.7	44.9
Liquid	50.2	34.2	37.3	20.1	30.1	34.1	60.8	40.5
Wax	16.5	34.0	21.2	18.9	7.0	8.5	14.3	14.2
Coke	0.9	1.0	1.5	8.6	0.5	0.3	2.2	0.4
Undegraded MWP[b]	8.0	13.6	0.4	2.6				
Reaction temperature at 450°C								
Gas[a]	48.7	35.9	45.9	68.3	73.4	61.0	49.9	58.8
Liquid	44.2	47.3	36.0	12.9	24.4	29.4	34.1	19.1
Wax	6.6	15.9	17.5	15.5	2.2	7.1	13.0	21.4
Coke	0.5	0.9	0.5	2.9	0	2.5	3.0	0.7
Undegraded MWP[b]			0.4	1.9				

[a] Calculated from mass balance [b] Based on MWP charge

Liquefaction of MWP in a refinery stream has been studied at a laboratory level [44]. Thus, MWP containing mainly polyolefines (Table 8.4) has been added into the feed of a hydrocracking plant, heavy vacuum gas oil (HVGO) and then the blend containing 20 wt% MWP has been converted to fuels by two-step processing. In the first step, dechlorination has been carried out by preheating at 350°C (dechlorination step) in a semi-batch reactor yielding a slurry of 91.2 wt% and a liquid 2.1 wt%. Then the dechlorinated mixture containing 120 ppm chlorine has been catalytically hydrocracked at temperatures between 425 and 450°C. The temperatures have been chosen on the basis of the hydrocracking process in the refinery. The catalysts used were HZSM-5, DHC-8 (commercial hydrocracking catalyst consisting of non-noble hydrogenation metals on a silica–alumina base) and a cobalt-loaded activated carbon catalyst, Co-AC. The product distribution from hydrocracking of MWP/HVGO blend in comparison to VGO alone is given in Table 8.5.

Both the temperature and the type of catalyst effected the product distribution. Different trends in product distribution were observed with the catalyst as the reaction temperature increased. As expected, HZSM-5 showed a high cracking activity, leading to more gas product formation. There was a continuous increase in gas yield by increasing temperature whereas liquid yield decreased dramatically. In contrast to the liquid yield, the amount of wax did not decrease at temperatures above 435°C. This shows that at higher temperature, further cracking reactions occurred, leading to gas formation and waxy compounds. However, hydrocracking of blends containing individual polymer (LDPE/HVGO, HDPE/HVGO, PP/HVGO) led to a greater amount of liquid and a smaller amount of wax being obtained than from the MWP/HVGO blend. This may be due to two reasons. One is that the degradation route of the individual polymer is different from that in the polymer mixture. The other cause may be the impurities in MWP, because the activity of HZSM-5 was effected by impurities. In contrast to HZSM-5, DHC-8 has shown catalytic activity at temperatures above 425°C. The increase in temperature led to the production of more liquid and the cracking of waxy compounds. The degradation route is as follows:

$$\text{Wax} \longrightarrow \text{Liquid} \longrightarrow \text{Gas}$$

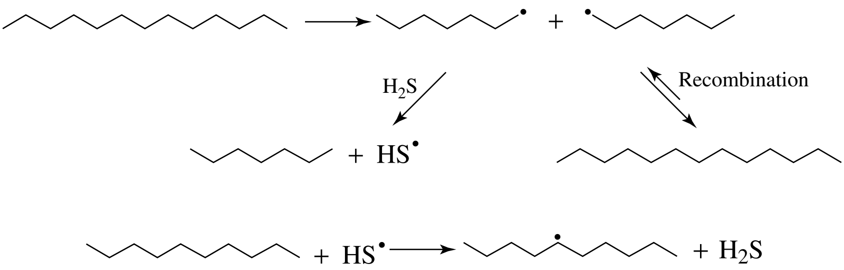
The studies on the hydrocracking of blends containing individual polymer showed that the catalytic activity of DHC-8 varied with the polymer type in the blend. Although the blends of LDPE/HVGO and PP/HVGO liquefied easily at 425°C over DHC-8, the HDPE/HVGO DHC-8 showed sufficient cracking activity only at 450°C. These results suggest that HDPE in blends, even at very low concentrations, such as 2.4%, plays an important role in controlling the rate of cracking of blends in the absence of a sufficient temperature and of catalytic activity. DHC-8 and HZSM-5 showed substantially different activities in coprocessing of HVGO with polymers due to the differences in their acidity. DHC-8 is an amorphous silica–alumina (ASA). It is known that the activity in ASA is attributed to both Lewis and Brönsted acid sites. The strongest sites are not the most favorable sites (in hydrocracking catalyst). The most favorable sites are the weak ones that are sufficiently strong to accomplish the desired chemical reactions. However, HZSM-5 has the stronger acid sites and is more effective in the degradation of polymer. Although acidic catalysts have good performance in conversion of pure polymers to liquid and gaseous fuels, the impurities in wastes are poisonous for acidic catalysts and/or lead to easy deactivation of catalyst in the case of catalytic liquefaction of waste plastics. This is because the basic nitrogen which occurs in waste plastics poisons the active site of acidic catalysts. A cobalt-loaded active carbon catalyst (neutral catalyst) has shown a better cracking ability than commercial DHC-8 catalyst in co-processing of MWP. Upon increasing the temperature, formation of gases increased. The yields of liquid and gas products increased, depending on the increase in the cracking of waxy compounds and waste plastics, when the temperature increased from 425 to 435°C. A further increase in the temperature led to cracking of liquids to gases.

In cracking over a metal-loaded activated carbon catalyst, hydrocarbons are cracked via a radical mechanism as in thermal cracking. However, cracking over Co-AC gave a very different product distribution when compared with thermal cracking. At 425°C, the liquid product is not generally obtained by thermal hydrocracking, whereas hydrocracking over Co-AC produced liquid product. Over Co-AC, the free radicals on the carbon surface initiate the cracking reaction by abstraction of hydrogen in hydrocarbons as follows.

$$\mathrm{R{-}CH_2{-}CH_2{-}CH_2{-}R + {}^{\bullet}AC \longrightarrow R{-}CH_2{-}{}^{\bullet}CH{-}CH_2{-}R + H{:}AC}$$

On the other hand, in radical degradations the concentration of free radicals can be controlled by H_2S [45]. In this study, H_2S is already present because the HVGO contains sulfur under hydrocracking conditions. In thermal hydrocracking, the hydrogen of H_2S is abstracted by the hydrocarbon radical to form a stable hydrocarbon and $HS^{\bullet}$. Subsequently the $HS^{\bullet}$ abstracts a hydrogen from the hydrocarbon. Thus, the lifetime of hydrocarbon radicals can not be reduced. However, in the presence of M-AC catalyst, $H^{\bullet}$ and $HS^{\bullet}$ are formed from H_2S. $HS^{\bullet}$ abstracts a hydrogen from the hydrocarbon or is stabilized on the supported metal catalyst by hydrogenation. These explanations can be shown schematically as follows.

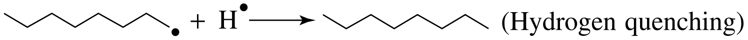
In the thermal case:



In the presence of Co-AC:

$$H_2S \xrightarrow{\text{Metal}} H^{\bullet} + HS^{\bullet}$$

$$HS^{\bullet} + H_2 \xrightarrow{\text{Metal}} H_2S + H^{\bullet}$$



In hydrocracking of HVGO alone the reason for decreased gas formation over Co-AC catalyst (compared with a thermal run) may be the fact that the activated carbon leads to the formation of more $H^{\bullet}$ or $HS^{\bullet}$ which terminates the radical degradation pathyways. However, in the case of a blend, in the absence of catalytic activity, hydrocarbon quenching (with radicals from derivated plastics) may be more pronounced than hydrogen quenching (with $H^{\bullet}$).

As in thermal runs, due to reaction between primary degradation products of HVGO and MWP, DHC-8 showed a lower cracking activity than that of hydrocracking of HVGO itself in the presence of DHC-8. This result is consistent with the results obtained from hydrocracking of blends containing single plastics. In contrast, in the presence of HZSM-5, the addition of MWP to VGO decreased the liquid yield whereas it increased the gas yield. This shows that presence of MWP led to overcracking reactions.

Over Co-AC, the effect of MWP on cracking properties of HVGO varied with temperature. At 425 and 435°C, similar effects were observed to those observed over HZSM-5; production of more gas and less liquid. It is a most important point that similar product distribution has been obtained from hydrocracking of HVGO and MWP/HVGO over Co-AC at 450°C.

The catalyst type also affects the quality of liquid fuel. The changes in the composition of liquids with temperature depend on the type of catalyst. The amount of naphtha fraction in the liquid fuel increased with temperature up to 435°C and then decreased (over

HZSM-5 due to overcracking of naphtha) or remained constant (over Co-AC and DHC-8). In hydrocracking of MWP/HVGO blend at 435°C, HZSM-5 produced liquid containing 70% naphtha (boiling point $<$ 172°C), 17% middle distillate (bp 172–232°C), whereas in the presence of DHC-8, the naphtha and middle distillate were 46 and 19% respectively.

At the same temperature of 435°C, Co-AC gave liquid containing more light compounds than DHC-8; 55% naphtha and 18% middle distillate. As expected, the liquid derived from thermal runs were heavier than that of catalytic runs at all temperatures.

Although in the case of hydrocracking of HVGO alone, DHC-8 commercial hydrocracking catalyst gave the lightest product, it did not give the best result for MWP/HVGO blend. It may be noted that in the presence of Co-AC, the liquids from MWP/VGO blend had lighter compounds than that from HVGO.

It is noteworthy that, although HZSM-5 is more active in hydrocracking of the MWP/HVGO blend, it favored aromatization reactions and inhibits desulfurization, even in the presence of H_2. The liquid fuel derived by hydrocracking over HZSM-5 at 435°C had the highest amount of sulfur (2.1 wt%) and aromatic compounds (28.0 wt%). In contrast, the aromatic content of liquids was 4.0 and 6 wt% for DHC-8 and Co-AC, respectively. As expected the liquid from DHC-8 contained the lowest sulfur amount (1.009 wt%) since it has been used in refinery for hydrocracking of HVGO. However, it showed a greater desulfurization effect in the hydrocracking of blends containing individual pure polymer. It may be concluded that impurities in wastes affected the HDS activity of DHC-8. Co-AC catalyst also had a hydrodesulfurization effect, produced a liquid containing 1.21 wt% sulfur. In addition, it should be noted that in the presence of Co-AC the liquids from blends containing both waste polymer and pure polymer had a similar sulfur amount.

3 CONCLUSIONS

As a result, MWP sorted from municipal solid wastes can be processed in a refinery, which has a dechlorination unit installed prior to the hydrocracking unit. Even though commercial catalysts showed satisfactory performance at high temperatures, neutral catalysts based on activated carbon can also be utilized for this purpose.

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9

Kinetic Model of the Chemical and Catalytic Recycling of Waste Polyethylene into Fuels

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1 INTRODUCTION

There are several physical and chemical methods to investigate the degradation of polymers, from methods without change of physical and chemical properties of polymers to degradation processes for the recovery of monomers. The initiation of degradation may be considerably different: heat (thermal degradation), heat and catalyst (thermocatalytic degradation), oxygen (oxidative degradation), heat and oxygen (thermo-oxidative degradation), radiation (photochemical degradation), radiation and oxygen (photo-oxidative degradation), chemicals (chemical degradation), microorganisms or enzymes (biodegradation or bioerosion), etc.

The common characteristic of these methods is that they cause irreversible changes in the structure of polymers. The decomposition of the framework of polymers results in decreasing molecular weight and significant changes of physical and chemical properties.

The widely known and thoroughly studied methods are thermal and thermocatalytic degradation, which are referred to in the literature as chemical recycling. Chemical recycling and chemical degradation are not the same, because chemical degradation means degradations caused by chemicals (acids, solvents, alkalis, etc.)

The study of chemical recycling and degradation of waste plastics has developed since the 1980s. During chemical recycling hydrocarbon macromolecules of polymers break down into smaller molecules owing to thermal or thermal and catalytic effects. According to researchers, the possibility of further utilization of cracked products is their fuel-like use; therefore the objective of researches is the production of hydrocarbons with similar properties to refinery streams (e.g. gasoline, kerosene, diesel oil, etc.). For this reason the

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formation of volatile products (gases, liquids) with suitable yield is a key issue during investigations.

There are some advantages of the application of catalysts, on the other hand it may cause difficulties (feeding of catalysts into the reactor, activity loss, etc.). Usually batch experiments were carried out on laboratory scale (1–5 g) using one or two types of polymers, which were virgin and not waste polymers, therefore the confrontation with problems of greater amounts of catalysts is probable in the immediate future.

Many polymers with different structure and properties may be used as raw materials in degradation (HDPE, LDPE, PP, PS, PVC, PET, PA, PUR, etc.) although polyolefins (HDPE, LDPE, PP) and polystyrene (PS) have the best properties from the point of view of their further utilization. Several reports have described the thermal and catalytic cracking of waste polymers. Two types of polymers have been widely investigated: polyethylene and polypropylene, because they represent 60–65% of all plastic wastes. The degradation of plastics means heating to high temperatures where macromolecules break into smaller fragments. Valuable mixtures of hydrocarbons (gas, liquid and residue) are obtained [1–6].

The structure of the hydrocarbons produced can be modified by the use of catalyst. Catalytic cracking consumes less energy than the noncatalytic process and results in formation of more branch-chain hydrocarbons. On the other hand the addition of the catalyst can be troublesome, and the catalyst accumulates in the residue or coke. There are two ways to contact the melted polymer and catalysts: the polymer and catalyst can be mixed first, then melted, or the molten plastics can be fed continuously over a fluidized catalyst bed. The usually employed catalysts are US-Y, and H-ZSM-5. Catalyst activity and product structure have been reported [7–11]. It was found that the H-ZSM-5 and FCC catalysts provided the best possibility to yield hydrocarbons in the boiling range of gasoline.

2 REACTION KINETICS OF DEGRADATION

Description of decomposition reactions during degradation of plastics is quite difficult, because they are very complex. Furthermore there are considerable differences between thermal degradation of waste plastics in the absence and presence of catalysts, but the type of the reactor or the amount of plastics is also important. Degradation in the presence of catalysts is called thermocatalytic degradation. Cracking experiments are done in batch reactors in 95% of cases [1–11] and within it the thermogravimetric analysis connected with different techniques (e.g. TG, DTG, DSC, TG-MS, DTG-MS, etc.) is predominant [12–17]. Only a few researchers have investigated the cracking of waste polymers under continuous or semi-continuous conditions [18–21]. One reason for this is that considerable amounts of wastes are needed for continuous cracking and difficulties emerge caused by the geometry of the reactor and greater amounts of materials (e.g. circulation, heat transfer, coking, fouling, etc.) or the feeding of catalysts, their separation from products and regeneration.

Some kinetic models for thermal or catalytic polymer degradation have been proposed. The commonly used approach is first-order kinetics to investigate the characteristics of degradation (Equation 9.1). In this approach at first the weight loss curve of polymers during the decomposition is determined, and overall rate constants are calculated

[12, 14–16, 22–25]. The objectives of experiments are the determination of the apparent activation energies and other reaction kinetic parameters (reaction rate, preexponential constant, etc.) of degradation resulting volatile products (gases and liquids). Besides the development of kinetic models the prediction of the yields or main properties of products in the knowledge of properties of the raw material are also important. The principal problem in this case is the derivation of reaction rate constant because some factors significantly affect the conversion of degradation (physical, geometrical, steric, etc.). Usually a constant value of reaction rate is postulated and first-order kinetic equation together with the Arrhenius equation is used. Relations become more difficult when considering autocatalytic reactions. Some correlations exist to calculate reaction kinetic parameters under dynamic circumstances [26, 27]. The activation energy and the preexponential constant are determined from the logarithmic form of the Arrhenius equation (Equation 9.2.).

$$-\frac{\mathrm{d}m}{\mathrm{d}t} = km^n \tag{9.1}$$

$$k = A_0 e^{-\frac{E}{RT}} \tag{9.2}$$

where m_0 is the weight of sample, n is the reaction order, k is the reaction rate coefficient, m is the weight of residue, t is the time of degradation, E is the activation energy and A_0 is the preexponential constant.

Relations might be simplified by using thermogravimetric and connected methods, but a new parameter is to be introduced. This new parameter is the heating rate. Table 9.1 shows some of the approaches used for the determination of kinetic parameters [28–30].

When comparing the equations in Table 9.1, it is found that the equations of Flynn–Wall, Horowitz–Metger and Friedmann gave excellent correlation in the case of degradation of polypropylene [29, 30]. Others created a software to calculate the reaction kinetic parameters using the first-order kinetic equation based on these equations. Key parameters were calculated with the minimization of differences between calculated and experimental results obtained directly by a thermogravimetric apparatus [24]. Good correlation between data was observed in case of HDPE and PS by using this software.

Table 9.1 Summary of approaches for the determination of kinetic parameters

Method	Equation
Flynn–Wall	$\Delta \ln \beta = -1052 \left(\frac{E_a}{R}\right) \Delta \left(\frac{1}{T}\right)$
Friedmann	$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = \ln A + n \ln(1-\alpha) + \min(\alpha) - \left(\frac{E_a}{RT}\right)$
Kissinger	$\ln\left(\frac{\beta}{T^2}\right) = -\frac{E}{RT} + \left[\ln\left(\frac{AR}{E}\right) - \ln F(x)\right]$
Ozarawa	$\ln \beta = -0.4567\frac{E}{RT} + \left(\log\frac{AE}{R} - \log F(x) - 2.315\right)$
Horowitz–Metger	$\ln\left[\ln\left(\frac{1}{1-\alpha}\right)\right] = \frac{E_a \Theta}{RT_s^2}$

The main problem in case of thermocatalytic cracking of polymers is the activity loss of catalysts; therefore first-order kinetics is applicable only with some simplifications in thermocatalytic cases. On the other hand there is a relation modelling the fluid catalytic cracking taking into consideration the catalyst deactivation in refineries [31]:

$$\eta = \exp[-\alpha C(c)] \tag{9.3}$$

where η is the activation loss of catalyst, $C(c)$ is the coking of catalyst and α is a constant depending on the type of catalyst.

Equation (9.3) was used to model the thermocatalytic degradation of waste polyethylene and polypropylene [22]. In this case researchers had to calculate η for each catalyst. On the other hand it is complicated; therefore researchers disregard the change of reaction rate and order caused by deactivation of catalysts in most experiments. The reaction rates and other reaction kinetic parameters are given in Table 9.2 [32].

There are also some empirical equations for describing the yields of products formed in the cracking reactions of polymers. One of them is the Atkinson and McCaffrey kinetic model, which derives the weight loss of polymer for their initial degree of polymerization, weight of sample and reaction rate. As a matter of fact the reaction rate constant is calculated by using a first-order kinetic equation [33, 34].

The temperature significantly affects the conversion of thermocatalytic degradation besides the characteristic of catalysts. The time–temperature superposition describes the dependence of reaction rate from temperature. The conversion can be increased both with degradation temperature and time. It means that the cracking time which is needed to achieve the same degree of conversion decreases with increasing temperature. The shift factor is the quotient of cracking times at different temperatures or the quotient of temperatures at different cracking times. The value of the shift factor is affected by the characteristics of the polymer and by the cracking conditions. There are two methods to derive the shift factors: the Arrhenius equation and the Williams–Landel–Ferry (WLF) equation. J.H. Chan and S.T. Balke calculated the value of shift factors in case of polypropylene degradation [35]. It was found that the product of reaction rate coefficients and cracking times at different temperatures is nearly constant. The shift factors and constants of the WLF equations can be calculated by the use of these similarities.

2.1 REACTION MECHANISM

As a matter of fact the cracking of C–C bonds takes place as the result of competition between reactions initiated by thermal and catalytic effects of thermocatalytic degradation. It means that thermal and catalytic reactions do not separate from each other, therefore in discussing thermocatalytic cracking of polymers one has to touch upon both the thermal and catalytic degradation reactions. It is well known, that the thermal (noncatalytic) cracking of plastics occurs by a radical mechanism, wherein the initiating radicals are formed by the effect of heat. Catalytic cracking, on the other hand, generally proceeds though carbenium ions, which are considered to be produced by the abstraction of hydride ion (Lewis acid) from the polymer or the addition of proton (Brösted acid) to the polymer macromolecule in the initial reaction step. Fragments formed in the first cracking reactions cracked further into lower-molecular-weight hydrocarbons on the active sites of the

Table 9.2 Reaction kinetic properties of thermal cracking of different polymers

Kinetic model	Equation	E_a(kJ/mol)	n	A (min^{-1})	Yield coefficient
$\mathrm{HDPE}\xrightarrow{k_1}\mathrm{V}+\mathrm{R}$	$\frac{\mathrm{d}[HDPE]}{\mathrm{d}t}=-A_1e^{\frac{-E_{a1}}{RT}}[\mathrm{HDPE}]^{n_1}$	250	0.65	1.71×10^{17}	
$\alpha_1\mathrm{LDPE}_1\xrightarrow{k_1}\mathrm{V}_1+\mathrm{R}$	$\frac{\mathrm{d}[LDPE_1]}{\mathrm{d}t}=-A_1e^{\frac{-E_{a1}}{RT}}[\mathrm{LDPE}_1]^{n_1}$	$E_{a1}=120$	$n_1=1.40$	$\mathrm{A}_1=1.34\times10^9$	$\alpha_1=0.10$
$\alpha_2\mathrm{LDPE}_2\xrightarrow{k_2}\mathrm{V}_2+\mathrm{R}_2$	$\frac{\mathrm{d}[\mathrm{LDPE}_2]}{\mathrm{d}t}=-A_2e^{\frac{-E_{a2}}{RT}}[\mathrm{LDPE}_2]^{n_2}$	$E_{a2}=220$	$n_2=0.60$	$\mathrm{A}_2=1.47\times10^{15}$	$\alpha_2=0.90$
$\mathrm{PP}\xrightarrow{k_1}\mathrm{V}+\mathrm{R}$	$\frac{\mathrm{d}[\mathrm{PP}]}{\mathrm{d}t}=-A_1e^{\frac{-E_{a1}}{RT}}[\mathrm{PP}]^{n_1}$	125	0.40	2.04×10^8	
$\alpha_1\mathrm{PS}_1\xrightarrow{k_1}\mathrm{V}_2+\mathrm{R}_2$	$\frac{\mathrm{d}[PS_1]}{\mathrm{d}t}=-A_1e^{\frac{-E_{a1}}{RT}}[\mathrm{PS}_1]^{n_1}$	$E_{a1}=120$	$n_1=1.60$	$A_1=1.06\times10^8$	$\alpha_1=0.10$
$\alpha_2\mathrm{PS}_2\xrightarrow{k_2}\mathrm{V}_2+\mathrm{R}_2$	$\frac{\mathrm{d}[\mathrm{PS}_2]}{\mathrm{d}t}=-A_2e^{\frac{-E_{a2}}{RT}}[\mathrm{PS}_2]^{n_1}$	$E_{a2}=185$	$n_2=0.76$	$A_2=2.32\times10^{13}$	$\alpha_2=0.90$
$\mathrm{PVC}\xrightarrow{k_1}a\mathrm{HCl}+b\mathrm{I}$	$\frac{\mathrm{d}[\mathrm{PVC}]}{\mathrm{d}t}=-A_1e^{\frac{-E_{a1}}{RT}}[\mathrm{PVC}]^{n_1}$	$E_{a1}=198$	$n_1=1.04$	$\mathrm{A}_1=3.57\times10^{18}$	$b=0.52$
$b\mathrm{I}\xrightarrow{k_2}c\mathrm{V}_1+e\mathrm{R}_1$	$\frac{\mathrm{d}[I]}{\mathrm{d}t}=b(A_1e^{\frac{-E_{a1}}{RT}}[\mathrm{PVC}]^{n_1}-A_2e^{\frac{-E_{a2}}{RT}}[I]^{n_2}$	$E_{a2}=143$	$n_2=1.15$	$\mathrm{A}_2=9.95\times10^{10}$	$e=0.36$
$e\mathrm{R}_1\xrightarrow{k_3}f\mathrm{V}_2+g\mathrm{R}_2$	$\frac{\mathrm{d}[\mathrm{R}_1]}{\mathrm{d}t}=e(A_2e^{\frac{-E_{a2}}{RT}}[I]^{n_2}-A_3e^{\frac{-E_{a3}}{RT}}[\mathrm{SR}_1]^{n_3}$	$E_{a3}=243$	$n_3=1.58$	$\mathrm{A}_3=5.77\times10^{16}$	$g=0.06$
	$\frac{\mathrm{d}[\mathrm{R}_2]}{\mathrm{d}t}=g(A_3e^{\frac{-E_{a3}}{RT}}[\mathrm{SR}_1]^{n_3}$				

V volatile products; I intermediates; SR_1 primary products; SR_2 secondary products catalyst. Unstable primary fragments are cracked in further decomposition reactions. The following elemental reactions take place both in thermal and thermo-catalytic cases:

a) initiation
b) formation of secondary radicals
  - depolymerization, formation of monomers;
  - favourable and unfavourable hydrogen transfer reactions;
  - intermolecular hydrogen transfer (formation of paraffins and dienes);
  - isomerization via vinyl groups;
c) termination by disproportionation or recombination of radicals.

In the presence of catalysts, heterogeneous catalytic cracking occurs on the surface interface of the melted polymer and solid catalysts. The main steps of reactions are as follows: diffusion on the surface of catalyst, adsorption on the catalyst, chemical reaction, desorption from the catalyst, diffusion to the liquid phase. The reaction rate of catalytic reactions is always determined by the slowest elementary reaction. The dominant rate controller elementary reactions are the linking of the polymer to the active site of catalyst. But the selectivity of catalysts on raw materials and products might be important. The selectivity is affected by molecular size and shape of raw materials, intermediates and products [36].

2.1.1 Initiation

The mechanism of initiation is partly radical in thermocatalytic degradation. The cracking of C–C bonds occurs by homolytic cracking of C–C bonds, at regions with structural faults or distortion of the electron cloud.

Catalytic cracking generally proceeds through a carbenium ion, which is considered to occur by the abstraction of hydride ion from polymer or the addition of proton on the polymer macromolecule in the initial step of the reaction (Figure 9.1).

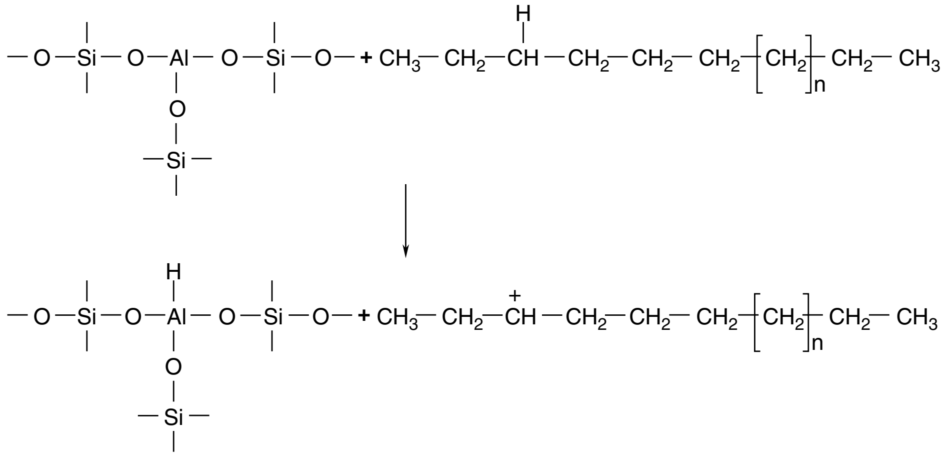


Figure 9.1 Initiation in thermocatalytic cracking

The framework of waste polymers might be cracked at C–C bonds at low temperature and both at C–C and C–H bonds at high temperature. The cracking of C–C bonds has lower energy consumption, than that of C–H, because it has lower bond energy, by 40–60 kJ/mol, than the C–H bond. The likelihood of cracking of a carbon chain is significantly affected by its substituents. In the case of polypropylene this means that the lower thermal stability is the consequence of methyl groups linked to the main carbon chain. Methyl groups have a positive inductive effect, but among others halogens and phenyl groups have the same property; e.g. the high yield of monomer in the case of degradation of polystyrene is attributed to this effect.

Table 9.3 shows the activation energies of elemental reactions in the case of polymer degradation. It is noticeable the initiating reactions have the highest potential barrier. This potential barrier can be decreased by the use of catalysts and it results a decrease of 50–100 kJ/mol in activation energy [37, 38, 39].

Tables 9.4 and 9.5 show some examples of thermal and thermocatalytic cracking on laboratory scale.

In the presence of catalysts the beginning of cracking of C–C bonds of macromolecules of polymer occurs at a lower temperature than in the absence of catalysts. This phenomenon could be explained by the acidic sites of the catalysts, because of to the considerably greater number of unstable molecular fragments formed at lower temperature in the presence of catalysts. Volatile products are formed from polymers with suitable yields only above 450°C without catalysts, but at 300–400°C using catalysts. On the other hand some noncatalytic cracking takes place at 400–450°C [37, 39, 41] because

Table 9.3 Activation energies of elementary steps in polymer degradation

Elementary steps	Activation energy (kJ/mol)
Initiation	284–336
Depropagation	21–77
Termination by disproportionation or recombination	4–10
Diffusion in molten state	27
Diffusion in solid state	41

Table 9.4 Some laboratory experiments of thermal pyrolysis

Investigator	Polymer	Reactor	Temperature (°C)	Products
K. Murata *et al.* [39]	HDPE, PP, PS	Continuous flow stirred reactor	350–450	Gas, oil
R. Aguado *et al.* [40]	PS	Conical spouted bed reactor	500–600	Gas, monomer
T. Moriya *et al.* [41]	HDPE	Bomb-type autoclave	400–425	Gas, oil
A. Karaduman *et al.* [42]	PS	Free-wall reactor	825	Aromatics
H. Bockhorn *et al.* [43]	HDPE, PP	Closed loop-type reactor	410–480	Gas, oil
W. Kaminsky *et al.* [44]	Mixed waste	Fluidized-bed reactor	600–750	Gas, oil, aromatics
N. Miskolczi *et al.* [45]	Mixed waste	Tube reactor	500–550	Gas, oil, aromatics
F.J. Mastral *et al.* [46]	HDPE	Fluidized-bed reactor	640–850	Gas, wax, oil

Table 9.5 Some laboratory experiment on catalytic pyrolysis

Investigator	Polymer	Experimental set-up	Catalyst concentration (%)	Catalyst
A. Marcilla *et al.* [15]	LLDPE, LDPE HDPE	Thermogravimetric apparatus with an initial sample mass 4–25 mg and a heating rate of 10 and 40°C/min in nitrogen atmosphere	2–9	MCM-41
Z.S. Seddegi *et al.* [7]	HDPE	The reactor containing 3 g of polymer was connected to a liquid condenser and gas collection bag. Gases and liquid was analyzed with GC	10–16	MCM-41
J. Aguado *et al.* [47]	LDPE	Screw kiln reactor with two furnaces (2 × 52 cm) and 250 g of polymer at 300°C under nitrogen atmosphere using 3.0–15.0 m^3/h	2	Al-MCM-41
P.A. Jalil *et al.* [5]	HDPE	Glass batch reactor under atmospheric condition. 3 g of HDPE pellets were used	3 and 6	MCM-41
R. van Grieken *et al.* [9]	LDPE	The degradation of 50 g of plastic was carried out in a batch reactor provided with a helicoidal stirrer at 120 rpm under nitrogen atmosphere		USY zeolite, activated carbon, silica–alumina, MCM-41, HZSM-5, Pd charcoal
S.Y. Kim *et al.* [3]	PS	Batch stirred tank reactor made of pyrex glass. A mixture of 100.0 g PS and 1 g catalyst was loaded inside the reactor	1	Clinoptilolite, HZSM-5, silica–alumina
E.-Y. Hwang *et al.* [11]	PP	Semi-batch reactor with nitrogen flow rate of 30 ml/min. A mixture of 3.0 g PS and 0.3 g catalyst was loaded inside a Pyrex vessel	10	Different clinoptilolites
G. de la Puente *et al.* [48]	LDPE	Riser simulator reactor	6.5	Equilibrium Engelhard FCC catalyst ASA
S. Karagöz *et al.* [49]	80% Vacuum Gas Oil and 20% HDPE	A 100 ml stainless steel shrank type batch autoclave was used	1	DHC-8 hydrocracking catalyst HZSM-5
S. Ali *et al.* [21]	HDPE	Fluidized-bed reactor under N_2	66.6	ZSM-5, US-Y, ASA, Fresh commercial FCC catalyst, Equilibrium Engelhard FCC catalyst

Table 9.5 (*continued*)

Investigator	Polymer	Experimental set-up	Catalyst concentration (%)	Catalyst
Y.-H. Seo *et al.* [5]	HDPE	The reactor was a 1.1 L round stainless steel bottle placed in a furnace	5	ZSM-5 (powder) Y-zeolite (powder) Y-zeolite (pellet) Mordenite (pellet) Silica–alumina (powder) Alumina (powder)
P.N. Sharrat *et al.* [19]	HDPE	Fluidized-bed reactor using nitrogen	40	HZSM-5
K. Takuma *et al.* [36]	LDPE	A fixed-bed tubular flow reactor system was used in helium atmosphere	10	H-gallosilicate HZSM-5
P. Carniti *et al.* [50]	PP	Thermogravimetric analysis		SiO_2, silica–magnesia, silica–titanate, mordenite, SALA, SAHA
Y. Sakata *et al.* [8]	HPDE, LDPE, PP, PET, PVC	Flow reactor under semi-batch conditions. The degraded products of plastics are passed through a fixed bed of catalyst	10	Silica–alumina, ZSM-5, KFS-16B
T. Masuda *et al.* [4]	HDPE-derived heavy oil	A fixed-bed type reactor	10	Ni-REY
J.-S- Kim *et al.* [3]	PS	A batch stirred tank reactor made of pyrex glass was used with 200 rpm stirring. 10 g polymer was cracked	1	Al_2O_3, Fe_2O_3, Fe/Al_2O_3, $Fe\text{-}K/Al_2O_3$, $Fe\text{-}Ba/Al_2O_3$, $Fe\text{-}Zn/Al_2O_3$, $Fe\text{-}Mg/Al_2O_3$
Uemichi *et al.* [21]	PE, PP	Flow reactor under nitrogen		Silica–alumina, activated carbon, metal-supported silica-alumina

the preferred compounds are aliphatic ones. It is well known that above 450–460°C the possibility of reactions of cyclization, aromatization and polycondensation increases considerably and this results growing concentrations of naphthenes and aromatics [36]. If waste polyolefins (LDPE, HDPE, PP) have to be converted into aliphatic olefins and paraffins the low temperature is a key parameter.

Another important parameter is the catalyst concentration. Thermocatalytic cracking of HDPE and MDPE over HZSM-5 and Y-zeolite catalysts was carried out in a cycled-spheres reactor. It was found that the required temperature of cracking could be decreased by 2% using a low concentration of catalysts, and by 16–20% in the case of greater catalyst concentration because the reaction rate increased with increasing catalyst concentration [51]. Not only the catalyst concentration, but also the temperature is a parameter that determines properties. Increasing temperature increases the yields of volatile products. At higher temperature more C–C bonds are cracked in consequence of their lower thermal stability. On the other hand not only the yields of volatile products are increasing at higher temperature, but also the yield of coke.

Smaller differences were found between thermal and thermocatalytic degradations in respect to yields and structure of products at higher temperatures (450–500°C), than at lower temperatures (400–420°C).

The composition of feed polymers also has an important effect on the properties of products. In the experimental work of Miskolczi *et al.* commercial waste plastics from the packaging, electronic and automotive industry and the agriculture were used as raw materials. The samples contained high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), ethylene–propylene copolymer (EPC), polystyrene (PS), polyamide 6.6 (PA 6.6) and polyvinyl chloride (PVC).

The decomposition of waste polymer was carried out in the tube reactor, which consisted of three main parts: an extruder, a reactor and a separator (Figure 9.2).

Each cracking reactor had the same geometric properties (e.g. length, diameter, etc.), and they were kept at the same cracking temperature. Inside the reactor the polymers were melted and their carbon chain cracked into low-molecular-weight fragments. In a separator the hydrocarbons formed were separated into volatile products and residue. The cracking characteristics and the change of product properties were investigated depending on temperature, residence time and composition of feed polymer. Therefore different temperatures (500, 525, 550°C) and residence times (15, 18, 23, 30 min.) were used.

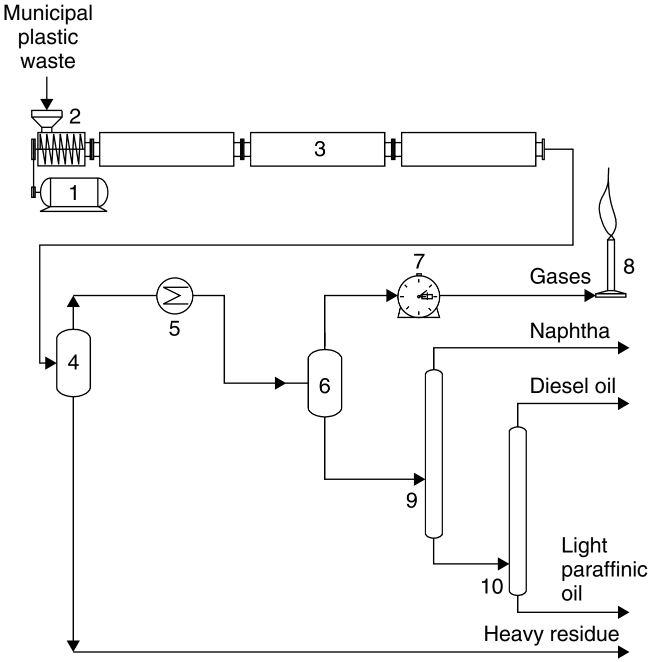


Figure 9.2 Cracking apparatus for cracking of municipal plastic waste: 1. motor; 2. extruder; 3. reactor; 4. separator; 5. condenser; 6. separator; 7. gas-flow meter; 8. flare; 9. atmospheric distillation; 10. vacuum distillation

The yields of valuable light products (mainly naphtha, diesel oil) increased both with residence time and temperature, which could be caused by the differences in the thermal stability of polymer chains. Moreover the yields of naphtha and diesel-oil-like fractions significantly increased with increasing concentration of PS in the feed MPW [54].

The composition of gases formed in cracking reactions of polymer blends contained mostly C_2, C_3 and C_4 hydrocarbons, which was the consequence of structure of polyethylenes and polypropylene. The concentration of olefins was higher than that of the paraffins of the same carbon number, because the possibility of β-scission reactions is greater than hydrogen transfer reactions in thermal degradation. The cracking parameters, apart from the composition of raw materials, did not significantly affect the composition of gaseous products. Calculated heating value of gases were 46–47 MJ/kg, which were quite high for gases used in energy generation (e.g. to provide the heat requirement of cracking with gas products of degradation).

Identifying of individual compounds in liquid products, especially branched molecules from polypropylene, is rather difficult, because of the cracking of polypropylene yields a great number of isomer compounds. The liquid product obtained by cracking of polyethylene consisted mostly of *n*-alkenes and *n*-alkanes, which were evenly distributed by carbon number, whereas the cracking of polystyrene yielded blends of aromatic compounds, styrene, ethylbenzene, benzene, toluene [45, 54].

By the separation of products obtained by thermal cracking of model municipal plastic wastes different fuel like fractions were separated: naphtha-like (N), diesel-like (DO) and light-paraffinic-oil-like fractions (LPO). The other properties of products obtained by cracking of MPW (20% HDPE, 20% LDPE, 10% EPC, 38% PP, 10% PS, 1% PA 6.6 and 1% PVC) are shown in Table 9.6.

The naphtha-like fraction contained C_5–C_{18} hydrocarbons, the main components being C_7–C_9 hydrocarbons, while that of C_9–C_{25} and C_{21}–C_{30} hydrocarbons in case of diesel-oil-like and light-paraffinic-oil-like fractions. The aromatic content was accumulated in the naphtha-like fraction and its concentration in others was below 1%. This is an advantageous property for further, fuel-like or petrochemical applications, because the aromatic content in white spirit does not cause problems, on the other hand the low aromatic and high branched hydrocarbon content in diesel gas oil is also an advantageous property. The concentration of aromatics increased both with cracking temperature, increasing residence time and PS content of the feed polymer blend. In the respect to aromatics the dominant concentration of ethylbenzene and styrene, the building elements of polystyrene, was found. It was significant that the concentration of aromatics in the product was significantly higher (20–27%) than the concentration of polystyrene in raw material (10%), because of lower activation energy of polystyrene than others. In the case of aliphatic compounds the triple sequence could be observed, which is typical of decomposition of polypropylene. Due to the polypropylene content of samples C_6, C_9, C_{12} hydrocarbons were present in the highest concentration. Each fraction had nearly half the olefin content. Due to aromatics in naphtha-like fraction their octane numbers were high. According to our previous experiences the formation of notable aromatics from polyolefins did not observe in this tube reactor system bellow 560°C [45, 54], because the reaction rate of cyclization and polycondensation, which resulted in aromatics, polycyclical compounds or coke, increased by leaps and bounds above 560°C.

Table 9.6 The composition and main properties of fuel-like products

Temperature (°C)	500			525			550		
Products	N	DO	LPO	N	DO	LPO	N	DO	LPO
Aliphatic olefin content (%)	37.9	45.3	40.6	38.8	45.5	41.9	37.1	44.2	41.7
Paraffin content (%)	44.3	54.7	59.4	43.6	54.9	58.1	42.5	54.8	58.3
Aromatic content (%)	17.8			17.6	0.6		20.4	1.0	
Benzene	0.8			0.7	0.0		0.9	0.1	
Toluene	0.3			0.3	0.1		0.9	0.1	
Ethylbenzene	2.7			2.2	0.2		2.1	0.3	
Styrene	12.2			13.0	0.1		14.5	0.2	
Xylenes	0.8			0.3	0.0		0.5	0.2	
Other	1.0			1.1	0.2		1.5	0.1	
Density (g/cm^3)	0.753	0.781	0.818	0.766	0.793	0.823	0.759	0.789	0.828
Flash point (°C)		98	217		98	219		94	216
Pour point (°C)	−47	−9	68	−43	−13	64	−49	−10	61
CFPP (°C)		−3			−4			−2	
RON	95			97			96		
MON	84			85			85		
Diesel index		69			68			69	
Cetane number		64			63			64	
Viscosity (mm^2/s, at 40°C)		4.4			4.3			4.3	
M (g/mol)	118	242		117	246		121	248	
C/H	6.0	6.1	6.2	6.1	6.2	6.2	6.0	6.1	6.1
Cl content (ppm)	47	239	216	45	240	217	52	253	224
S content (ppm)	14	11	15	9	11	11	10	10	14
N content (ppm)	218	458	761	224	440	759	222	462	771

The fraction of diesel-oil-like hydrocarbons had also a triple sequence and the main aliphatic compounds may be characterized with carbon numbers 12, 15, 18, 21, 24, 27. In contrast with the experimental results of naphtha diesel oil had considerably lower concentration of aromatics. In the case of each MPW sample its concentration was not more than 1%, because aromatics with lower boiling point stayed in the naphtha-like fraction. Similarly, as mentioned above, the diesel-oil-like fraction also had favourable properties for further fuel-like application. The olefin content was a bit smaller than in case of naphtha-like fractions, because cracking reaction resulting olefins (e.g. β-scission) produced hydrocarbons with a shorter length of carbon chain. Both cetane numbers and diesel indexes of products were high enough, while the CFPP was rather low.

It was found that the light-paraffinic-oil-like fractions had olefin and paraffin content without aromatics and naphthenes. These fractions are appeared in solid phase at room temperature due to their hydrocarbon structure with boiling point 250–380°C.

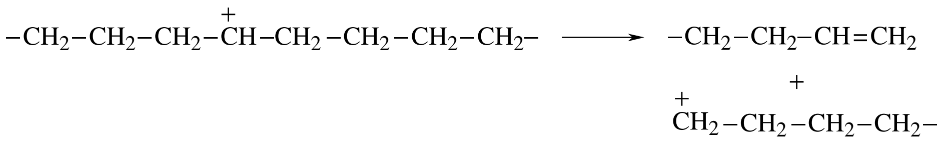
In the residue fractions aromatics were present as oligomers of styrene with higher carbon number, which could not distilled from melted polymers. These fractions were wax-like and their melting points were about 100°C, and they had the highest molecular weight, about 2500 g/mol, which decreases a bit with increasing concentration of polyamide and polyvinyl chloride waste plastics. This phenomenon could be attributed to the greater degradation of MPW, in consequence of initiating effect of radicals from, e.g. PVC on C–C bond cracking. Mechanical impurities and water content were not detected in theses fractions. Their calorific values were about 41.3 MJ/kg, which is quite high for application of these fractions for energy production.

Unfortunately the favourable properties of fractions were decreased in consequence of increasing concentration of PA 6.6 and PVC, because both the concentration of nitrogen and chlorine increased. This is a disadvantageous property for further utilization; therefore the removal of chlorine and nitrogen needs to be solved.

2.1.2 Formation of Secondary Unstable Compounds

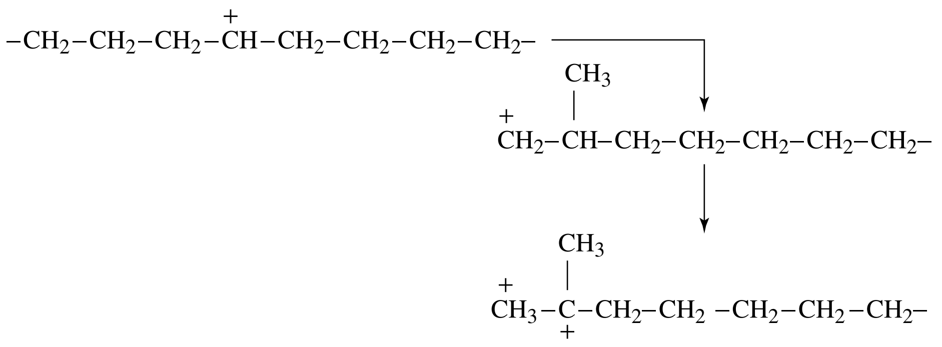
Unstable molecular fragments (radicals and ions) formed in the initiating reaction take part in further decomposition reactions with uncracked macromolecules of polymer or radicals and ions, resulting, among others, in secondary instable compounds of lower molecular weight. Generally the β-scission of primary radicals and ions results in oligomers and perhaps monomer. It was found that generally intermolecular hydrogen transfer reactions followed by β-scission take place, particularly at lower temperature. This reaction leads to formation of stable radicals and ions. At higher temperature the polymer chain cracked to a greater degree; therefore the primary unstable fragments react with alkanes. It is important to note that the probability of formation of aromatics by Diels–Alder reactions is greater. In these reactions, e.g. polyenes might be the precursors of benzene at higher temperature. In the olefins it is found that the double bond moves toward the end of the framework in the case of nonbranched structures, and that of tertiary carbons in of branched structures. Terminal double bonds turn into internal ones in the case of catalytic cracking, but this is not typical in thermal cracking.

(A) β-scission



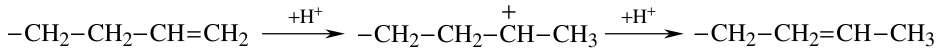
$$-CH_2-CH_2-CH_2-\overset{+}{C}H-CH_2-CH_2-CH_2-CH_2- \longrightarrow -CH_2-CH_2-CH=CH_2 + \overset{+}{C}H_2-CH_2-CH_2-CH_2-$$

(B) Isomerization of carbon framework



$$-CH_2-CH_2-CH_2-\overset{+}{C}H-CH_2-CH_2-CH_2-CH_2- \longrightarrow \overset{+}{C}H_2-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_2-CH_2-CH_2-CH_2-CH_2- \longrightarrow CH_3-\underset{+}{\overset{CH_3}{\overset{|}{C}}}-CH_2-CH_2-CH_2-CH_2-CH_2-$$

Isomerization of double bond



$$-CH_2-CH_2-CH=CH_2 \xrightarrow{+H^+} -CH_2-CH_2-\overset{+}{C}H-CH_3 \xrightarrow{+H^+} -CH_2-CH_2=CH-CH_3$$

(C) Hydrogen transfer reactions

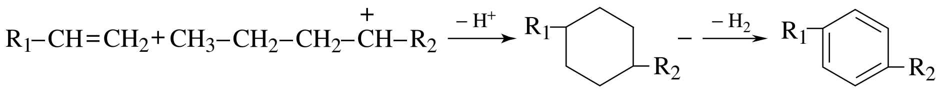
Intermolecular hydrogen transfer reactions

$$-CH_2-CH_2-CH_2^+ + -CH_2-CH_2-CH_2-CH_2- \longrightarrow \begin{array}{c} -CH_2-CH_2-CH_2- \\ + \\ -CH_2-CH_2-CH_2-CH_2^+ \end{array}$$

Intramolecular hydrogen transfer reactions

$$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2^+ \longrightarrow -CH_2-CH_2-CH_2-CH_2^+-CH_2-CH_2-CH_2-$$

(D) Cyclization and aromatization



Generally the concentration of iso-paraffins and olefins increased with decreasing temperature because the increase in further degradation of branched hydrocarbons is greater, than that of non-branched with increasing temperature. A similar phenomenon could be observed in the case of catalysts possessing a weak hydrogenation property accompanied by considerable acidity, because the olefin intermediates formed are isomerized in greater ratio on the acidic sites of catalysts. On the other hand not only the probability of isomerzation, but catalyst activity is decreases with decreasing of the acidity of catalysts.

2.1.3 Termination with Recombination or Disproportionation

Primary and secondary unstable molecular fragments formed in the cracking reactions could be stabilized in several ways. Recombination or disproportionation of unstable fragments is one simple way. As a result of recombination the molecular weight and branching of products might be significantly increased. It is important to note that both recombination and disproportionation are second-order reactions according to reaction kinetics.

Cyclization, aromatization or polycondensation are other ways of termination. Basically cyclic alkenes, alkenes, mono and polynuclear arenes or coke are formed in these reactions. Termination reactions are principally controlled by the properties of polymers and the temperature.

3 CATALYSTS

3.1 MONOFUNCTIONAL CATALYSTS

Monofunctional catalysts are catalysts having only the cracking property. Their structure may be crystalline or amorphous. Typical crystalline cracking catalysts are zeolites. Amorphous catalysts are alumina-silicate, magnesium-silicate, titanium-silicate, titanium-alumina-silicate, titanium−alumina, silica−alumina dispersed in alumina, alumina-borate and other oxides with acidic characteristic. Usually the acidity of catalysts and the C–C cracking function is increasing in the order Al_2O_3 <Al_2O_3-halogen<SiO_2-Al_2O_3 <zeolite.

Zeolites are natural or artificially produced microporous crystalline silica−alumina with ion-exchange, molecule filter or sorption properties. The production of artificial zeolites is carried out at controlled parameters (temperature, pressure, pH, etc.) by the reaction of stoichiometric silica-halides or tetrahydro-silicate and sodium-alumina. The other important parameter is the reaction time because the degree of crystallinity and pore structure of zeolites is basically affected by the reaction time. The structure of zeolite is composed of AlO_4 and SiO_4 tetrahedra which are connected with others through common oxygen atoms. In the final step of formation of catalyst cations without catalytic activity (tetrahedral and alkali-earth metals) have been replaced into elements possessing catalytic activity (lanthanum, cerium, neodinium, etc.). Nevertheless generally inactive cations are replaced by hydrogen ions. Cations are first changed with $NH_4{}^+$, which are transformed by the heat treatment.

Compared with amorphous catalysts, zeolite-based catalysts have the following advantages: better thermal stability, better selectivity in respect to volatile products and resistance to catalyst poisoning, greater acidity (resulting in greater cracking activity). In general ZSM-5, mordenite, X, Y, β, ω, mezoporous zeolites (e.g. MCM-41) were used.

The high surface area and porosity of catalysts play an important role in forming of the structure of cracked hydrocarbons. There are several properties of catalysts that are important to cracking (acidic sites of macropores, micropores). The catalyst selectivity is affected by the crystalline structure of zeolites and their characteristics.

Cracking of large macromolecules of polymers gets started at the amorphous acidic sites of the catalysts, then further cracking may proceed on the crystalline part of the catalysts if molecules have such small size that they can get into the pores of the catalyst. Strong acidity favours the cracking of heavier fractions. Acidity of catalysts is expressed by the ratio of Si/Al. The acidity increases with greater Si/Al. One method of increasing the acidity of the catalyst is to decrease of alumina content (e.g. with ammonium-hexafluoro-silicon or silicon-tetrachloride). Furthermore the pore size and ion-exchange property decreases while acidity and thermal stability increase with decreasing concentration of aluminium. Table 9.7 shows the main properties of some preferred polymer cracking catalysts.

As mentioned above the structure of zeolite and its pore size fundamentally determine the cracking property of the catalyst. The difference in activity of mordenite and zeolite catalysts (e.g. HZSM-5, Y-zeolite) is unambiguously due to variation in structure [1]. Mordenite contains pores of relatively large size (about 7 × 8 Å), while the pores of

Table 9.7 Physicochemical properties of the catalysts [9, 11, 47, 48]

Catalyst	HZSM-5	β-zeolite	FCC	MCM-41	SA	HY	HNZ
Commercial name	HZSM-5 catalyst	β-zeolite catalyst	Engelhard FCC catalyst	MCM-41 catalyst	Silica alumina	Y zeolite catalyst	Clinoptilolite catalyst
Si/Al	31	39	12.9	45	36	3	4.0
Pore size (nm)	0.55	0.64		2.4	2–12	0.74	
BET area (m^2/g)	361	613	151	1164	261	583	271
Surface area (m^2/g)	7	25		73		9	
Pore volume (cm^3/g)	0.18	0.35	78	0.79	0.97	0.26	0.107
Micropore volume (cm^3/g)	0.17	0.24				0.23	
Crystal size (μm)	3	0.20		0.2–2		0.50	
Acidity (mequiv of NH_3/g)	0.52	0.32		0.22	0.24	0.37	
$T_{max.}$ (°C)	470	422		338	302	300	

ZSM-5 are smaller (about 5 × 5 Å). The pore size basically determines the length of products. Generally the greater the pore size the longer the hydrocarbons formed. Not only the pore size of catalysts is important, but also their geometry. As is well known the acidity of catalysts mainly determinates the cracking behaviour of C–C bonds and the probability of β-scission. However, the amorphous part of catalysts fosters the isomerization and aromatization reactions. The high yield of gases observed with the use of amorphous silica–alumina without 3D structural pores is explained with its great acidity. On the other hand the low coking is the consequence of the catalyst surface which is free from complicated pore structure on which the coke can be deposited with difficulty.

It is important to note that the reaction rate of thermocatalytic cracking decreases with reaction time. In general it is the consequence of the blocking of active sites of catalysts by coking.

The ZSM-5 catalyst shows quite high selectivity in the formation of paraffins and olefins and branched hydrocarbons, while the yield of gases is also high. Both high yields of gases and lighter liquids are the consequence of the large microporous surface area.

Another important parameter is the catalyst grain size and its distribution. There is less area for cracking of C–C bonds in the case of greater catalysts particle size. For example lighter hydrocarbons are formed with considerably higher yield in cracking reactions of waste polymer over smaller sized catalyst [1]. Furthermore, higher concentration of unsaturated hydrocarbons was found due to more β-scission. On the other hand some other catalysts show great efficiency in the formation of unsaturated hydrocarbons: ZSM-5, silica–alumina, MCM-41.

The further utilization of products obtained by degradation of polymers (wastes and by-products of the plastic industry) is not solved yet. One possibility of their utilization is fuel-like application or mixing in fuels as blending components. It is important to

Table 9.8 The change of properties of products

Property	Presence of catalysts	Increasing temperature
Density	⇓	⇓
Viscosity	⇓	⇓
RON	⇑	⇑
MON	⇑	⇑
Cetane number	⇑	-
Pour point	⇓	-
S content	-	-
N content	-	-

⇓: decreasing in property, ⇑: increasing in property, -: no change in property

note that before blending the high olefin content is to be saturated with hydrogen, or hydroisomerized. These steps result in a high-quality synthetic diesel fuel, with high cetane number, and theoretically free from sulfur, nitrogen and metals. In practice these fractions generally have very low heteroatom content, even if the raw material was pure and not waste, because some polymers contain, e.g. sulphur containing anti-flame or antioxidant additives etc. Therefore the determination of practical properties (density, viscosity, pour point, RON, MON, cetane number, impurities etc.) of products obtained by cracking of polymers is important. However, there are considerably few references in respect to these properties. One reason of this fact is that the measurement of practical properties needs a relatively large quantity of products, not produced in most experimental work. The change of some main properties of products is shown in Table 9.8.

It can be stated that generally the presence of catalysts is favourable and increasing temperature might be favourable for further fuel-like utilization in respect of products in the same boiling point range. The decrease of density, viscosity and partly the pour point is due to the greater cracking of C–C bonds. On the other hand the isomerization of carbon framework may also cause a decrease in the pour point.

The octane number is a quite important property of the products. The octane number of light liquid fractions increases in the presence of catalysts, but considerable differences could be observed in respect to RON and MON depending on the catalyst properties. The research octane number of light liquids changed between 60 and 115 in the case of cracking at 415°C in a batch reactor using different catalysts [1, 11]. Principally the concentration of aromatics, *n*-aliphatics and branched hydrocarbons determines the octane number. Increasing concentration of branched compounds and aromatics resulted in higher RON and MON. On the other hand too high a concentration of aromatics is unfavourable because of their high sensibility.

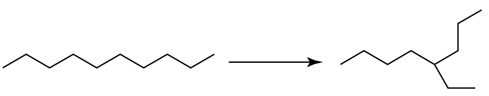
3.2 BIFUNCTIONAL CATALYSTS

Bifunctional catalysts have a cracking function and an other (e.g. hydrogenation) function. Generally the bifunctional catalysts used for thermocatalytic degradation of polymers are usually impregnated transition metals on silica–alumina or zeolite. The cracking and isomerization function is provided by an acidic support, whereas the other is provided by metals. The hydrogenation or aromatization activity of catalysts is determined, among other factors, by metal type, amount of metal used, the degree of metal dispersion, the location of metal on support or metal–support interaction. On the other hand the concentration of metal across the diameter of catalyst grains also important. There are three cases of concentration distribution: eggshell (metals only on the inside of support), eggwhite (the maximum concentration of metal between one-half and one-quarter of grain diameter) and eggyolk (the maximum concentration of metal within one-half of grain diameter). At the same metal content considerable differences were observed in the concentration distribution in the catalysts.

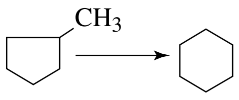
Numerous metals have been evaluated as bifunctional catalysts. Those used are noble metals and non-noble or transition metals. Platinum and palladium have the highest catalytic activity. The noble metal content is usually 1% or less, whereas that of non-noble metals is larger 1–30%. The concentration of dispersed metal on supports plays an important role in the activity of the catalyst, e.g. the activity of hydrogenation/dehydrogenation increases then decreases with the concentration of metals. There are some typical reactions of bifunctional catalysts.

(A) Isomerization

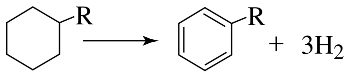
Paraffin isomerization



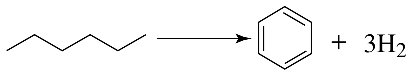
Naphtene isomerization



(B) Dehydrogenation



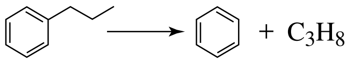
(C) Dehydrocyclization



(D) Hydrocracking

$$C_{10}H_{22} + H_2 \longrightarrow C_4H_{10} + C_6H_{14}$$

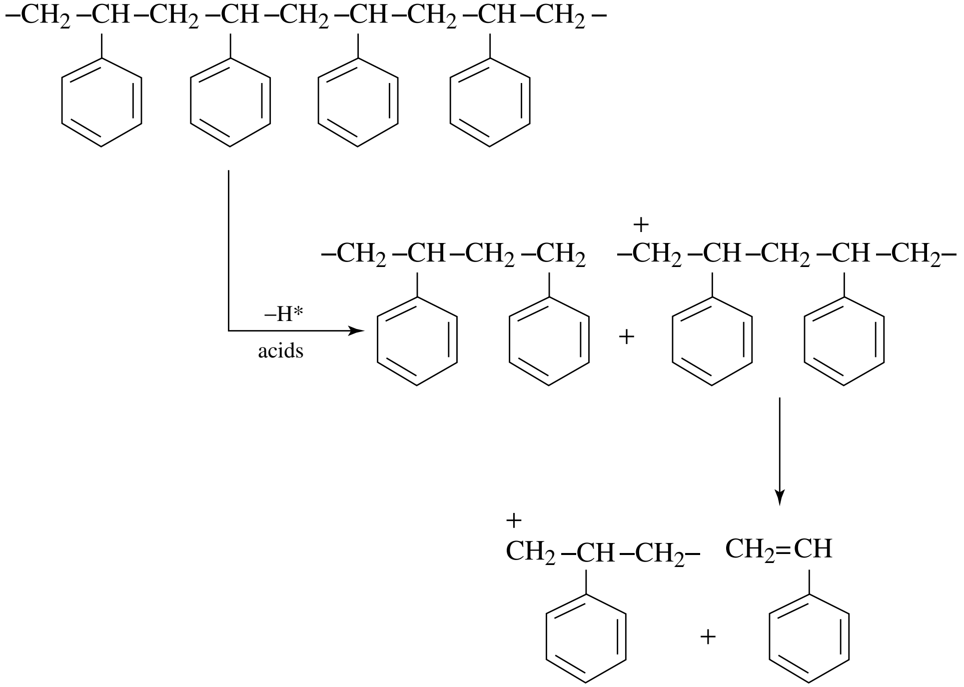
(E) Dealkylation



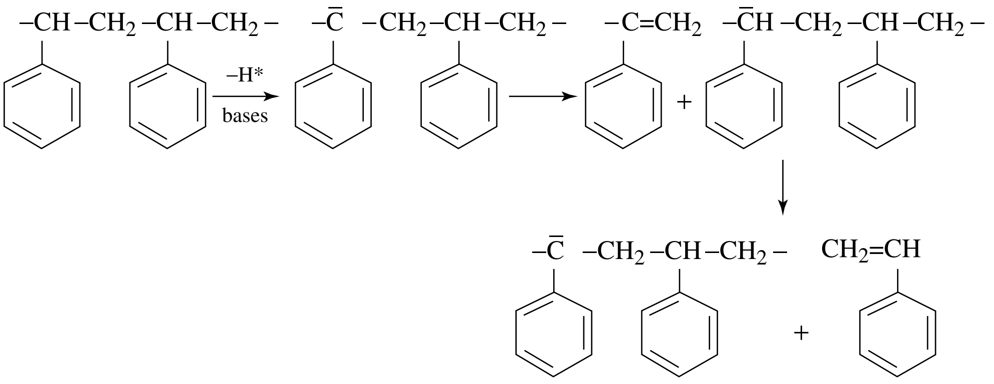
It is known that not only the quality of metals, but also their location on the support is an important parameter in respect to cracking behaviour. For example it was found during the investigation of platinum-impregnated Al_2O_3, SiO_2-Al_2O_3 and activated carbon that using Al_2O_3 support the yield of aromatics was significantly higher than in other cases and the yields of *i*-alkenes was 2.26 and 5% with the use of Al_2O_3, SiO_2-Al_2O_3 and activated carbon, respectively [52].

3.3 SOLID ALKALIS

Solid alkalis might catalyse the cracking reactions of polymers as is the case with acidic catalysts. According to experimental work solid alkalis catalyse the degradation of polystyrene more efficiently than acidic catalysts [53]. This phenomenon could be explained by differences in the cracking mechanism of polymers. The main components in the oils obtained by solid acids were styrene monomer and dimer. Since cracking of hydrocarbons on solid acids has been explained in terms of β-scission of C–C bonds [19, 20], these were probably produced by β-scission of C–C bonds in the PS main chains as follows:



On the solid bases, the fraction of styrene monomer found in the product oils increased to about 75 wt%, and the fraction of styrene, including both monomer and dimer, increased to about 90 wt%. Partially because there was no formation of benzene and indane derivatives in the oils obtained using solid bases or by simple thermal degradation, and partially because of the considerable proportions of styrene dimer in those oils, it can be concluded that the degradation on solid bases probably proceeds by a route similar to that for the simple thermal degradation reaction, i.e. by depolymerization. Thermal degradation of PS starts with a random initiation to form polymer radicals [21, 22], but the catalytic degradation on solid bases may start with the formation of carboanions by the elimination of a hydrogen atom of the PS adsorbed on base sites as follows:



The difference in the fraction of residues formed by thermal degradation and by catalytic degradation on solid bases is due to the fast degradation of the vaporized fragments of PS on base sites. Studies on the relationship between base strengths and their catalytic activities for HCl elimination of 1,1,2-trichloroethane revealed the important role of base sites for hydrogen atom elimination from 1,1,2-trichloroethane [23]. Although the base strengths of solid bases employed in this work have not yet been measured, the higher yields of styrene from PS may be ascribed to the stronger base sites on the surface of the solid bases. From some alkalis BaO proved to be the most efficient, and polystyrene was converted into monomer with the yield of more than 90% at 623 K.

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PART III

Quality of Fuels

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10

Production of Gaseous and Liquid Fuels by Pyrolysis and Gasification of Plastics: Technological Approach

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1 INTRODUCTION

The carbonization of a product consists in heating it in a confined atmosphere, i.e. in the absence or lack of oxygen. When heating a material above 300°C in the absence of air, the organic material decomposes in three phases: gas, liquid and solid.

In the *pyrolysis processes*, a thermal degradation occurs between 400 and 600°C in the complete absence of oxygen. These processes are characterized by the indirect heating of the material through the furnace wall (or pipes). The pyrolitic products, the solid (mix of char metals and mineral matter) and the hot gases (condensable and noncondensable mixture), are collected. Their relative proportions depend on the nature of the material, the applied technology and the pyrolysis conditions, i.e. temperature, pressure, heating rate, etc. The reductive atmosphere of the furnace is mainly a function of the pyrolitic gas composition.

In the *gasification processes*, the material is directly heated at higher temperatures (800–1000°C) by partial combustion of the contained carbon into carbon monoxide. A limited amount of air (or oxygen) is admitted to the furnace according to the stoichiometry (formation of CO_2 and H_2O) so that the reductive atmosphere in the furnace is governed by the ratio CO/CO_2.

Wood carbonization is a very well known process, used in the past for the production of charcoal in primitive extractive metallurgy. In this case, the volatile matter and the water are extracted from the wood, leaving solid charcoal.

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The carbonization of a sample proceeds progressively from the outside to the inside: it will depend on the heat transfer to the material, but also on the heat transfer inside the material. The residence time at the selected temperature is then of major importance in order to complete the carbonization. For each kind of material, the residence time has to be increased with its dimensions. If the residence time is too low, incompletely carbonized material will be found at the heart of the piece.

Slow reactions at very low temperature maximize the solid yields, as in charcoal production since antiquity. Changing the heating rate, temperature, pressure and residence time leads to substantial modifications in the proportions of the gas, liquids and solids. High heating rates (up to 1000 K/min) minimize the char formation and rapid quenching favours the condensation of the liquid phase before the cracking into gaseous products. Table 10.1 gives a general overview of the different kinds of processes (hydrogenation and reactive processes are not included).

It is then very difficult to compare the gas, liquid and solid yields obtained for a specific material by different authors as the operating conditions can be very different (mass between a few milligrams to few grams, heating rate from a few K/min to tens of K/sec, etc.).

The use of polymers has increased by a factor of about three since 1980 and life-cycle analysis shows that energy and raw material saving could be reached by the reprocessing of plastics recovered from waste streams. Today, PVC, PE and PET are easily sorted from different waste streams for reprocessing, but all sorting plants evolve large quantities of mixed plastics. The main conditions for efficient material reprocessing concern the purity of the recycled feedstock, i.e. the quality of the sorting process. For a lot of waste streams, as well as for sorting plant refuse, it is not economic to separate the different kinds of polymers. This explains the large amount of plastic waste landfilling in Europe. When easy and cheap plastic waste sorting is feasible to produce high-quality secondary products, material reprocessing is the best solution. When wastes containing large quantities of plastics are not suitable for sorting, the main alternative to landfilling is incineration, but the high net calorific value of this kind of waste could be a major problem. For mixed plastics low in PVC, energy valorization (upgrading) in cement kilns or in the steel industry is useful. An alternative way consists in pelletizing the mix in order for it to be gasified, but the preparation costs are relatively high.

Another cleaner alternative consists in producing solid, liquid and gaseous fuels by pyrolysis. The solid fuel could be upgraded by mechanical separation of metals and minerals in order to produce a cheap feedstock to a classical gasifier. Moreover, selected additions during pyrolysis could entrap pollutants such as chlorine and heavy metals [1–3].

The main advantage of pyrolysis over direct combustion in a waste-to-energy unit is a tremendous reduction in the volume of product gases (10- “to” 20-fold). This leads to a significant reduction in the complexity of the exhaust gas purification system. Moreover, pyrolysis of waste containing plastics could be performed with less charge preparation, so that minerals and metals are easily separated during the solid fuel conditioning and less ash are produced.

The thermal degradation of polymers has been extensively studied for different purposes, performed by analytical pyrolysis for information on the kinetics and mechanisms of degradation and has been extended during the last few decades to studies of the catalytic effects taking place under pyrolysis of complex waste materials [4,5].

Table 10.1 Pyrolysis processes

Process	Feed size	Moisture	Heating rate	Residence time	Temperature (°C)	Pressure	Products
Slow carbonization	Large		Very low	Days	450–600	Atmospheric	Charcoal
Slow pyrolysis	Medium <200 mm	<15%	10–100 K/min	10–60 min	450–600	Atmospheric/vacuum	Gas, oil, char
Fast pyrolysis	Small <1 mm	<10%	Up to 1000 K/s	0.5–5 s	550–650	Atmospheric	Gas, oil, (char)
Flash pyrolysis	Small <1 mm	<10%	Up to 10 000 K/s	<1 s	450–900	Atmospheric	Gas, oils, (char)

Table 10.2 Influence of operating conditions on carbonization yields of polyethylene

	Slow (500°C)	Fast (500°C)	Slow (700°C)	Fast (700°C)
Gas (wt%)	10	10	15	50
Liquid (wt%)	88	90	85	50
Solid (wt%)	2	0	0	0

This section is dedicated to a survey of the literature on carbonization product yields. Very large discrepancies can be seen between the results obtained by different authors in the carbonization yields for the same material (Table 10.2).

The following section reviews the literature data summarizing the behaviour during carbonization of five individual polymers, i.e. polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene terephthalate (PET). For each polymer, results will first be presented for flash pyrolysis then for slow pyrolysis by the isothermal and dynamic methods.

In slow pyrolysis, temperatures are generally lower than for flash pyrolysis, but residence time is longer. Meanwhile, there are two different methods. One method is the *isothermal–static method* where the charge is directly heated at a given temperature and maintained during a certain time while in the *dynamic method* (TGA) the charge is progressively heated.

2 LITERATURE REVIEW ON PLASTICS CARBONIZATION

The thermal decomposition of polymers which generates degradation products has been largely studied during the last few years and a review of these results will be presented. The literature shows the results on mass balance for the different products issued from the polymer carbonization as well as phase composition, decomposition mechanisms and kinetic data. Different techniques are used (dynamic or isothermal measurements) such as thermogravimetry (TGA) or batch small-size pyrolysis reactors fixed-bed (static), fluidized-bed (FB) and circulating extruder at atmospheric or low pressure. The products issued from different technologies are classified in two main categories ‘slow’ and ‘fast/flash’ pyrolysis. In summary, the review of the results from the literature performed at laboratory scale shows the strong dependence of the carbonization products in relation to the main process parameters such as final temperature, pressure, heating rate and residence time. A choice of several important polymers is made with regard to their common use with the purpose of comparing the different carbonization processes able to produce substitution fuels.

The physical characteristics of the plastic input influence the carbonization process. In static conditions, the heating rate of small particles is higher than for large particles. In this case, difficulties could occur for the extrapolation from small-scale carbonization data to pilot- and industrial-scale units. The physical and chemical properties of the material are of great importance in order to be able to evaluate the heat transfer from the reactor inside the material.

2.1 POLYETHYLENE (PE)

For *flash pyrolysis* of PE, the mass balance at different temperatures is presented in Table 10.3. G, L and S are respectively the gas, liquid and solid phases.

An increase in temperature will favour the quantity of gas phase and will decrease the liquid phase. The composition of the liquid fraction is presented in Table 10.4.

In the gas fraction, the main products are methane, ethylene, ethane and propene. It is shown that by increasing the temperature, the propane and propene content decreases while methane and ethylene increase.

The molar fraction of the monomer (ethylene) does not vary regularly with the temperature. Kaminsky [11] and Conesa [12] find respectively 24 and 34% of methane between 650 and 790°C. Some discrepancies are observed in the results of Scott [6]; 45–55% of methane is found in the same range of temperature; this can be explained by differences in operating conditions (heating rate, residence time, etc.).

In the oil fraction, the main products (at 740°C) are benzene, toluene, naphthalene and other aromatics [11].

Slow pyrolysis PE decomposition is presented in Table 10.5.

Table 10.3 PE flash pyrolysis: mass balance

Conditions		Parameters		Mass balance			References
Reactor type	*p* (atm)	*T* (°C)	*m* (g)	G (%)	L (%)	S (%)	
FB	1	515			89.8	5.9	6
FB	1	530		7.6	92.4	0	7
FB	1	550	3	11.4	66.7		8
FB	1	550	3	21.4	53.2		8
FB	1	654		17.5	73.5	1.1	6
RCR	1	650		80	20		9
FB	1	730		51.2	37.5	2.1	6
FB	1	740		59.1	39.2	1.8	10
FB	1	740		59.9	39.8	0.9	10
FB	1	740		58.6	39.6	1.8	11
FB	1	760		55.8	42.4	1.8	11
FB	1	780		51.2	46.2	1.8	11
FB	1	790		61.5	32.8	0.2	6
FB	1	800	1	66.2	28.3	5.5	12

FB fluidized bed; RCR rotating cone Reactor

Table 10.4 PE flash pyrolysis: gas phase composition

T (°C)	H_2 (%)	CH_4 (%)	C_2H_6 (%)	C_2H_4 (%)	C_3H_8 (%)	C_3H_6 (%)	C_4H_{10} (%)	C_4H_8 (%)	Other (%)	CO_2 (%)	CO (%)	References
550	1.9	7.3	8.0	25.7	5.4	21.1	2.6	25.2	2.5	0	0	8
760	1.4	42.7	12.0	35.8	0.1	10.0	0.7	2.9	0.4	0	0	11
800		44.2	4.5	46.7	0.2	4.0	0.2	0.3	0	0	0	12

Table 10.5 PE slow pyrolysis decomposition: mass balance

Conditions		Parameters		Mass balance			References
Reactor type	p (atm)	T (°C)	m (g)	G (%)	L (%)	S (%)	
TGA	10^{-8}	405	0.1	2.5	86.1	11.4	13
TGA	10^{-8}	450	0.1	3.1	95.5	1.4	13
Static	4–35	430		7.9	90.8	1.3	14
TGA	1	430	0.02			72*	15
TGA	1	440	0.02			47*	15
TGA	1	450	0.02			28*	15
TGA	1	460	0.02			10*	15
TGA	1	470	0.02			3*	15
TGA	1	480	0.02			0*	15
Static		700		16.8‡	79.7‡		16
Static		700		15.0#	84.3#		16

‡ HDPE; # LDPE; static: fixed-bed (batch static reactor)
* Value estimated using the TGA graph

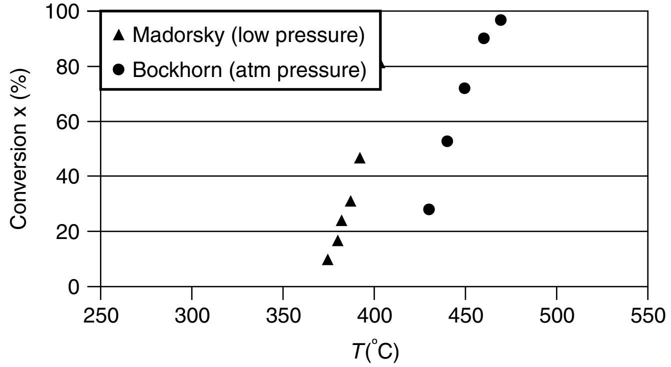

Figure 10.1 PE slow pyrolysis conversion yield (%)

The conversion yield (x) is expressed by the ratio of the weight loss over the initial mass. The evolution of the conversion yield versus the temperature is represented in the Figure 10.1.

Figure 10.1 shows that the conversion is more efficient at lower temperature under vacuum [13] than at atmospheric pressure under an inert atmosphere [14, 15]. This is explained by the fact that volatilization is favoured at lower pressure.

In slow pyrolysis by the dynamic method, the temperature domain is generally large and in this case, the main parameter is the heating rate. Table 10.6 indicates the temperature interval for the decomposition of the PE defined between the temperatures T_5 and T_{95}. These two temperatures are defined respectively as the temperature at which the conversion starts (T_5 at 5% conversion) and T_{95} (close to the end of conversion, at 95%). The maximum rate of conversion occurs between T_5 and T_{95}, at $T_{\max}$.

According to Wu [17], the decomposition interval lies between 390 and 490°C. The lower temperature range found by Anderson [18] is related to lower pressure conditions.

Table 10.6 PE slow pyrolysis (dynamic method): characteristic parameters

Conditions		Parameters		Temperature			References
Reactor	p (atm)	Heating rate (K/min)	m (g)	T_5 (°C)	T_{95} (°C)	T_{max} (°C)	
TGA	1	10	0.02	420*	490*	470*	15
TGA	1	1	0.004	390–400*	450–460*		17
TGA	1	2	0.004	400–410*	465–470*		17
TGA	1	5.5	0.004	420–425*	490*		17
TGA	10^{-3}	5	0.1	<340*	460*		18

* Values estimated using the TGA graph

The initial temperature for the decomposition of LDPE is lower than that of HDPE [17]. For the two types of PE, total degradation occurs at 490°C. The gas phase composition in slow pyrolysis is presented in Table 10.7.

At 425°C, at a pressure of 10^{-4} mmHg, the main component is propylene, in larger proportion than ethylene [20]. At higher temperature, the formation of alkanes is favoured.

In *slow pyrolysis,* the gas phase contains less methane and ethylene and more ethane and propane than by *flash pyrolysis* (see Tables 10.4 and 10.7). The product yields obtained in the literature by different authors for the PE for slow pyrolysis (Pinto, Madorsky, Bockhorn, Tsuji and Williams) and fast pyrolysis (Kaminsky, Williams, Scott and Conesa) are respectively presented in Figures 10.2 and 10.3.

Table 10.7 PE slow pyrolysis: gas phase composition

T (°C)	H_2 (%)	CH_4 (%)	C_2H_6 (%)	C_2H_4 (%)	C_3H_8 (%)	C_3H_6 (%)	C_4H_{10} (%)	C_4H_8 (%)	Other (%)	CO_2 (%)	CO (%)	References
425	0	27.2	9.1	11.6	18.3	22.4	5.3	6.0	0			19
500	6.49	7.53	13.8	13.2	17.4	28.9	7.5	5.2	0			20
500	5.69	2.93	11.2	5.6	20.7	15.5	20.8	15.7	0			20
700‡	0.7	11.3	13.2	18.4	7.8	27.2	1.3	2.1	0			16
700#	0.3	7.6	11.1	26.6	8.9	26.6	2.1	13.3	3.4			16

‡ HDPE; # LDPE

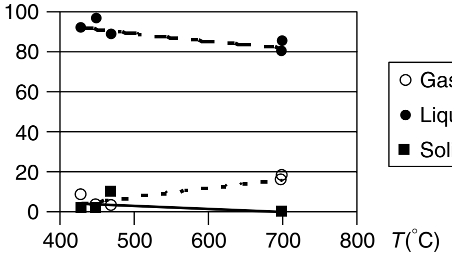

Figure 10.2 PE slow pyrolysis: product yields (%)

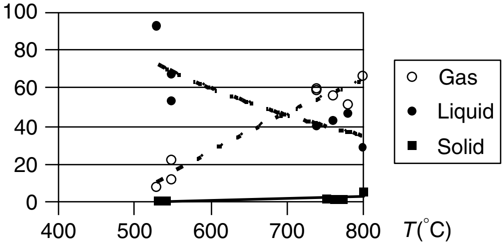

Figure 10.3 PE flash pyrolysis: product yields (%)

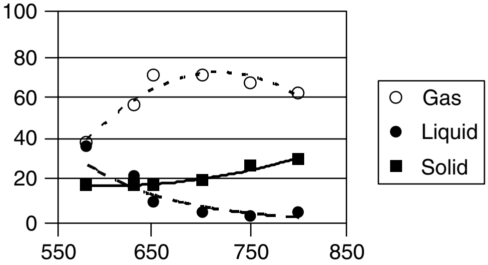

Figure 10.4 PE gasification: product yields (%)

During the slow pyrolysis of polyethylene, for a temperature increase from 400 to 700°C, the yield in liquid phase remains higher than 80% with a very small increase in the yield of gas phase (less than 20%). On the other hand, in flash pyrolysis of polyethylene, an increase of temperature from 550 to 700°C leads to a decrease of the yield in the liquid phase to less than 40% with an increase in the yield of the gas phase up to 60%.

In the 1970s Sawagushi *et al.* [21] presented results and validated a kinetic approach to the intensity function in the case of *steam gasification* of PE in a fixed-bed reactor. These results are presented in Figure 10.4.

The maximum total gas yield reaches 75% at 700°C. In comparison with pyrolysis, thermal gasification of polymers is also a suitable process because its products are of simpler composition and have a narrower range of molecular weights.

By a *two-stage pyrolitic gasification* process (470 and 800°C), it is possible to improve the quality of the gaseous products and the gas yield. In these conditions, the gas yield reaches 80% [22].

2.2 POLYPROPYLENE (PP)

The *flash pyrolysis* of PP is realized at temperatures higher than 500°C. The mass balance at different temperatures is presented in Table 10.8.

These results show that for temperatures in the range of 750°C, the proportions of the three phases produced are constant. Gas and liquid fractions are close to 50% while the solid fraction is less than 2%. The composition of the gas phase is presented in Table 10.9.

Table 10.8 PP flash pyrolysis: mass balance

Conditions		Parameters		Mass balance			References
Reactor type	p (atm)	T (°C)	m (g)	G (%)	L (%)	S (%)	
FB	1	510		6.3	93.7	0	7
FB	1	550	3	6.5	69.8		8
FB	1	740		49.6	48.8	1.6	11
FB	1	760		51.4	46.9	1.7	11

FB: fluidized-bed

Table 10.9 PP flash pyrolysis: gas phase composition

T (°C)	H_2 (%)	CH_4 (%)	C_2H_6 (%)	C_2H_4 (%)	C_3H_8 (%)	C_3H_6 (%)	C_4H_{10} (%)	C_4H_8 (%)	Other (%)	CO_2 (%)	CO (%)	References
550	3.7	6.8	6.9	22.8	10.3	16.6	4.0	30.0	0			8
740	1.4	56.9	8.1	28.0	0.2	7.5	0.8	0.8				11

At lower temperature, Williams [8] finds mainly ethylene, propane, propene and butene as major components. Kaminsky [11], at higher temperature, finds mainly methane and ethylene.

In *slow pyrolysis*, the experiments are conducted at constant temperature and the mass balance is presented in Table 10.10.

In order to be able to compare the results, the conversion yields are presented in Figure 10.5 after a residence time of 30 min in the reactor.

As for polyethylene, working at low pressure [23,24] shows that the decomposition of polypropylene occurs at lower temperature compared with the results at atmospheric pressure [25,26]. In both pressure conditions, the solid fraction is very weak for temperatures higher than 400°C.

Table 10.10 PP slow pyrolysis: mass balance

Conditions		Parameters		Mass Balance			References
Reactor type	p (atm)	T (°C)	m (g)	G (%)	L (%)	S (%)	
TGA	10^{-8}	328	0.006	1.5	6.7	91.8	23
TGA	10^{-7}	400	1	14.5	65.7	19.8	24
TGA	10^{-8}	410	0.006	11.2	85.2	3.6	23
TGA	1	410	0.04			65	25
TGA	1	420	0.04			42	25
TGA	1	430	0.04			25	25
TGA	1	440	0.04			10	25
TGA	1	450	0.04			1	25
TGA	10^{-8}	500	0.006	17.5	82.1	0.4	23
Static		700	3	13.6	84.4	0.2	16

Static: fixed-bed (batch static reactor)

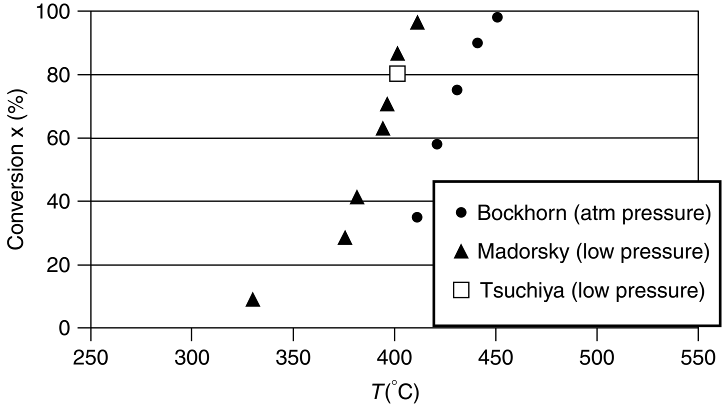

Figure 10.5 PP slow pyrolysis: conversion yield (%)

Table 10.11 PP slow pyrolysis (dynamic method): characteristic parameters

Conditions		Parameters		Characteristic temperatures			References
Reactor type	p (atm)	Heating rate (K/min)	m (g)	T_5 (°C)	T_{95} (°C)	T_{max} (°C)	
TGA	1	1	0.004	360*	440*		17
TGA	1	2	0.004	375*	455*		17
TGA	1	5.5	0.004	390*	480*		17
TGA	1	5	0.02	340	481	456	27
TGA	1	10	0.02	354	489	469	27
TGA	1	15	0.02	371	494	477	27

* Values estimated using the TGA graph

By slow pyrolysis, the dynamic method is more appropriate to estimate the decomposition interval for the polypropylene decomposition. Table 10.11 indicates the temperature interval for the decomposition of the PP defined between the temperatures T_5 and T_{95}

When the heating rate increases, the temperature interval for the decomposition is displaced to higher temperatures. It can be seen that the decomposition of PP is totally achieved at 490°C. Large quantities of the monomer are produced at low temperature and it decreases at higher temperature. Ethylene becomes the main component in the gas phase. Details of the gas phase composition are given in Table 10.12.

Table 10.12 PP slow pyrolysis: gas phase composition

T (°C)	H_2 (%)	CH_4 (%)	C_2H_6 (%)	C_2H_4 (%)	C_3H_8 (%)	C_3H_6 (%)	C_4H_{10} (%)	C_4H_8 (%)	Other (%)	CO_2 (%)	CO (%)	References
400	0	11.0	13.4	0	5.5	61.1	0.2	8.8				28
500	1.58	14.9	26.4	0.84	4.9	47.9	0.4	2.4				20
700	0.4	6.8	10.6	25.8	7.3	25.9	1.7	9.5				16

At higher temperature (700°C), in *slow pyrolysis,* the gas phase contains less methane and more propane, propene and butene than by *flash pyrolysis* (see Tables 10.9 and 10.12).

The product yields obtained in the literature by different authors for the PP for slow pyrolysis (Bockhorn, Pinto, Tsuji and Williams) and fast pyrolysis (Kaminsky and Williams) are respectively presented in the Figures 10.6. and 10.7.

The carbonization of polypropylene is similar to that of polyethylene. During slow pyrolysis of polypropylene and for a temperature increase from 400 to 700°C, the yield in the liquid phase remains higher than 80% with a very small increase in the yield of gas phase (less than 20%). On the other hand, in flash pyrolysis of polypropylene, an increase of temperature from 550 to 700°C leads to a decrease of the yield in the liquid phase down to 40% with an increase of the gas phase up to 60%. As presented for PE (see Section 2.1), Sawagushi *et al.* [21] present the results of *steam gasification* of PP in a fixed bed reactor (Figure 10.8).

The maximum gas yield reaches 65% at 650°C whereas the carbon deposit increases up to 20–30%. These results show that the liquid yield decreases more rapidly than by flash pyrolysis. By a *two-stage pyrolitic gasification process* (450 and 800°C), it is possible to improve the quality of the gaseous products and the gas yield. In these conditions, the gas yield reaches 74% [22].

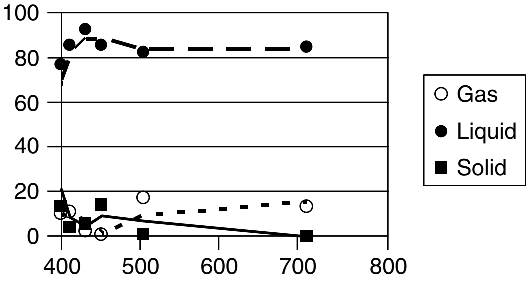

Figure 10.6 PP slow pyrolysis: product yields (%)

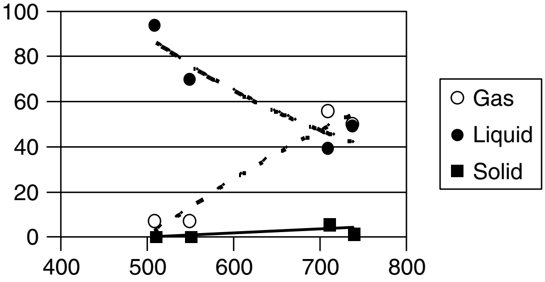

Figure 10.7 PP flash pyrolysis: product yields (%)

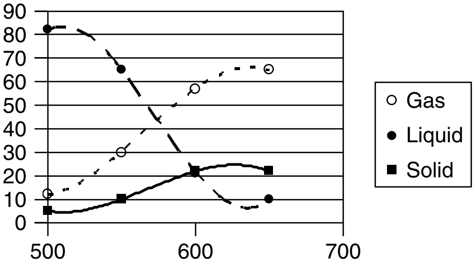

Figure 10.8 PP gasification: product yields (%)

Table 10.13 PS flash pyrolysis: mass balance including the yield of monomer, styrene

Conditions		Parameters		Mass balance				References
Reactor type	p (atm)	T (°C)	m (g)	G (%)	L (%)	S (%)	Styrene (%)	
FB	1	520		0.1	23.0	0	76.8	29
FB	1	532		11.5	12.3	0	76.2	6
FB	1	550	3	0.7	71.4	0		8
FB		580		9.9	24.6	0.6	64.9	11
FB	1	615		15.7	10.6	0	72.3	6
FB	1	708		15.2	7.7	0	75.6	6

FB: fluidized-bed

2.3 POLYSTYRENE (PS)

For the *flash pyrolysis* of PS, the results in mass balance are presented in Table 10.13. The yield of monomer is added because styrene is the major component during the carbonization of PS.

A significant liquid phase is observed during the flash pyrolysis of polystyrene with styrene as the main component [8]. Except for one experiment by Kaminsky [11] the yield in styrene formed during the flash pyrolysis of PS (between 520 and 710°C) is near 75%. The major other products are aromatic compounds (oligomeric styrenes) [11].

The conversion yield x of polystyrene by *slow pyrolysis* after a residence time of 60 min is presented at different temperatures in Table 10.14.

By the dynamic method, the temperature intervals (T_5 and T_{95}) are determined and the results are shown in Table 10.15 for PS.

From these results an average interval for the decomposition of PS is estimated between 330 and 425°C.

The main product yield (after slow or flash pyrolysis) is the liquid phase and Sawagushi[31] found that this is mainly composed styrene monomers, dimers and trimers. For a residence time of 60 min, increasing the temperature from 310 to 350°C increases the monomer fraction up to 78%. Table 10.16 shows the proportions of these three components in the liquid phase as a function of the temperature.

Table 10.14 PS slow pyrolysis: mass balance

Conditions		Parameters		Mass balance			References
Reactor type	p (atm)	T (°C)	m (g)	G (%)	L (%)	S (%)	
TGA	10^{-9}	335	0.006			95	30
TGA	10^{-9}	345	0.006			88	30
TGA	10^{-9}	350	0.006			82	30
TGA	10^{-9}	360	0.006			43	30
TGA	10^{-9}	365	0.006			59	30
Static	1	700	3	3.4	83.8	3.5	16

Table 10.15 PS slow pyrolysis (dynamic method): characteristic parameters

Conditions		Parameters		Characteristic temperatures		References
Reactor type	p (atm)	Heating rate (K/min)	m (g)	T_5 (°C)	T_{95} (°C)	
TGA	1	1	0.004	330*	390*	17
TGA	1	2	0.004	345*	405*	17
TGA	1	5.5	0.004	336*	425*	17
TGA	10^{-3}	5	0.1	370*	415*	18

* Values estimated using the TGA graph

Table 10.16 PS slow pyrolysis: liquid phase composition (styrene)

T (°C)	Styrene			References
	Monomer (%)	Dimer (%)	Trimer (%)	
310	25.0	28.3	46.7	31
330	60.2	13.1	26.6	31
350	78.4	9.4	12.2	31

The styrene fraction is similar to that in flash pyrolysis at higher temperature [6,11]. McNeill[32] studied the volatilization of PS under vacuum.

The survey of the literature results for the behaviour of polystyrene during slow pyrolysis (Koo, Pinto, Takai, Tsuji and Williams) and for fast pyrolysis (Kaminsky, Scott and Williams) are respectively presented in Figures 10.9 and 10.10.

It can be seen that during slow and fast pyrolysis of polystyrene, if the temperature increases respectively from 400 to 700°C and 550 to 700°C, the yield in the liquid phase remains higher than 80% with a relatively stable yield in the gas phase, less than 20%.

By a *two-stage pyrolitic gasification* process (450 and 800°C) [22], the gas yield is very low because styrene monomer, dimer and trimer hardly decompose in these conditions.

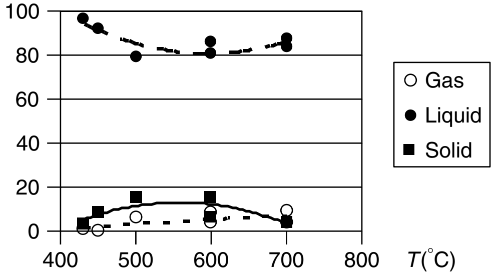

Figure 10.9 PS slow pyrolysis: product yields (%)

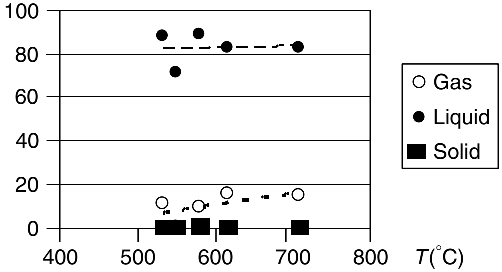

Figure 10.10 PS flash pyrolysis: product yields (%)

2.4 POLYVINYL CHLORIDE (PVC)

For *the flash pyrolysis* of PVC, the mass balance is presented in Table 10.17. The mass fraction of the hydrogen chloride is included as it is one of the main products in the gas phase.

In the same temperature range, the solid fraction found by Williams [8] is quite large, with a low fraction of HCl compared with the results of Scott [6]. This could be explained if carbonization is not totally complete in the first case. A higher temperature, the solid fraction is reduced in favour of the gas and oil fractions. In the gas phase, the part of HCl nearly reaches its theoretical yield. According to Williams [8] the oils contain principally benzene and toluene respectively 22.1 and 9.6% by mass.

The results of the PVC decomposition in *slow pyrolysis* are presented in Table 10.18.

Bockhorn *et al.* [33,15] and Gimenez *et al.* [34] find a plateau between 310 and 380°C for about 40% (at 2 K/min) conversion which corresponds to the release of HCl.

Table 10.17 PVC flash pyrolysis: mass balance

Conditions		Parameters		Mass balance				References
Reactor type	*p* (atm)	*T* (°C)	*m* (g)	G (%)	L (%)	S (%)	HCl (%)	
FB	1	520		28.3	6.3	9.1	56.0	6
FB	1	550	3	3.9	22.1	13.5	31.7	8
FB	1	740		6.8	28.1	8.8	56.3	11

Table 10.18 PVC slow pyrolysis: mass balance

Conditions		Parameters		Mass balance			References
Reactor type	p (atm)	T (°C)	m (g)	G (%)	L (%)	S (%)	
TGA	1	270	0.01			64*	15
TGA	1	290	0.01			57*	15
TGA	1	300	0.01			48*	15
TGA	1	310	0.01			45*	15
TGA	1	400	0.01			20*	15
TGA	1	410	0.01			12*	15
TGA	1	420	0.01			6*	15
TGA	1	440	0.01			3*	15
Static	1	700		55.4	31.7	13.8	16

* Values estimated using the TGA graph

According to Williams [16] (at 25 K/min), after the dehydrochlorination step, a second decomposition step starts at about 400°C [35–37]. This is explained by the rupture of polyenic chains produced during the first step and the formation of benzene-derived compounds [15]. The conversion yield x in *slow pyrolysis* of PVC is presented at different temperatures in Figure 10.11.

By the dynamic method, Miranda [38], working between 1 and 20 K/min, finds a plateau at 36% conversion. A weight loss of 64% is higher than the theoretical loss of HCl. This is explained by some benzene formation during the dehydrohalogenation step. The temperature at which the second decomposition step occurs is higher if the heating rate increases.

According to Miranda [38], the proportion of solid depends strongly on the heating rate (6.9–12.4% for heating rates respectively from 1 to 20 K/min). Analysis of the solid by Williams [16] reveals a carbon content of 90.2% with only 2.9% ash.

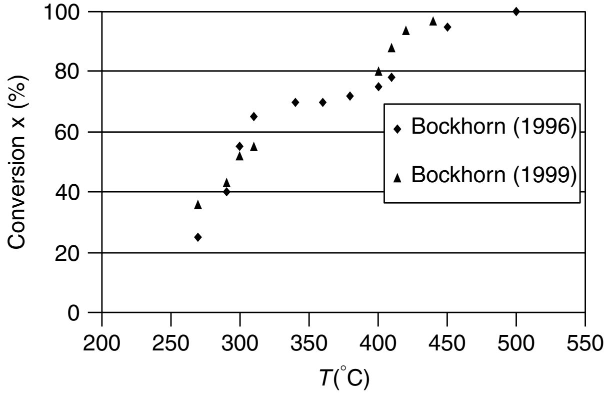

Figure 10.11 PVC slow pyrolysis: conversion yields (%)

2.5 POLYETHYLENE TEREPHTHALATE (PET)

Mass balance is presented in *flash pyrolysis* of PET at different temperatures in Table 10.19. Results of Williams [8] and Kaminsky [11] show that the decomposition of PET produces about the same quantities of gas and liquid with a proportion of solid around 10%.

The composition of the gas phase is given in Table 10.20. According to Williams [8], the gases contain carbon oxides (nearly 90%). These results are confirmed by those of Kaminsky [11].

In the oils, benzene and toluene are the major components [11]. Bednas [39] finds aldehydes (formaldehyde and acetaldehyde) as major components at 700°C. If the temperature rises 900°C, the amount of acetaldehyde decreases and carbon monoxide becomes more important in proportion then carbon dioxide [39]. This is explained by the decomposition of acetaldehyde in methane and carbon monoxide.

The results of the PET decomposition in *slow pyrolysis* are presented in Table 10.21.

As for flash pyrolysis, the proportion of solid remains important. The carbon content is estimated at 84.9% with 5.9% ash [16].

The conversion yields *x* of PET [40–42] are presented at different temperatures in Figure 10.12. It is important to take into account that the results by Dzieciol concern a thermo-oxidative degradation in air (flow of 0.025 m^3/h for 20 min).

By the dynamic method, the results for PET are presented in Table 10.22 where the conclusions are determined on the basis of TGA diagrams.

Table 10.19 PET flash pyrolysis: mass balance

Conditions		Parameters		Mass balance			References
Reactor type	*p* (atm)	*T* (°C)	*m* (g)	G (%)	L (%)	S (%)	
FB	1	550		49.1	39.4	12.8	8
FB	1	768	3	50.8	40.0	7.1	11

Table 10.20 PET flash pyrolysis: gas phase composition (%)

T (°C)	H_2 (%)	CH_4 (%)	C_2H_6 (%)	C_2H_4 (%)	C_3H_8 (%)	C_3H_6 (%)	C_4H_{10} (%)	C_4H_8 (%)	Other (%)	CO_2 (%)	CO (%)	References
550	2.1	1.8	0	3.1	0	2.6	0	0	0	37.8	52.6	8
768	9.2	14.6	0.4	0	0.1	0.1	0	0	0.1	37.5	38.1	11

Table 10.21 PET slow pyrolysis: mass balance

Conditions		Parameters		Mass balance			References
Reactor type	*p* (atm)	*T* (°C)	*m* (g)	G (%)	L (%)	S (%)	
FB	1	700	3	38.7	41.3	15.6	16

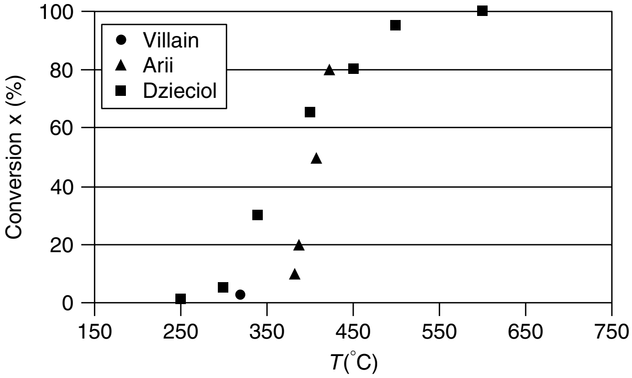

Figure 10.12 PET slow pyrolysis: conversion yields (%)

Table 10.22 PET slow pyrolysis (dynamic method): characteristic parameters

Conditions		Parameters		Characteristic temperatures			References
Reactor type	p (atm)	Heating rate (K/min)	m (g)	T_5 (°C)	T_{95} (°C)	T_{max} (°C)	
TGA	1	10	0.02			430*	43
TGA	1	1–10	0.001	370*	450*		42
TGA	1	10		400	450	430	44

* Values estimated using the TGA graph

Table 10.23 PET slow pyrolysis: gas phase composition (%)

T (°C)	H_2 (%)	CH_4 (%)	C_2H_6 (%)	C_2H_4 (%)	C_3H_8 (%)	C_3H_6 (%)	C_4H_{10} (%)	C_4H_8 (%)	C_4H_8 (%)	CO_2 (%)	CO (%)	References
700	12.4	3.6	0.1	4.0	0.2	0.2	0	0	0	41.4	38.1	16
850	0	11.6	0	2.6	0	0	0	0	0	36.5	48.7	45

The temperature interval estimated on the basis of these results lies between 370 and 430°C.

The gas phase composition is shown in Table 10.23. It consists mainly of carbon oxides and consequently has a very low net calorific value.

2.6 PLASTIC MIXTURES

Two types of approach exist to study the behaviour of plastic mixtures during pyrolysis. On one hand, some authors [46] work on plastic waste mixtures while other authors [47] work on simulated mixed plastic waste prepared with a specific composition. The proportions of the different polymers are based on mean values related to real waste mixtures.

Table 10.24 Plastic mixtures composition and flash pyrolysis: products (%)

T (°C)	PE (%)	PP (%)	PS (%)	PVC (%)	PET (%)	Other (%)	G* (%)	L** (%)	Wax (%)	S (%)	References
500	62.5	7.29	13.5	11.46	5.21	0	11.6	37.8	17.3	2.8	48
550	62.5	7.29	13.5	11.46	5.21	0	25.9	38.5	18.6	5.9	48
600	62.5	7.29	13.5	11.46	5.21	0	44.7	34.3	8.7	7.6	48
650	62.5	7.29	13.5	11.46	5.21	0	89.6	20.5	0		48
700	62.5	7.29	13.5	11.46	5.21	0	69.3	18.4	0		48
717	67.6		1	1.7	9.3	20.4	40.4	19.0		40.6	49
730	65		25	1.2	2.8	6	35	51.3		13.2	50
738	65		25	1.2	2.8	6	38	50		12	50
787	67.6		1	1.7	9.3	20.4	39.7	23.2		37.1	50
790	57		19	14	5	5	43.7	30.9		25.4	11

* Gas with HCl; ** L: liquid phase or oil

Table 10.24 summarizes the product yield after *flash pyrolysis* of the simulated mixed plastics in relation to pyrolysis temperature.

Williams [48,8] finds an increased production of gas formation on increasing the temperature up to 650°C. There was no more wax formed from 650°C [48]. The amount of HCl measured decreased from 1.8 to 0.5% in this temperature range. Scott *et al.* [6] pyrolysed plastic waste in a fluidized-bed at 580°C with a HCl production of 34.6%, suggesting that the PVC content was in higher proportion in the plastic mixture input.

The theoretical yield of pyrolysis products calculated on the basis of the additivity of individual plastic pyrolysis at 550°C is in good agreement with the products yields for the mixed plastics pyrolysis. However, with increase of the pyrolysis temperature, the char and gas yield are higher (with a decrease of oil and wax yields), suggesting that there are some interaction of the plastics in the mixture during pyrolysis [8]. Increasing the pyrolysis temperature leads to an increase of the aromatics, and a decrease of alkanes, alkenes and alkadienes in the oils.

Using *slow pyrolysis*, the results of Koo *et al.* [51] (atmospheric pressure, 20 g, 48 K/min and 70 min) of various proportions of PE/PS at 5 and 700°C are presented in Figures 10.13 and 10.14.

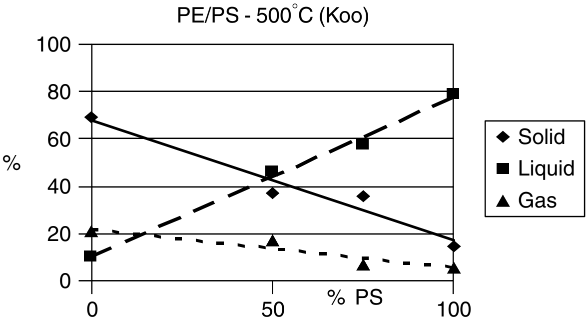

Figure 10.13 PE/PS product yields: 500°C

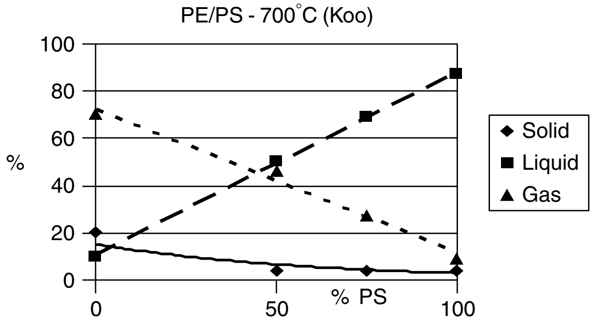

Figure 10.14 PE/PS product yields: 700°C

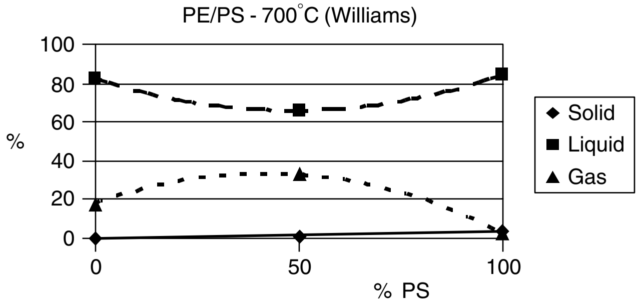

Figure 10.15 PE/PS product yields (%): 700°C

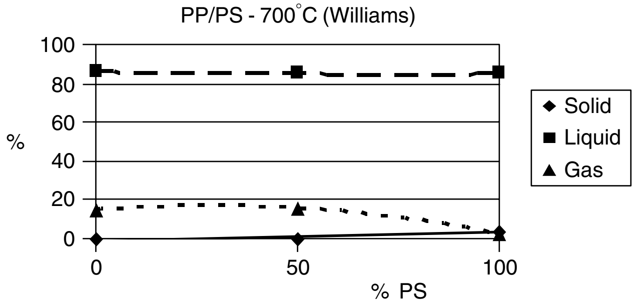

Figure 10.16 PP/PS product yields (%): 700°C

Mechanisms of degradation of blends of PS and PP have been studied by DSC and the kinetics of degradation of the blends matched with that of virgin PP for more than 50% PP [52]. On the other hand, the results of Williams [53,54] (atmospheric pressure, 3 g, 25 K/min and 60 min) for 1:1 mixtures of PE/PS, PP/PS,PVC/PS and PET/PS at 700°C are presented in Figures 10.15–10.18. These results show a deviation from additivity in the case of PE/PS mixtures.

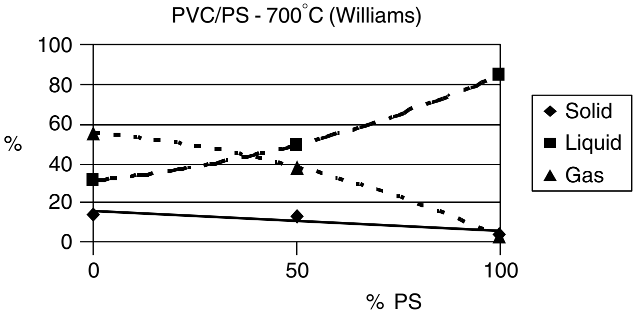

Figure 10.17 PVC/PS product yields (%): 700°C

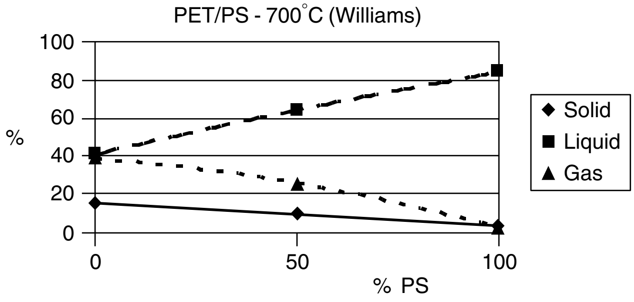

Figure 10.18 PET/PS product yields (%): 700°C

The results of Williams (Figure 10.15) show that for PE/PS mixtures (1:1) more gas and less liquid are produced than by the pyrolysis of the individual polymers at 700°C. This is in contradiction to Koo's results (Figure 10.14). For pure PS, the results are quite similar. The main differences are found for pure PE in the in proportions of gas and liquid phases (Figures 10.14 and 10.15). The contradiction in these results could be explained by the fact that the experimental conditions are quite different (3 g, 25 K/min for Williams and 20 g, 48 K/min for Koo) and that PE is more sensitive to the experimental conditions (see Figures 10.2 and 10.3). Indeed, the hot gas and oils are rapidly extracted co-currently from the reactor with the nitrogen flow [16] in the experiments of Williams whereas they are extracted counter-currently and remain longer in the hot zone of the reactor, being partially cracked into smaller entities, in Koo's experiments [51]. For the other binary mixtures of plastics, there is less deviation from additivity.

Dodson *et al.* [55] using TGA found a stabilization effect of PS when mixed with PVC heating up to 500°C (10 mg sample, 10 K/min). In a pilot extruder, Kuwabara *et al.* [56] show higher dechlorination rates of PVC mixtures with PE, PP and PS rather than the binary systems PE–PVC. HCl seems to inhibit the pyrolytic reaction of PE, resulting in a lower conversion rate [57].

Differences between flash and slow pyrolysis have been pointed out, especially for PE and PP. Products yields by slow pyrolysis at high temperature (700°C) are similar to those in flash pyrolysis at low temperature (500°C). Flash pyrolysis at higher temperature increases the gas yields.

The results in the literature for most of the polymers show that, at atmospheric pressure, the pyrolysis temperature does not have to exceed 600°C to reach total carbonization. Parameters such as heating rate and residence time will differ among different authors and some discrepancies still exist for the individual polymers. On the other hand, for polymer mixtures, interaction between polymers appears during pyrolysis between polymers with more gas produced and a better quality of the oils. These interactions are not yet explained.

3 TECHNOLOGICAL APPROACH

Pyrolysis and gasification are thermal degradation or carbonization processes [58–60] working at medium temperatures under controlled atmosphere. Pyrolysis processes involve indirect heating and recovery of pure pyrolysis products. Gasification processes involve direct heating and lead to the dilution of the pyrolitic gases by partial combustion products and nitrogen. A predictive carbonization model is presented in order to estimate the solid and gas yields during the pyrolysis of the waste mixture and also the net calorific value of the char and the gases.

The scaling-up of the results from the predictive model and from laboratory-scale results have to take into account the different types of technologies.

3.1 PREDICTIVE CARBONIZATION MODEL [61]

Let us consider that a mixed waste contains different components, each being characterized by its water content W, volatile matter VM* and ash content A* (the last two being on a dry basis). Assuming that each component behaves independently and using the hypothesis of additivity, it is possible to estimate the product yields after carbonization. Moreover, this model takes into account the different carbonization yields for each component (according their physical and chemical properties). From the C, H, O analysis of each component (easier than that for the rough mixture), it is possible to estimate the net calorific value of the char and the gases from the waste pyrolysis.

Taking into account the proximate analysis of the input material (water content W, volatile matter VM* and ashes content A^*), it is possible to estimate the fixed carbon $\mathrm{C_F}^*$:

$$\mathrm{C_F}^* = 100 - \mathrm{VM}^* - A^* \quad \text{and the dry matter DM} = 100\text{-}W.$$

Assuming that, during slow carbonization, the volatile matter is oriented with the water in the gas phase and that the fixed carbon is in the solid phase with the ashes, the mass balance could be estimated:

Mass of gas phase:

$$M_{\mathrm{G}} = \mathrm{VM} + \mathrm{W} \quad \text{with} \quad \mathrm{VM} = \mathrm{VM}^* \frac{\mathrm{DM}}{100}$$

Mass of solid phase (char):

$$M_\mathrm{S} = \mathrm{C_F} + A \quad \text{with} \quad A = A^* \frac{\mathrm{DM}}{100} \quad \text{and} \quad C_\mathrm{F} = 100 - \mathrm{VM} - A$$

If the temperature and/or the residence time are too low, the carbonization will be incomplete and some volatile matter will remain in the char. If φ is the proportion of VM entrapped in the char, the carbonization yield is $\alpha = 1 - \varphi$. One possible way of estimating the carbonization yield could be a TGA analysis at low heating rate for the same input material. Sampling is then the main problem for milligram sample analysis. Therefore, the use of larger scale TGA devices up to 5 g is recommended [58]. This model has been validated for used tyres, biomass, Tetrapak® boxes, mix of plastic wastes, etc. and gives rather good agreement (less than 10% difference) with experimental results for slow pyrolysis [62].

3.2 SCALE-UP

Moving from batch experiments to continuous reactors, one major problem is to ensure a good flow of the material inside the reactor (mechanical aspect). The efficiency of the global process depends not only on the material transport in the reactor, but also on the heat transfer to and inside the material. The feed preparation is then essential as well as the characterization of the eventual side material (water, metals, minerals, pollutants, etc.).

The different pyrolysis and gasification technologies, selected in relation to the waste input, generate different kinds of products that will have to be upgraded into substitution fuels. The solid fuel could be upgraded by mechanical separation of metals and minerals in order to produce a cheap feedstock to a classical gasifier. Moreover, selected additions during pyrolysis could entrap pollutants such as chlorine and heavy metals [2,3,63,64].

Interactions during pyrolysis of waste containing plastics in the presence of wood contaminated by chlorine and heavy metals have been studied at laboratory scale. The chlorine capture and the inhibition the chlorination of heavy metals has been validated at pilot scale [1].

The quality of the gases and oils has to be certified by analytical tests in order to be accepted for valorization as substitutions fuels [5].

The results in slow pyrolysis for various waste at laboratory scale (PE, PVC, sorting residues, wood, tyres, Tetrapak, etc.) are in very good agreement (less than 10% difference) with those obtained at pilot scale (Cutec Institute, Clausthal, 25 kg/h; Thide, Vernouillet, 500 kg/h and Traidec, Ste Foy l'Argentière, 500 kg/h). Furthermore they also give good agreement with industrial practice for slow pyrolysis (Noell, Salzgitter, 2-5 t/h, and others).

3.3 PYROLYSIS TECHNOLOGIES

The different technologies involve *indirect heating* and are characterized by the method of heat transfer to the material and by the method used for mixing the charge in the furnace. *Slow pyrolysis* can be performed in rotary kilns, or in static furnaces equipped with moving blades or screws for mixing the material and increasing the heat transfer. *Fast or flash pyrolysis* is usually performed in fluidized-bed furnaces or in vortex ablative furnaces. As pyrolysis is a pretreatment, the gas, liquids and solids issued from this treatment will need a post-treatment for further valorization.

3.3.1 Slow Pyrolysis

Rotary kilns are in common use all over the world for various applications. This technology was developed since the 1980s by Karl Kiener, Noell, Mannesmann (actually Technip), Babcock, Mitsui, VTA (Veba Öl), PKA, and Thide. For external heating, all technologies propose fuel or natural gas burners except for Babcock (Burgau Plant, Germany) and Thide (Nakaminato, JPN, Arras Plants; France) who adopted the furnace heating by exhaust gas issued from pyrolitic gas combustion. PKA proposed burners fed by cracked pyrolitic gases. Several pilot installations exist and are electrically heated. Some processes use a water-tight system for the char recuperation. Minerals and metals could be easily discarded from the char either by dry screening, or by wet elutriation.

All the processes developed during the 1980s included series of condensers in order to recover the different fractions of hydrocarbons contained in the pyrolitic gases. They were efficient, but this gas post-treatment was not economically viable according to petroleum prices. The hot pyrolitic gases are usually burned in a post-combustion chamber, part of the energy being used for the furnace heating, the rest for steam production. A simple gas cleaning system is present in order to fulfil the emissions regulations. One of the main problems encountered is tar deposits in the gas extraction pipes. Therefore, the main approach today is to keep the gases hot (heated pipes) and to burn the hot pyrolitic gases directly. In the PKA system, the pyrolitic gases are cracked and converted in noncondensable hydrocarbons. Now, according to increasing fossil fuels market prices, the recovery of hydrocarbons from the pyrolitic gases becomes more and more realistic.

The dimensions of these kilns are related to the nature of the material input and the capacity. Different furnace modelling approaches are recently proposed in the literature [65–67]. The design of the kiln is calculated to obtain complete carbonization of the product. Then, the power of the boiler is dimensioned according to the energy valorization choice. So, a plant is characterized either in terms of output power, or in terms of capacity for a defined waste input. Table 10.25 gives examples of different rotary kiln dimensions

Rotary kilns are commonly used for different waste streams such as contaminated soils, petroleum residues, car shredder refuse, municipal solid waste (MSW) mixed with sludge and industrial waste, used tyres, etc.

Moving-bed furnaces can be classified in three families:

- fixed vertical cylindrical furnaces equipped with rotating moving blades (Okadora, Japan). Many installations exist in Japan for different waste streams, including tyres and waste plastics;
- fixed horizontal cylindrical furnaces equipped with moving blades (Cosa, formerly Alcyon, Taiwan). One installation for tyre pyrolysis;
- horizontal tubes equipped with Archimedean screws (Compact Power, UK). The pyrolitic products are immediately transferred in a steam gasification reactor

Table 10.25 Examples of rotary kilns dimensions

Waste nature	Capacity (t/h)	Length (m)	Diameter (m)	Constructor
Various	5.3	28	2.8	Noell Salzgitter (1983)
Mixed plastics	1.5	28	2.8	Noell Salzgitter (1983)
Tyres	2	28	2.8	Noell Salzgitter (1983)
MSW	2.5	18	2.2	PKA
Composite material		13	1.3	Pyropleq-Technip (1990)
MSW	3	17	2.2	Siemens-Goldshöfe
MSW	5	20	2.9	Mitsui-Seibu R21
MSW	7.5	23	3.2	Mitsui-Siemens
MSW	4.0			Thide (2003)
Tyres	2.0–2.5	11.5	1.8	VTA (2004)

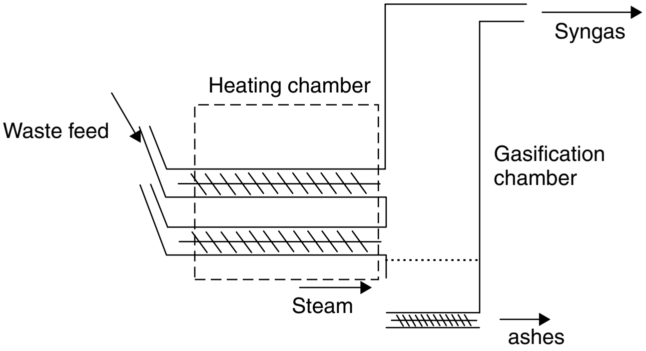

Figure 10.19 Screw pyrolyser followed by gasification

(Figure 10.19). Demonstration plant 1 t/h for hospital waste and many runs on different waste streams.

- horizontal hearth equipped with moving blades (Pyrovac, Canada). One plant is devoted for biomass pyrolysis. A lot of experience on tyre pyrolysis.

The furnaces are generally heated by the exhaust gases issued from the combustion of the pyrolitic gases. Cosa adopted an electrical heating system and Pyrovac a circulating molten salt system.

3.3.2 Fast Pyrolysis

Fast pyrolysis (and flash pyrolysis) needs a very high heat transfer to and inside the material. Fluidized-bed technology is therefore well adapted for this purpose [68–70]. New developments in this field involve vortex ablative pyrolysis technology. In both cases, high heat transfer within the material needs strict charge preparation (fine grinding).

The *entrained flow reactor* is usually used for biomass, but can be used for mixed plastics. A stoichiometric air–propane burner produces the inert hot flue gas that flows upwards through the vertical reactor and entrains the particles while heating. The Georgia Institute of Technology has developed an entrained flow reactor for biomass (6.4 m height,

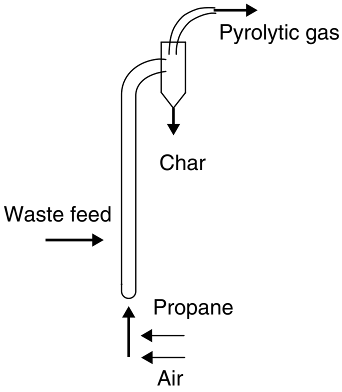

Figure 10.20 Entrained flow reactor

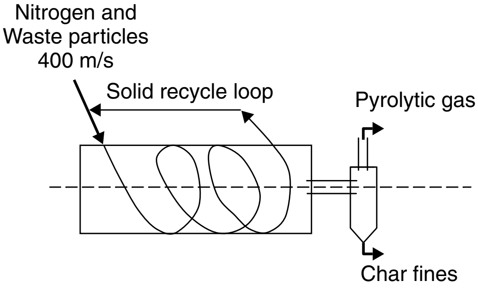

Figure 10.21 Vortex ablative reactor

0.15 m diameter) with a capacity of 500 kg/h (Figure 10.20). The thermal energy of the flue gas is used to heat the particles and provide the heat for pyrolysis reactions. A typical carrier-gas to input mass ratio is about 4:7. It seems that a large quantity of nitrogen is needed.

In the *vortex ablative reactor*, the waste particles are entrained in a nitrogen flow (a few m/s) and enter the preheated cylindrical reactor tangentially. As the residence time in the reactor is rather low, incompletely converted solid particles are separated and recycled in the system. The liquid oil film on the wall evaporates rapidly before cracking. The vortex ablative reactor developed by SERI (Golden, CO) has a length of 0.7 m and a diameter of 0.13 m (Figure 10.21). This technology can also be used for plastic waste [71].

As these technologies have been developed for small particles, scaling-up to a few t/h is of major interest.

3.4 GASIFICATION TECHNOLOGIES

Gasification differs from pyrolysis in that oxygen is introduced in the reactor (air, steam, or pure O_2) and reacts partly at high temperature with some carbon available in the waste.

The partial combustion produces the heat necessary for the process inside the furnace and in the gasification reactions, the waste is *directly heated*.

By pure oxygen gasification, the gas contains mainly carbon monoxide and tars. On the other hand, by air gasification, a large amount of nitrogen is present, and a low-calorific gas is produced (4–6 MJ/m^3). By steam gasification there is a formation of a syngas rich in CO and H_2. (10–15 MJ/m^3). Combined steam and oxygen gasification is also used in order to have better temperature control of the process (steam gasification is endothermic). From 15 to 20 MJ/m^3 can be reached for the gas produced by steam gasification under pressure. Gasification also produces ash. Some gasifiers operate under high pressure.

3.4.1 Types of Reactor

The different gasifier types are listed here:

- shaft gasifiers: air or oxygen (updraft and downdraft);
- fluidized-bed gasifiers: air–oxygen or steam (bubbling and circulating);
- multiple hearth: air;
- rotary kilns: air.

The quality of the gasification products are related to the material input and will differ according to the technologies used. Tar formation can be a major problem in some cases. For a well-defined material input, the choice of the technology will depend on the products (gas or liquids) valorization method.

During *updraft gasification* (fixed-bed reactor), the waste moves slowly towards the bottom and the airflow counter-currently to the waste flow. Hot gases are generated at the bottom and pass through the down-flowing waste. Gasification occurs progressively in the fixed bed, the gases, tars and moisture are entrained towards the top and do not reach the hot zone of the furnace. There is less thermal breakdown so that the produced gas can be rich in heavy oils and tars.

In *downdraft gasification* (fixed-bed reactor), the air and the waste flow co-currently down. The gasification occurs within the bed with the formation of gas, oils and tars reaching progressively the high temperature zone so that thermal breakdown occurs. These products react afterwards in the gasification zone with oxygen and/or steam, producing hydrogen and light hydrocarbons with fewer tars (pilot plant Grüssing, Germany).

In the *bubbling fluidized bed*, the material stays in the bed during the gasification process. The pyrolitic gas, oils and tars are entrained with the fluidizing gas with less thermal breakdown of the tars. Ash contributes to the bed formation.

In the *circulating fluidized bed*, high fluidizing velocities are needed and the solids are elutriated. They are separated from the gases and recycled to the reactor in order to achieve the gasification process. Ash is discarded continuously. Mixed plastic pellets are gasified by this process in a Lurgi CFB gasifier at SVZ (Schwarze Pumpe, Germany). In Rüdersdorf, Germany, a CFB gasifier produces a gas fuel for firing a lime kiln.

In *multiple hearth furnaces*, the waste is fed into the top and moves down through the hearths by the rotation of rabbling arm. Air is injected at the bottom and at different levels so that the flue gas mixed with the pyrolitic gases flow counter-currently upstream, heating the waste. Ash is extracted at the bottom of the furnace. A Nesa furnace has been installed to produce fuel gas at the Origny cement kiln plant (Rochefort-sur Nenon, France).

The *rotary kiln* consists of an inclined cylinder lined with ceramics. The waste introduced at the front end is mixed by the rotation of the kiln (a few rpm) and is heated progressively when moving down and carbonizing while pyrolitic gases are released. The fixed carbon with the minerals reach the other cylinder end where a controlled air input (under-stoichiometry) gasifies the carbon into CO. The counter-current flow of hot carbon monoxide and nitrogen progressively heat the waste and are mixed with the pyrolitic gases. Complete combustion occurs in a post-combustion chamber (Basse Sambre-ERI furnaces in Budapest and Iceland).

3.4.2 Examples of Industrial Plants Treating Plastic waste

The gasification process is particularly effective for the treatment of plastics. The reducing atmosphere and the presence of hydrogen leads to an instant breakdown of the molecular structure of the plastic to form CO and H_2 while any halogen compounds are released for capture in the gas clean-up system [72].

SVZ (Sekundärrohstoff Verwertungszentrum Schwarze Pumpe) is a centre for the reuse of secondary raw material. This plant consists of seven downdraft fixed-bed gasifiers and two entrained flow reactors [73]

The *Lurgi fixed-bed grate gasifiers (FBG)* have been derived from Lurgi fixed-bed gasification technology [74]. They are designed to process solid waste. With 3.6 m diameter, they operate with a mixture of steam and oxygen at a pressure of 24 bar. Each gasifier has a capacity range between 8 and 14 t/h (depending on feedstock composition). Solid waste such as plastics, rubber, fluff, are treated, as well as sewage sludge, contaminated wood, residues of paint, household waste. Prior agglomeration of the feed by briquetting or pelletizing is required for a good porosity of the charge inside the reactor and a good counter-current flow of the descending fuel through the charge.

The *British Gas/Lurgi slagging gasifier (BGL)* has been integrated into SVZ installations in order to increase the gasification capacity. This gasifier operates under pressure and provides the gasification of large particles and assures the vitrification of the inorganic matter.

The *Lurgi multi-purpose gasifier (MPG)* is an entrained flow gasifier used for liquid wastes (tars, oils, solvents, emulsions and also the tars and oils generated by the fixed bed reactors, and even slurries).

The SVZ plant produces synthetic gas or fuel gas at atmospheric or elevated pressure, with the recovery of minerals in slag. There is a partial gas conditioning (CO shifting), a gas purification system with flue gas desulphurization. This plant is characterized by a high thermal efficiency and a flexible feedstock. A 120 000 t/a methanol plant is associated with it.

In the *Pernis* plant, Texaco has adopted a downdraft reactor fed with oxygen and/or steam according to the waste feed input. This technology has been developed for coal, heavy oils, petroleum coke, orimulsion, wastes and mixed plastics. End products could be energy (combined cycles), hydrogen, ammonia or methanol according the type of feed [75].

Texaco has recently adapted its gasification process to plastics waste [76]. The project is to develop a capacity of 40–50 kt/yr in Pernis (Netherlands). This process consists in two parts; a liquefaction step and an entrained bed gasifier. The plastic waste is depolymerized in the liquefaction step into synthetic heavy oil and some condensable and noncondensable gases. The oil and the condensable gas are injected in the gasifier (mixed oxygen–steam gasification between 1200 and 1500°C). The main components of the syngas are CO and H_2 with smaller amounts of methane, carbon dioxide and water. In this project, the aim is to sell the syngas to the chemical industry. The process is classified as feedstock recycling for mixed plastic waste [77].

Noell have develop different gasification technologies based on 'Noell entrained-flow gasification' (with cooling screen and quench, with cooled walls or with cooling screens) [78,79]. This company is also developing a process combining pyrolysis and gasification, the Noell conversion process. The Noell-KRC gasification facilities are located in Freiberg, Germany.

The different pyrolysis and gasification technologies, consisting of the production of solid, liquid and/or gaseous fuels, have achieved a significant industrial throughput and could be a clean alternative to the direct combustion of plastics.

3.5 FUEL VALORIZATION

3.5.1 By Pyrolysis

According to the principle of indirect heating, the pyrolitic gases are not diluted by nitrogen or by combustion products. Tables 10.26 and 10.27 give some examples of refuse-derived fuels obtained by pyrolysis of different waste streams [80].

Product yields from mixed plastics pyrolysis are about 2.9% char, 75.1% oils and 9.6% noncondensable gas [16,48]. Calorific values of the oils are about 40 MJ/kg.

When PVC is present in the starting mixture, its thermal degradation occurs in two steps [81]. Bockhorn *et al.* [33] showed that the first step starts at about 200°C with dehydrochloration [82]. Hydrochloric acid is formed during the first stage of carbonization and can react with hydrocarbon radicals to produce organochlorinated compounds in the gas phase [3]. During co-pyrolysis and gasification of PVC with cellulose derived material (wood and straw), McGhee *et al.* [83] showed that char yields are greater than those produced by pyrolysis of individual components because of the reaction of HCl with

Table 10.26 Examples of RDF issued by pyrolysis at 500°C for different waste streams

Waste	Gas + oils (kg/t)	Char (% ashes) (kg/t)	Metals and minerals (kg/t)
Tyres	550	300 (15%)	150
Sorting refuse 1*	350 + 310 kg water	80 (31%)	260
Sorting refuse 2*	370 + 170 kg water	60 (31%)	400
Sorting refuse 3*	700	180 (42%)	120
Mixed waste with PCB-PCDD-PCDF	280	720 (51%)	
ASR 1	538	205 (64%)	257
Paper recycling refuse (dry)	700	200 (33%)	100
MSW	390 + 200 kg water	240 (40%)	170

* With mixed plastics

Table 10.27 Examples of energy content of RDF issued by pyrolysis of different waste

Waste	Gas + oils (MJ/kg)	Char (MJ/kg)
Tyres	38	28
Sorting refuse 1*	20	20
Sorting refuse 2*	16	20
Sorting refuse 3*	28	5.5
Mixed waste with PCB-PCDD-PCDF	9	3.3
ASR	31	10
Paper recycling refuse (dry)	23	21
MSW	13	18

* With mixed plastics

cellulose below 330°C. The chars produced in these conditions are relatively unreactive. When lignin is present in the waste, these compounds could be adsorbed on the char [84]. Addition of basic compounds during pyrolysis leads to the formation of calcium chloride in the char that can be leached out by washing [1]. This approach has been tested at pilot and industrial scale [85].

3.5.2 By Gasification

The syngas produced by air gasification has a rather low heating value, between 4 and 6 MJ/m^3 according to the nature of the gasified material. With oxygen gasification, the gas can reach 8–14 MJ/m^3. The best results are obtained by steam gasification (up to 18 MJ/m^3).

The raw gas generally contains tars and fine char particles. The advantages in using the produced gas fuel directly by combustion in a boiler or in a furnace are that these hot gases do not have to be cleaned to a great extent. The installed piping and burners have to be able to tolerate some contaminants in order to avoid fouling or clogging. When the gas is used in gas turbines or prime movers in order to generate power or electricity, they have to be cleaned to high specification [86].

The gasification of the char issued from the pyrolysis of different waste streams is shown in Table 10.28. From the ash content of the char, it is possible to evaluate the quantity of syngas produced by steam gasification of the chars issued from the pyrolysis of the different waste streams. The combination of the syngas and the pyrolytic gases allows evaluation of the total potential energy recovered by gasification.

It can be seen that a significant proportion of the energy content of the waste is recovered by the gasification of the char and that the ultimate residue is decreased in comparison with the quantity of bottom ash produced compared with direct incineration. Solid plastic waste represents a significant stream for conversion back to energy [89].

There is a need to choose the best technology, well adapted to the local situation (waste dispersion and end-products market). Taking into account the revenues from tipping fees for waste elimination and the sale of the energy and/or the end-products, the operating

Table 10.28 Energy recovered in syngas and pyrogas [87,88]

Waste	Syngas production (kg/t_{waste})	Energy in syngas (GJ/t_{waste})	Energy in pyrogas (GJ/t_{waste})	Total energy recovered (GJ/t_{waste})
tyres	525	9.2	20.9	30.1
Sorting refuse 1	28	0.5	7	7.5
Sorting refuse 2	21	0.4	5.9	6.3
Sorting refuse 3	126	2.2	19.6	21.8
Mixed waste with PCB-PCDD-PCDF	990	17.3	2.5	19.8
ASR	282	4.9	16.7	21.6
Paper recycling refuse (dry)	275	4.8	16.1	20.9
MSW	330	5.8	5.1	10.8

costs and the transport costs, a clean economic solution could be a pyrolysis or gasification plant with on-site energy valorization or production of substitute fuels.

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11

Yield and Composition of Gases and Oils/Waxes from the Feedstock Recycling of Waste Plastic

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1 INTRODUCTION

Plastic polymers make up a high proportion of waste and the volume and range used is increasing dramatically. Thermoplastics are by far the most common type of plastic, comprising almost 80% of the plastics used in Europe, they are also the most easily recyclable. The consumption of plastics in Western Europe is of the order of 38 million tonnes per year and the majority is used in the production of plastic packaging, household and domestic products, electrical and electronic goods. There is also significant consumption of plastics for the building and construction industry and automotive industry. Figure 11.1 shows the distribution of plastics end-use in Western Europe by sector [1].

It is estimated that only about 50% of the plastics produced in Western Europe each year are available for collection and recycling. Of this collectable waste plastic, about 15%, representing about 3 million tonnes, is recycled in Western Europe. A further 23% of the plastics available for collection is incinerated with other wastes, mainly as municipal solid waste and the ‘recovery’ of the plastic in such cases is via energy recovery. The remainder of the plastic waste is disposed of, mainly to landfill. Table 11.1 shows the main industrial/commercial and municipal waste sectors which produce the waste plastic and the routes for recycling, energy recovery and disposal [1].

The separated recycled plastic material is processed by the end user by being granulated or pelletized, melted or partially melted and extruded to form the end product. The recycled plastic may be added to virgin plastic during the process. Outlets for single types of recycled plastics include for example, high-density polyethylene for dustbin sacks, pipes and garden furniture, polyvinyl chloride for sewer pipes, shoes, electrical fittings

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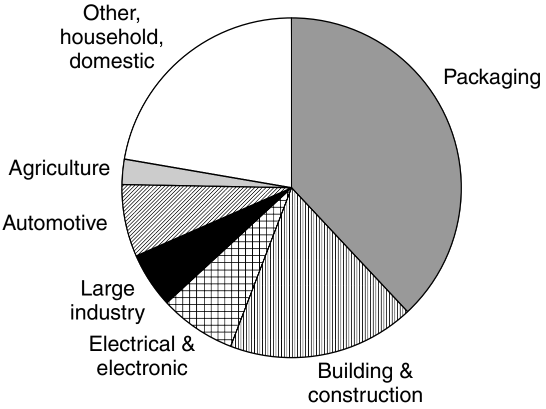


Figure 11.1 Plastics end-use in Western Europe by sector [1]

Table 11.1 Consumption and waste management of plastics by sector for Western Europe [1]

Sector	Consumption (1000 t)	Waste (1000 t)	Recycling (1000 t)	Recovery (1000 t)	Disposal (1000 t)
Agriculture	953	286	161	0	125
Automotive	2669	851	61	35	755
Building and construction	6710	530	58	0	472
Industry	5969	4130	1418	441	2271
Electrical and electronic	2783	854	34	4	816
Household	19039	13324	1087	4103	8139
Total	38123	19980	2819	4583	12578

and flooring and polyethylene terephthalate for egg cartons, carpets, fibre filling material and audio cassettes [2]. Applications for plastic mixtures have included plastic fencing, industrial plastic pallets, traffic cones, playground equipment and garden furniture. Other uses for recycled plastic products include their use in the construction industry for pipes, damp-proof membranes, plastic lumber and plastic/wood composites [3].

The low-grade uses for mixed plastic recycled materials has led to research into feedstock recycling or pyrolysis of plastics where the plastic waste materials are processed back to produce basic petrochemicals that can be used as feedstock to make virgin plastic [4]. The process has the advantage that, in addition to the processing of single plastic types, mixed plastics can also be used since all of the feedstock is reduced to petrochemicals. Feedstock recycling can be via hydrogenation at high temperature and pressure or via pyrolysis in an inert atmosphere at atmospheric pressure to thermally degrade the plastics. Pyrolysis of plastics thermally degrades the plastic, breaking the bonds of the polymer to produce lower-molecular-weight oligomers and monomers. The vapours resulting from the process are condensed to produce an oil/wax hydrocarbon product which has a high degree of purity and can be refined at the petroleum refinery to produce a range of petrochemical products, including virgin plastic.

The key process parameters that control the product yield and composition include the heating rate and temperature of pyrolysis. The heat is supplied by indirect heating such as the combustion of the gases or oil or directly by hot gas transfer. Very slow heating rates coupled with a low final maximum temperature maximizes the yield of char, for example, the production of char from wood in the form of charcoal involves a very slow heating rate to moderate temperatures. The process of carbonization of waste results in reduced concentrations of oil/tar and gas product and are regarded as by-products of the main charcoal forming process. Moderate heating rates in the range of about 20–100°C/min and maximum temperatures of 600°C give an approximate equal distribution of oils, char and gases. This is referred to as conventional pyrolysis or slow pyrolysis. Because of the slow heating rates and generally slow removal of the products of pyrolysis from the hot pyrolysis reactor, secondary reactions of the products can take place. Generally, a more complex product slate is found. Very high heating rates of about 100–1000°C/s at temperatures below 650°C and with rapid quenching lead to the formation of a mainly liquid product, referred to as fast or flash pyrolysis. In addition, the carbonaceous char and gas production are minimized. The primary liquid products of pyrolysis are rapidly quenched and this prevents breakdown of the products to gases in the hot reactor. The high reaction rates also cause char-forming reactions from the oil products to be minimized [5, 6].

At high heating rates and high temperatures the oil products quickly break down to yield a mainly gas product. Typical yield of gas from the original feedstock hydrocarbon is 70%. This process differs from gasification which are a series of reactions involving carbon and oxygen in the form of oxygen gas, air or steam to produce a gas product consisting mainly of CO, CO_2, H_2 and CH_4. Table 11.2 shows the typical characteristics of different types of pyrolysis [5, 6].

Plastic polymers make up a high proportion of waste and the volume and range used is increasing dramatically. The two main types of plastic are thermoplastics which soften when heated and harden again when cooled and thermosets which harden by curing and cannot be remoulded. The six main plastics in municipal solid waste are, high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene terephthalate (PET). In addition there are

Table 11.2 Typical characteristics of different types of pyrolysis [5, 6]

Pyrolysis	Residence time	Heating rate	Reaction environment	Pressure (bar)	Temperature (°C)	Major product
Carbonization	hrs-days	Very low	Combustion products	1	400	Charcoal
Conventional	10 s–10 min	Low–moderate	Primary/ secondary products	1	<600	Gas, char liquid
Flash-liquid	<1 s	High	Primary products	1	<600	Liquid
Flash-gas	<1 s	High	Primary products	1	>700	Gas
Ultra	<0.5 s	Very high	Primary products	1	1000	Gas, chemicals
Vacuum	2–30 s	Medium	Vacuum	<0.1	400	Liquid

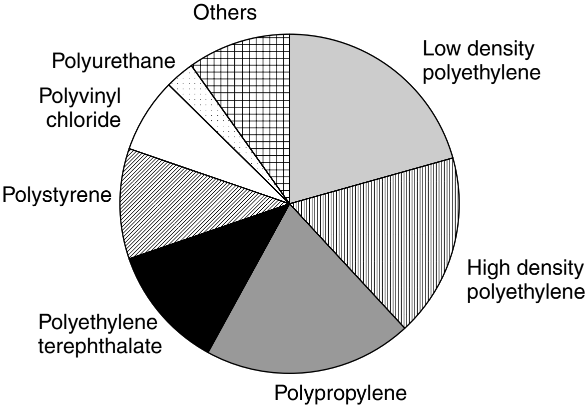


Figure 11.2 The main plastic types found in municipal solid waste [1]

a range of thermoset plastics, including polyester, polyurethane, polyamide, polycarbonate, phenolic and epoxy resins. Thermoplastics are by far the most common types of plastic comprising almost 80% of the plastics used in Europe, they are also the most easily recyclable. In many countries, plastic is collected from commercial and industrial sources as separate plastic fractions, much of which is recycled directly back into the plastic product manufacturing process. Although plastics make up between 5 and 15wt% of municipal solid waste it comprises 20–30% of the volume. The plastics in municipal solid waste are mainly in the form of plastic film and rigid containers. Plastic film comprises about 3–4 wt% of the household waste stream and is almost impossible to recycle. However, plastic containers are more easily collected separately or segregated from the waste stream. Figure 11.2 shows the proportion of the main plastic types found in municipal solid waste [1].

The detailed analysis of the derived oil/wax and gas products from the pyrolysis of plastics in relation to process conditions and different types of plastic is essential in providing data for the assessment of the feedstock recycling process. In addition, the yields and composition of gases and oils from the pyrolysis of mixed plastic waste are important in assessment of the process and to determine the possibility of any interactions between the plastics during pyrolysis.

2 FEEDSTOCK RECYCLING OF PLASTICS

2.1 PRODUCT YIELD

2.1.1 Product Yield from the Feedstock Recycling of Single Plastics

Table 11.3 shows the yield of gas, oil/wax and char from the fixed bed pyrolysis of the main polyalkene plastics, polyethylene and polypropylene, found in municipal solid waste [7–15]. Table 11.4 shows the gas, oil/wax and char from the pyrolysis of other plastics [7–9, 14–17]. All of the plastics produced an oil/wax and gas and in some cases a char. The product yield related directly to the type of plastic, the reactor type

Table 11.3 Product yield from the pyrolysis of polyalkene plastics

Feedstock	Reactor type	Temperature (°C)	Gas (wt%)	Oil/wax (wt%)	Char (wt%)	Reference
PE	Fluidized-bed	760	55.8	42.4	1.8	[9]
PE	Fluidized-bed	530	7.6	92.3	0.1	[9]
LDPE	Fluidized-bed	700	71.4	28.6	0.0	[10]
LDPE	Fluidized-bed	600	24.2	75.8	0.0	[10]
LDPE	Fluidized-bed	500	10.8	89.2	0.0	[10]
LDPE	Fixed-bed (batch)	700[1]	15.1	84.3	0.0	[7]
HDPE	Fixed-bed (batch)	700[1]	18.0	79.7	0.0	[7]
LDPE	Fixed-bed (batch)	500[1]	37.0	63.0	0.0	[15]
LDPE	Ultra-fast pyrolysis	825	92.9	5	2	[11]
HDPE	Fixed-bed (batch)	450	13.0	84	3	[12]
HDPE	Fixed-bed (batch)	430	9.6	69.3	21.1	[13]
HDPE	Vacuum	500	0.9	97.7	0.8	[14]
LDPE	Vacuum	500	2.7	96.0	1.0	[14]
LLDPE	Fluidized-bed	730	58.4	31.2	2.1	[8]
LLDPE	Fluidized-bed	515	0.0	89.8	5.9	[8]
PP	Fixed-bed (batch)	380	24.7	64.9	10.4	[13]
PP	Fixed-bed (batch)	700[1]	15.3	84.4	0.2	[7]
PP	Fluidized-bed	740	49.6	48.8	1.6	[9]
PP	Vacuum	500	3.5	95	<0.1	[14]
PP	Fixed-bed (batch)	500[1]	55.0	45.0	0.0	[15]

[1] Final temperature

and the process conditions, particularly pyrolysis temperature. The product oil produced from pyrolysis varies considerably in colour. For example, it has been reported that at temperatures of approximately 500°C, the polyalkene plastics, PE, HDPE, LDPE and PP produce a light-coloured waxy product [7]. Polyvinyl chloride produces a black oil, polystyrene produces a red/brown oil and polyethylene terephthalate produces a dark, almost black, viscous oil [7]. The condensable products derived from the thermoset plastic polyester/styrene resin used in composite production, consisted of a yellow/brown, low-viscosity oil, which accounted for approximately 80 vol% of the total condensable yield, a pale yellow wax and some water. Thermal decomposition of a thermoset phenolic resin used in a composite plastic generated a yellow/brown oil (50%), water (45%) and wax, whereas epoxy resin produced a viscous, dark brown/orange oil with some water (10 vol %) [18].

The distinction between the yield of condensed hydrocarbon wax and oil is a consequence of the pyrolysis reaction system, temperature, condensation collection system and condensation temperature. For example, fluidized-bed pyrolysis of various plastics at 550°C in a fluidized-bed reactor with rapid cooling of the condensate using water-cooled condensers produced an oil/wax ratio of 1.23 for HDPE, 0.50 for LDPE, 0.82 for PP, 4.75 for PS and 1.48 for PET [19]. In addition, it was shown that PVC produced 100% oil and no wax [19]. Kaminsky *et al.* [9] pyrolysed polyethylene in a fluidized-bed reactor at 530°C and reported an oil yield of 50.3 wt% and a wax yield of 42 wt%. Miranda *et al.* [14] for the vacuum pyrolysis of various plastics reported 88 wt% conversion of LDPE to wax and 8 wt% to an oil. For HDPE, the conversion was 92.3 wt% to wax and

Table 11.4 Product yield from the pyrolysis of other plastics

Feedstock	Reactor type	Temperature (°C)	Gas (wt%)	Oil/wax (wt%)	Char (wt%)	Reference
PS	Vacuum	500	<0.1	99.3	0.4	[14]
PS	Fixed-bed (batch)	700[1]	3.4	83.8	3.5	[7]
PS	Fluidized-bed	500	0.2	99.7	<0.1	[16]
PS	Fluidized-bed	580	9.9	89.5	0.6	[9]
PS	Fluidized-bed	600	0.7	98.7	<0.2	[17]
PS	Fluidized-bed	532	11.5	88.5		[8]
PS	Fluidized-bed	708	15.2	83.3		[8]
PVC	Vacuum	520	58.5[a]	32.4	8.5	[14]
PVC	Fixed-bed (batch)	700[1]	55.8[b]	31.7	13.8	[7]
PVC	Fluidized-bed	740	63.1[c]	28.1	8.8	[9]
PVC	Fluidized-bed	520	84.6[d]	6.3	9.1	[8]
PET	Fixed-bed (batch)	500[1]	73.4	9.1	18.5	[15]
PET	Fixed-bed (batch)	700[1]	38.7	41.3	15.6	[7]
Thermoset plastics						
Polyurethane	Fluidized-bed	760	37.9	56.3	0.3	[9]
Polyester	Fluidized-bed	768	50.8	40.0	7.1	[9]
Polyamide	Fluidized-bed	760	39.2	56.8	0.6	[9]
Polycarbonate	Fluidized-bed	710	26.5	46.4	24.6	[9]

[1] Final temperature
[a] Includes 58.2 wt% HCl
[b] Includes 52.9 wt% HCl
[c] Includes 56.3 wt% HCl
[d] Includes 56.0wt% HCl

5.4 wt% to oil, for PP the conversion to wax was 70 wt% and 25 wt% oil. They also showed that when polystyrene was pyrolysed in the vacuum reactor, 58.6 wt% light oil was produced and 40.7 wt% heavy oil [14].

Table 11.3 shows that, in most cases, the three polyalkene plastics produced very similar product yields, with high yields of wax, and hydrocarbon gas and negligible char yields. Higher temperatures of pyrolysis result in thermal cracking of the oil/wax to produce increased concentrations of gas. For example, Kaminsky *et al.* [9] reported an oil/wax yield of 92.3 wt% and 7.6 wt% gas, at a pyrolysis temperature of 530°C in a fluidized bed. However at the higher temperature of 760°C, the oil/wax was thermally degraded to produce 42.4 wt% oil/wax and 55.8 wt% gas.

In addition to temperature, the type of pyrolysis reactor is also important in determining product yield. High heating rates with short hot-zone residence times and rapid quenching of the products are regarded as favouring the formation of oil/wax products. Such conditions are typically found in fluidized-bed reactors. The pyrolysis gases and vapours are removed from the hot reactor and condensed before further reaction breaks down the higher-molecular-weight species into gaseous products. Therefore, the removal of pyrolysis products from the hot zone reduces the extent of secondary reactions which are known to increase the yield of char and gas at the expense of oil formation [20, 21]. For example, Cypres and Bettens [20] increased the rate of removal of pyrolysis vapours from a secondary hot zone by increasing the flow of nitrogen carrier gas. They found that this increased the yield of oil by reducing the secondary reactions. Primary vapours are first produced in the pyrolysis process, the characteristics of which are most influenced by heating rate. These primary vapours then degrade to secondary tars and gases, the proportion and characteristics of which are a function of temperature and time. Higher oil/wax yield may also be produced where the volatile products are quickly removed from the hot zone by, for example, nitrogen purge gas [7, 22] or under vacuum pyrolysis conditions [14]. Under fast pyrolysis conditions, at high temperature the major product is gas due to thermal cracking of the oil/wax. For example, Table 11.3 shows that fluidized-bed ultra-fast pyrolysis at high temperatures produces mainly gas from low-density polyethylene.

Table 11.4 shows the product yield of gas, oil/wax and char from the pyrolysis of other single plastics, including thermoplastics and thermoset plastics. Pyrolysis of polystyrene under moderate temperatures of between 500 and 600°C produces high levels of oil. Even at higher temperatures above 700°C, there is a high conversion of the polymer to oil. In fact the oil mainly consists mainly of the monomer styrene [8, 9, 23, 24].

Polyvinyl chloride produces a significantly lower yield of oil compared with the polyalkenes and polystyrene (Table 11.4). This reduction in oil yield is attributable to the conversion of the chlorine in the PVC molecule to hydrogen chloride gas under pyrolysis conditions. For example, Miranda *et al.* [14] report a hydrogen chloride gas yield of 58.2 wt%, Williams and Williams [7] report a hydrogen chloride yield of 52.9 wt%, Kaminsky *et al.* [9] a yield of 56.3 wt% hydrogen chloride and Scott *et al.* [8] a hydrogen chloride yield of 56.0 wt% in the gas. In addition, a significant proportion of char is produced during the pyrolysis of PVC.

The pyrolysis of polyethylene terephthalate produces large quantities of gas dominated by carbon dioxide and carbon monoxide, in addition to a wax and significant yield of char. Polyethylene terephthalate is characterized by a high proportion of oxygen in its chemical structure, unlike the other common polyalkene plastics (HDPE, LDPE, PP), polystyrene and polyvinyl chloride. The high oxygen content leads to the formation of mainly carbon dioxide and carbon monoxide and also to a wax which is characterized by high concentrations of oxygenated compounds.

Research on the pyrolysis of thermoset plastics is less common than thermoplastic pyrolysis research. Thermosets are most often used in composite materials which contain many different components, mainly fibre reinforcement, fillers and the thermoset or polymer, which is the matrix or continuous phase. There has been interest in the application of the technology of pyrolysis to recycle composite plastics [25, 26]. Product yields of gas, oil/wax and char are complicated and misleading because of the wide variety of formulations used in the production of the composite. For example, a high amount of filler and fibre reinforcement results in a high solid residue and inevitably a reduced gas and oil/wax yield. Similarly, in many cases, the polymeric resin is a mixture of different thermosets and thermoplastics and for real-world samples, the formulation is proprietary information. Table 11.4 shows the product yield for the pyrolysis of polyurethane, polyester, polyamide and polycarbonate in a fluidized-bed pyrolysis reactor [9].

2.1.2 Product Yield from the Feedstock Recycling of Mixed Plastics

The pyrolysis of mixtures of single plastics and real-world plastic derived from municipal solid waste has been investigated by several researchers and the yield of gas, oil/wax

Table 11.5 Product yield from the pyrolysis of mixed plastic

Feedstock	Reactor type	Temperature (°C)	Gas[a] (wt%)	Oil/wax (wt%)	Char (wt%)	Reference
Plastic mixture	Vacuum	520	6.3	91.8	1.3	[14]
Plastic mixture	Fixed-bed	700[1]	9.6	75.1	2.9	[27]
Plastic mixture	Fluidized-bed	600	44.7	43.2	7.6	[28]
Plastic mixture	Fixed-bed	500	85.2	12.5	3.0	[15]
MSW plastic	Fluidized-bed	787	43.6	26.4	25.4	[9]
MSW plastic	Fixed-bed	430	25	59	16	[22]

[1] Final temperature
[a] Gas yield includes HCl

and char are shown in Table 11.5 [9, 14, 15, 22, 27, 28]. The plastic mixture represents pure single plastics which are mixed to produce a mixture typically representative of the proportions of those plastics found in municipal solid waste. Table 11.5 shows that such mixtures of single plastics tend to produce lower char product yields compared with the pyrolysis of plastics derived from real-world municipal solid waste. This suggests that plastics derived from real-world municipal solid waste contains perhaps contamination and also plastics other than the common plastics of municipal solid waste, that is, polyethylene, polypropylene, polystyrene, polyvinyl chloride and polyethylene terephthalate. Perhaps including a proportion of thermoset plastics. Higher temperatures of pyrolysis produce increased concentrations of gas, as was found for the pyrolysis of single plastics. For example, Williams and Williams [28] examined the influence of temperature between 500 and 700°C on the product yield and product composition from the fast pyrolysis of mixed plastic waste in a fluidized bed. They found that the gas yield increased from 9.79 to 68.81 wt% as the temperature of pyrolysis was increased from 500 to 700°C. In addition, there was a corresponding decrease in oil/wax yield from 55.07 to 18.44 wt%. They also examined the influence of temperature on the separate yield of oil and wax, they found that the wax yield was 17.28 wt% (31.4% of the total oil/wax yield) at 500°C and decreased to 0.0 wt% at 700°C.

2.2 GAS COMPOSITION

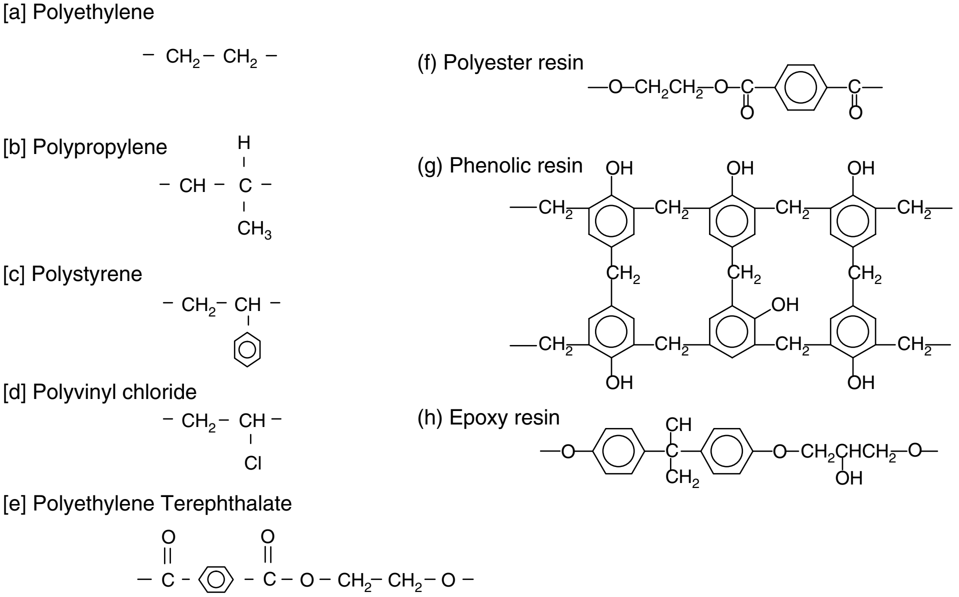
2.2.1 Gas Composition from the Feedstock Recycling of Single Plastics

Table 11.6 shows the composition of gases derived from the pyrolysis of individual single plastics from various researchers [7–9, 11, 19, 27]. The three polyalkene plastics, HDPE, LDPE and PP, behave quite similarly in that the main gases to be formed are alkene gases derived from the thermal degradation of their similar polyalkene chemical structure as shown in Figure 11.3. Ethene, and propene are the most common hydrocarbon gases. However, Kaminsky *et al.* [9], using higher temperatures of pyrolysis, found increased concentrations of methane compared with fixed-bed pyrolysis [7]. The thermal degradation of polyalkenes has been described as a random scission process whereby during degradation the rupture of bonds takes place at purely random points along the polymer chain length [29, 30]. Thus, all the bonds which remain intact at any one stage in the

Table 11.6 Gas composition from the pyrolysis of single plastics

	Reactor type	H_2 (wt%)	CH_4 (wt%)	C_2H_6 (wt%)	C_2H_4 (wt%)	C_3H_8 (wt%)	C_3H_6 (wt%)	C_4H_{10} (wt%)	C_4H_8 (wt%)	CO_2 (wt%)	CO (wt%)	HCl (wt%)	Reference
HDPE	Fixed-bed	0.12	1.90	2.21	6.08	1.31	4.56	0.22	0.36				[7]
PE	Fluidized-bed	0.8	23.8	6.7	20.0	0.08	5.6		0.6				[9]
LDPE	Fixed-bed	0.05	1.14	1.67	4.00	1.33	4.00	0.32	2.00				[7]
LDPE	Ultra-fast		22		28		18						[11]
LLDPE	Fluidized-bed		4.6	2.2	19.4	0.8	12.0	13.1[1]					[8]
PP	Fixed-bed	0.05	0.93	1.45	3.52	1.00	3.53	0.23	1.29				[7]
PP	Fluidized-bed	0.7	28.2	4.0	13.9	0.09	3.7		0.4				[9]
PS	Fixed-bed	0.04	0.53	0.08	0.26	0.02	0.05	0.00	0.06				[7]
PS	Fluidized-bed		0.06		0.04								[9]
PVC	Fixed-bed	0.12	0.77	0.47	0.15	0.24	0.19	0.11	0.15			52.93	[7]
PET	Fixed-bed	0.31	0.71	0.03	1.41	0.13	0.09	0.00	0.00	22.71	13.29	0.00	[7]
Polyester	Fluidized-bed	0.3	3.8	0.2		0.05	0.1			26.9	17.4		[9]
Polyurethane	Fluidized-bed	0.7	16.1	1.8	7.2	0.2	1.3		0.1	1.8	34.0		[9]
Mixed plastic	Fixed-bed	0.08	0.97	1.01	1.67	0.70	0.83	0.14	2.20	2.06		2.31	[27]
Mixed plastic	Fluidized-bed	0.22	2.87	2.39	5.65	1.26	5.53	0.24	6.35			1.42	[19]

[1] Total of C_4 gases



[a] Polyethylene

[b] Polypropylene

[c] Polystyrene

[d] Polyvinyl chloride

[e] Polyethylene Terephthalate

(f) Polyester resin

(g) Phenolic resin

(h) Epoxy resin

Figure 11.3 Repeating chemical structures of some common plastics

degradation process have the same probability of being broken, leading to the formation of polymer fragments of varying sizes. Since the bond energy of the C=C bond is much higher than the other bonds found in the polymer structure [31], there is a tendency to form alkenes in the derived product stream. The alkene gases, ethene, propene and to some extent butene represent the low-molecular-weight range of the random scission process. The alkane gases, methane, ethane, propane and butane are also present in significant concentrations, again formed as part of the random scission process of the thermal degradation of the polymer. The derived gases have a significant calorific value and it has been suggested that the gases may provide the energy requirements for the pyrolysis process, enhancing the economic viability. No carbon monoxide or carbon dioxide were formed from the pyrolysis of the polyalkenes since there is no oxygen present in the polymer.

Polystyrene gives a low gas yield overall, since there is a much higher conversion of the plastic to oil/wax. The derived gas composition consists mainly of alkene gases, ethene, propene and butene and also methane.

Polyvinyl chloride gave hydrogen chloride as by far the main gas. The C–Cl bond in the PVC structure has a lower bond energy than other bonds in its structure and upon heating has a tendency to break first. As a consequence, PVC thermal degradation begins around 150°C which is a much lower temperature than the other common plastics. The intermolecular chain transfer reaction which follows leads to dehydrochlorination and hydrogen chloride is produced [32]. Once dehydrochlorination is complete, PVC yields hydrocarbon gases consistent with the thermal degradation of a vinyl polymer. Table 11.6 shows that the main hydrocarbon gases were hydrogen, alkanes and alkenes.

The pyrolysis of polyethylene terephthalate produces a gas consisting mainly of carbon dioxide and carbon monoxide, due to the high oxygen content of the original plastic polymer (Figure 11.3). In addition, much lower, but significant, concentrations of ethene and propane are formed. Carbon dioxide is formed from the decarboxylation of the PET, carbon monoxide may be formed via either decarboxylation or reaction between carbon dioxide and char [33].

Pyrolysis of polyester produces a large conversion of the polymer to carbon dioxide and also carbon monoxide [9]. The generation of carbon monoxide and especially carbon dioxide seen at all pyrolysis temperatures is due to the large number of ester bonds in the resin. The pyrolysis of polyurethane in a fluidized bed at 700°C produced mainly carbon monoxide and methane [9]. Thermogravimetric decomposition studies of polyurethane where pyrolysis takes place in a fixed bed of sample have been shown to produce mainly carbon dioxide and carbon monoxide [34]. It has been suggested that the carbon dioxide is produced by the breaking of the urethane bond and that degradation begins at around 250°C [35]. Significant yields of methane and ethane have been reported at temperatures above 600°C [36]. In addition, it has also been reported that hydrogen cyanide can be formed during pyrolysis, from the isocyanates used in polymer production [36].

2.2.2 Gas Composition from the Feedstock Recycling of Mixed Plastics

Table 11.6 also shows the gas composition from the pyrolysis of mixed plastic waste representative of the plastics found in municipal solid waste. The major gases were hydrocarbons with smaller amounts of carbon dioxide and hydrogen chloride. The major hydrocarbons produced were the alkene gases, ethene, propene and butene and the alkane gases, methane, ethane, propane and butane. The carbon dioxide is produced due to the presence of the PET. Hydrogen chloride, is produced from the PVC present in the mixture of plastics. The interaction of the various single plastics in a mixture has been investigated [7]. The data suggest that less hydrogen, methane and ethane and more butane are formed than would be expected from the theoretical estimates derived from the pyrolysis of single individual plastics.

2.3 OIL/WAX COMPOSITION FROM THE FEEDSTOCK RECYCLING OF SINGLE PLASTICS

The oil/wax from the feedstock recycling of plastics has potential uses either as direct use as a fuel, for further upgrading to higher-quality petroleum refined substitute fuels or as a chemical feedstock. As such, the detailed analysis of the oil/wax is important. There are several routes and levels of analysis. For example, infrared analysis such as Fourier transform infrared (FTIR) spectrometry provides a broad analysis of the chemical groups found in the oils/wax. Similarly, the molecular weight range of the oils provides an indication of the distillation potential of the oils to produce refined fuels. Analysis of the oils for their potential as directly useable fuels requires standard fuel tests developed for the petroleum industry. Detailed identification of individual compounds in the oil/waxes requires analytical techniques such as liquid chromatography, gas chromatography and mass spectrometry.

2.3.1 Fourier Transform Infrared Spectrometry of Oils/Waxes

Figure 11.4 shows the functional group compositional analysis by Fourier transform infrared (FTIR) spectrometry of the oil/wax derived from the fixed bed pyrolysis of HDPE, LDPE and PP [7]. Figure 11.5 shows the functional group compositional analysis of oil derived from the fixed-bed PVC, PS and PET analysed by FTIR spectrometry [7]. Figure 11.6 shows the functional group compositional analysis of the six main mixed plastics found in municipal solid waste, in their relative proportions [27]. Figure 11.7 shows the functional group compositional analysis of oil/wax from the fixed-bed pyrolysis of polyester resin, phenolic resin and epoxy resin [18].

Figure 11.4 shows that the polyalkene plastics, HDPE, LDPE and PP, gave very similar FTIR spectra since their polymer structures are very similar and their thermal degradations are likely to produce similar compounds in the derived oil/wax [7]. The peak at 3050 cm^{-1} is an indication of the presence of =C–H stretching vibrations typical of alkene functional groups. The peaks between 3000 cm^{-1} and 2800 cm^{-1} indicate the presence of $-CH_3$, $-CH_2$ and C–H functional groups which are indicative of aliphatic species such as alkanes and alkenes. The C=C absorbance peak between 1625 cm^{-1} and 1675 cm^{-1} confirms that alkene groups are present in the oil/wax. The presence of peaks in the region of 1350–1500 cm^{-1} due to the deformation vibrations of C–H bonds confirm the presence

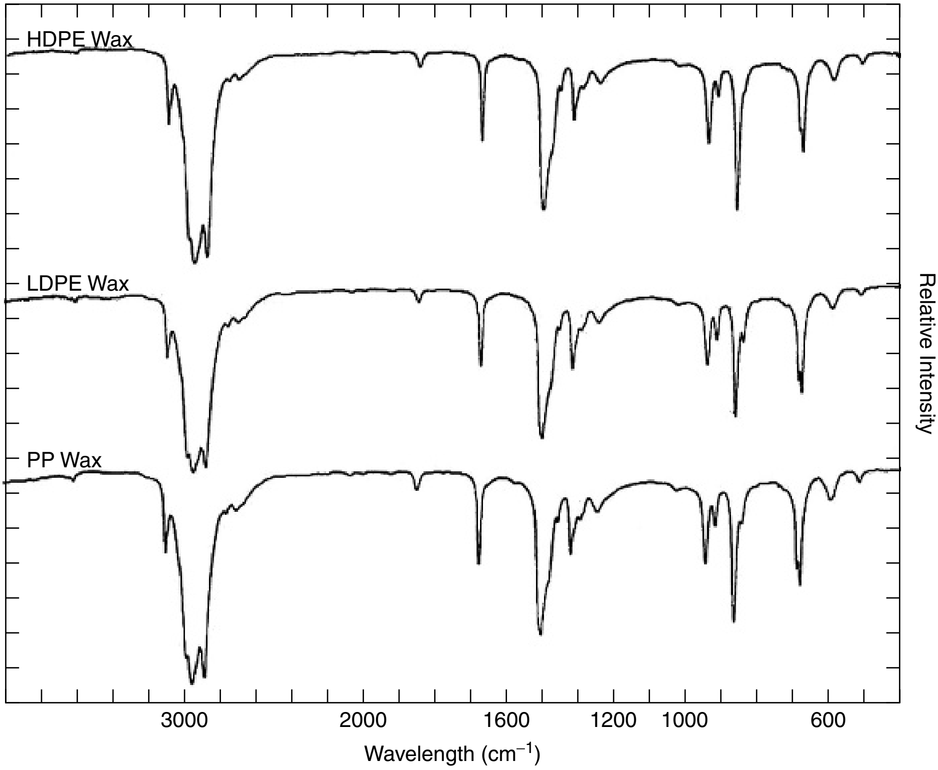


Figure 11.4 Fourier transform infrared spectra of the waxes derived from the pyrolysis of high-density polyethylene, low-density polyethylene and polypropylene

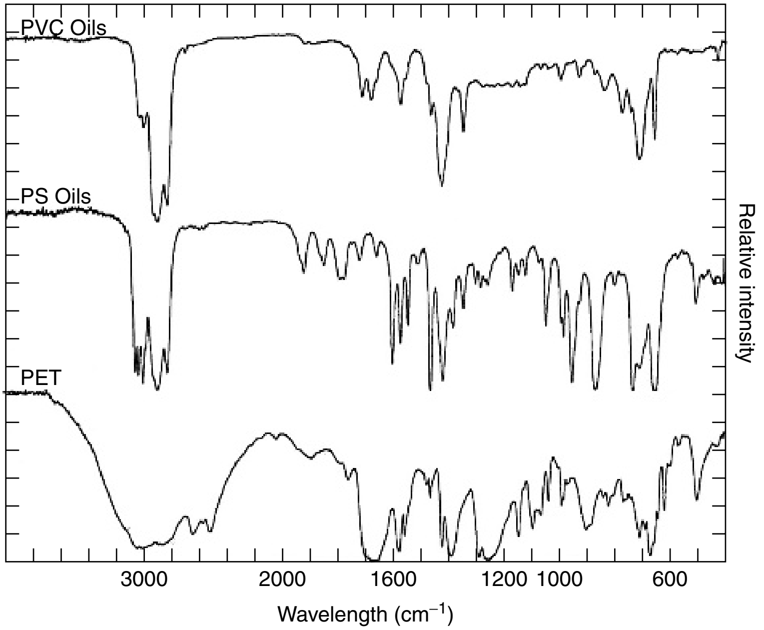


Figure 11.5 Fourier transform infrared spectra of the oils/waxes derived from the pyrolysis of polyvinyl chloride, polystyrene and polyethylene terephthalate

of aliphatic groups. The peaks located at 980 and 920 cm^{-1} represent CH stretching and deformation vibrations of alkene structures. Two peaks between 720 and 730 cm^{-1} indicate C–H cyclic deformations which suggest either aromatic or more likely –CH_2 which has split due to interaction in long molecular chains representing the presence of long oligomer chains. The overall spectra of the polyalkene pyrolysis oil/wax is therefore dominated by the presence of alkane and alkene compounds as has been found by other workers [37, 38].

Figure 11.5 shows that the functional group compositional analysis of the pyrolysis oil/waxes derived from the fixed-bed pyrolysis of PVC, PS and PET is very different from the polyalkene plastic pyrolysis oil/waxes. The spectra of the PVC pyrolysis oil/wax shows that the characteristic peaks of alkanes and alkenes are present as described for the polyalkene plastics. Since the PVC plastic polymer is based on a similar backbone structure to the polyalkene plastics, a similar degradation product oil/wax composition may be expected. However, the spectra for PVC in Figure 11.5 show that there are additional peaks in the region of 675–900 cm^{-1} and 1575–1625 cm^{-1}. The presence of these peaks indicates the presence of mono-aromatic, polycyclic aromatic and substituted aromatic groups. Benzene has been identified as a major constituent in oils derived from the pyrolysis of PVC whilst other aromatic compounds identified included alkylated benzenes and naphthalene and other polycyclic aromatic hydrocarbons [19, 32, 39]

The pyrolysis oil/wax derived from the fixed-bed pyrolysis of PS produced a strong presence of both aromatic and aliphatic functional groups. The presence of CH_3 and CH_2 are indicated by the peaks between 3000 and 2800 cm^{-1} and the peak in the region of

1350–1500 cm^{-1} due to the presence of C–H bonds confirm the presence of aliphatic groups. In addition, there are strong peaks present in the region of 675–900 cm^{-1} and three strong peaks between 3000 and 3050 cm^{-1} showing a very significant presence of aromatic compounds in the oil/wax. It has been shown that pyrolysis oil/wax from PS produces a mainly aromatic oil [8, 40], consequently the aliphatic functional groups indicated by the FTIR spectra probably indicates that these aliphatic groups are present as alkyl groups attached to aromatic rings.

The FTIR analysis for the oil/wax derived from PET pyrolysis produced a complex spectrum which included oxygenated functional groups in addition to aliphatic and aromatic groups. The oxygen atoms, aromatic ring and aliphatic groups in the original polymer structure leading to a very complex composition of compounds in the resultant pyrolysis oil/wax. The broad peak between 3300 and 2900 cm^{-1} may be due to intramolecular OH or hydrogen bonded OH groups. The presence of such groups, coupled with the presence of C=O stretching vibrations between 1650 and 1850 cm^{-1} indicates the presence of carboxylic acids and their derivatives. The presence of the C=O peaks between 1650 and 1850 cm^{-1} may also indicate the presence of ketones and aldehydes. Aromatic groups are indicated by the peaks between 675 and 900 cm^{-1} and 1575–1625 cm^{-1}.

Figure 11.6 shows the FTIR spectra for the pyrolysis oil from the pyrolysis of mixed plastics. The plastic mixture simulating that found in municipal solid waste. Since almost 70% of the plastic mixture was composed of the polyalkene plastics, HDPE, LDPE and PP, it would be expected that the thermal degradation products of these plastics will dominate the mixed plastic oil/wax composition. However, since polystyrene and polyvinyl chloride produce an aromatic oil/wax product on pyrolysis, then a significant aromatic content in the oils and waxes derived from the pyrolysis of the mixed plastic waste might also be expected. Figure 11.6 shows that the chemical groups found in the individual plastics pyrolysis oils are also found in the mixed plastic pyrolysis oil. However, it has been suggested that there is some interaction between the reaction products of the individual polymers to produce a significantly different chemical composition compared with what might be expected be mere addition of the individual polymer product compositions [7, 27].

Figure 11.7 shows the FTIR traces from oils/waxes derived from the fixed-bed pyrolysis of some thermoset plastics, polyester resin, phenolic resin and epoxy resin. The spectra produced from the polyester oil/wax featured a strong, broad peak at 3432–3437 cm^{-1}, derived from O–H stretching. The breadth of the peak suggests carboxylic acid groups, while the relatively clear definition and high peak centre wavenumber suggests the presence of alcoholic compounds. Very prominent absorption peaks at 1720 and 1285 cm^{-1} were assigned to C=O and C–O stretching respectively and were consistent with the presence of carboxylic acid, carbonyl and/or ester groups [41]. Other studies have identified all of these types of oxygenated compounds in the decomposition products of polyester [26, 42]. Groups of sharp peaks at 1500–1630 cm^{-1} and 700–910 cm^{-1} were due to skeletal vibrations and out-of-phase C–H bending of aromatic rings respectively [41]. This evidence, together with the relatively low ratio of methyl groups to methylene groups at 2960 and 2930 cm^{-1}, suggest a highly aromatic structure with little alkylation or chain branching. Taken as a whole, the spectra suggest that the oil/wax comprises mainly unchanged lengths of polyester chain, with changes in functional group where chain scission has

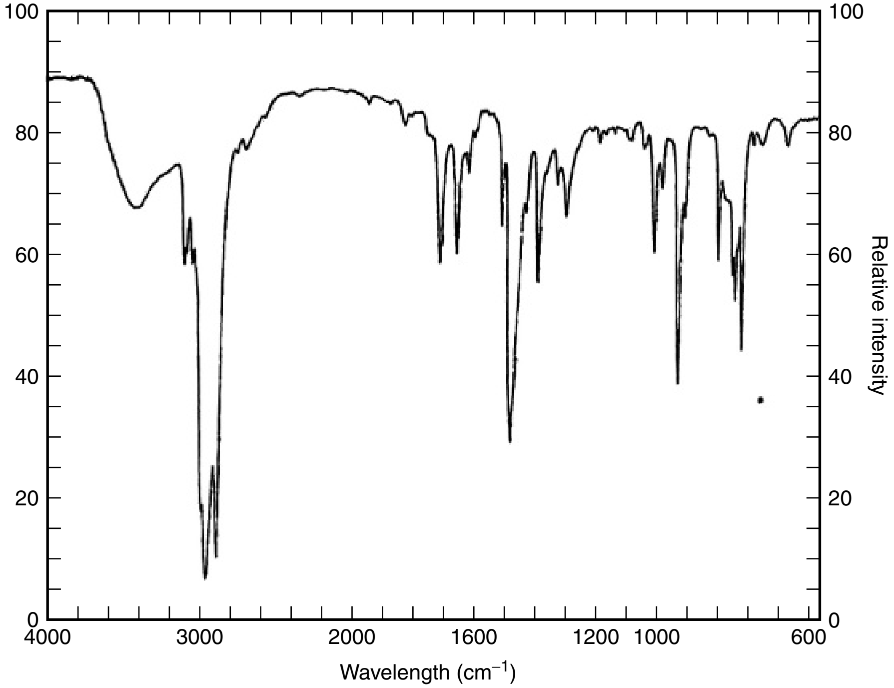


Figure 11.6 Fourier transform infrared spectra of the oil derived from the pyrolysis of mixed plastics

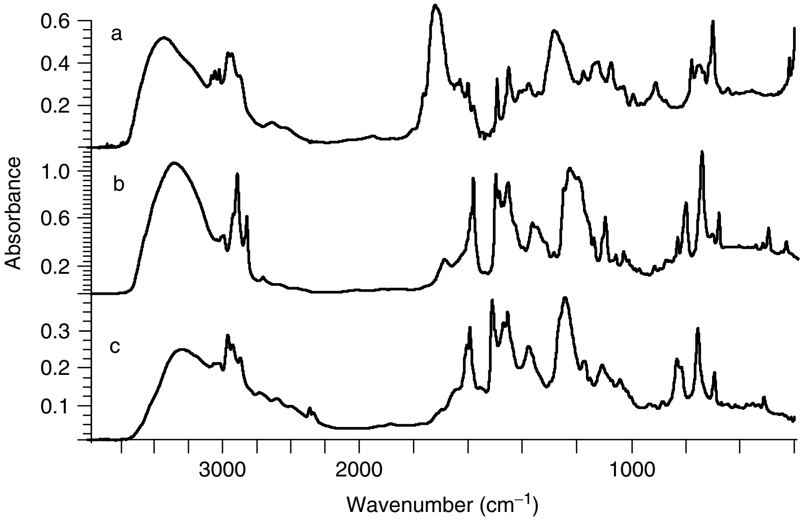


Figure 11.7 Fourier transform infrared spectra of the oils/waxes derived from the pyrolysis of polyester resin (a), phenolic resin (b) and epoxy resin (c)

occurred. As scission is most likely at the oxygen-containing groups [26, 43], one would expected to find a range of oxygenated functional groups present in the oils.

The oil derived from the phenolic resin used in a composite plastic sample produced a strong, more clearly defined hydroxyl peak at 3381–3385 cm^{-1}. The spectra showed large groups of peaks attributable to aromatic rings. A very strong peak at 1244 cm^{-1} and a less strong peak at 1379 cm^{-1} were attributed to C–O stretching/O–H bending interactions observed in phenols [41]. Strong peaks at 2925 and 2854 cm^{-1} caused by asymmetrical and symmetrical stretching of the C–H bond indicated a high proportion of methylene groups, whilst the proportion of methyl groups was comparatively low, indicating a relatively low degree of aromatic alkylation or aliphatic chain branching. These data therefore suggest that these samples were predominantly comprised of phenol, phenol derivatives and short lengths of the polymer chain.

The oil/wax from pyrolysis of epoxy resin composite produced similar spectra to those seen from the phenolic sample [18]. The hydroxyl stretch peak was broader, suggesting the presence of carboxylic acid groups, although no carbonyl groups were present to support this supposition. The ratio of methyl groups to methylene groups was higher than in the phenolic sample, suggesting greater alkylation of the phenolic units or branching of aliphatic chains than in the former case. These results are consistent with the structure of typical epoxy resins.

2.3.2 Molecular Weight Range of Pyrolysis Oils/Waxes

The molecular weight (MW) range of an oil/wax gives an indication of the boiling point range of the product which is a useful parameter in petrochemical process engineering to determine the compatibility of the recycled plastic product with the conventional petrochemical feedstocks derived from crude petroleum oil. Molecular weight range is determined by, for example, size exclusion chromatography, which is also known as gel permeation chromatography.

Figure 11.8 shows the molecular weight distribution for the waxes derived from the fluidized-bed pyrolysis of various plastics. There was no wax produced for the pyrolysis of polyvinyl chloride. The molecular weight range for the oils for polyvinyl chloride, together with the analysis of the oils for polyethylene terephthalate and polystyrene are shown in Figure 11.9. Table 11.7 shows data for the molecular weight range of oils and waxes derived from the pyrolysis of single plastics in a fluidized-bed reactor using a refractive index (RI) detector [19]. The MW distribution is usually determined as number and weight average MW, in addition the polydispersity of the oils was also calculated. The number average molecular weight M_n is defined as the average molecular weight according to the number of molecules present of each species [44]. The weight average molecular weight M_w is the sum of the product of the weight of each species present and its molecular weight divided by the sum of the weights of the species. The difference in the values of M_n and M_w indicates the polydispersity of the sample; the closer the two measured average molecular weights, the narrower the molecular weight distribution. Single compounds have a polydispersity in the range 1.0–1.1.

Table 11.7 shows that there was a shift to higher molecular weight distribution for the waxes compared to the oils, which is apparent when the number and weight average data of Table 11.7 are examined which show a distinct increase in value for the waxes

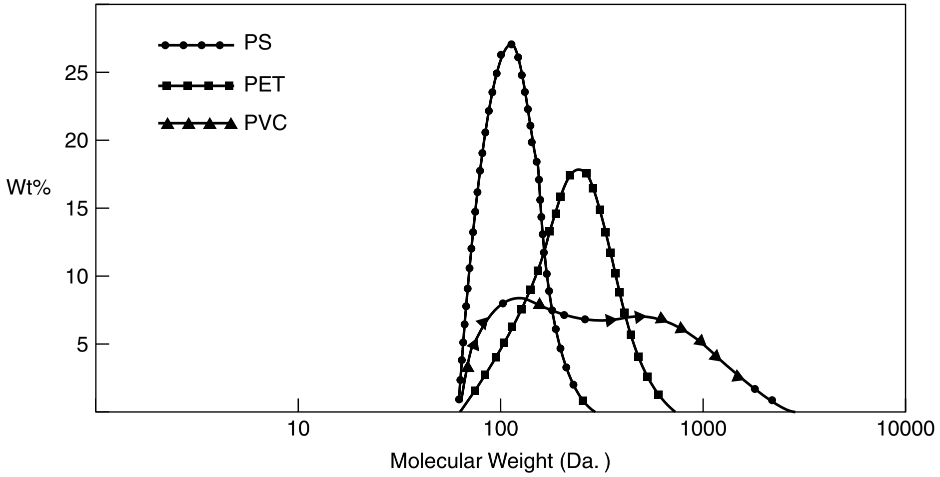


Figure 11.8 Molecular weight distribution of the oils derived from the fluidized-bed pyrolysis of polystyrene, polyvinyl chloride and polyethylene terephthalate

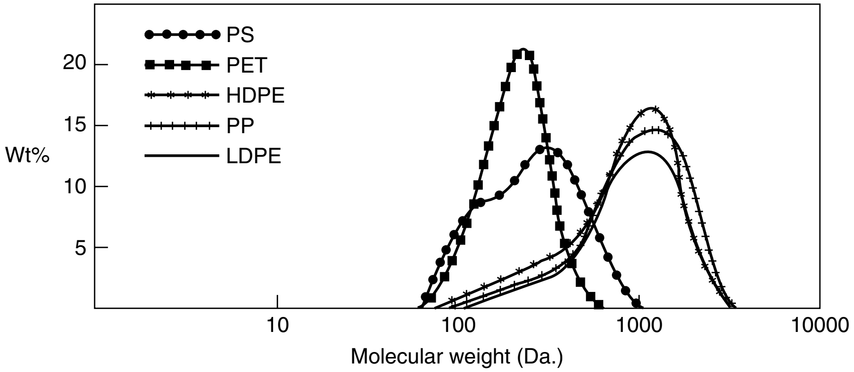


Figure 11.9 Molecular weight distribution of the waxes derived from the fluidized-bed pyrolysis of high-density polyethylene, low-density polyethylene, polypropylene, polystyrene and polyethylene terephthalate

compared with the oils. The waxes for the polyalkene plastics HDPE, LDPE and PP show a similar molecular weight distribution, ranging from a molecular weight of 100 to over 2000 Daltons with a peak molecular weight of approximately 1100 Da. Polystyrene wax showed a much lower molecular weight distribution from 80 to 190 Da. However, the main product from polystyrene pyrolysis was an oil which had a molecular weight range from 60 to 250 Da. Styrene has a molecular weight of 104 which accounts for the mostly low molecular weight nature of the oil sample. The molecular weight distribution of the pyrolysis oil from PVC was very wide, ranging from 60 to over 2000 Da, indicating that the polymer degradation had produced very high molecular weight compounds present in the oils. No wax was formed with PVC. Oil derived from PET pyrolysis gave a molecular weight distribution from 60 to approximately 800 Da. Table 11.7 also shows the

Table 11.7 Molecular weight data for oils and waxes from the fluidized-bed pyrolysis of individual plastics at 550°C [19]. (Reproduced by permission of the Energy Institute)

Product	HDPE	LDPE	PP	PS	PVC	PET
Oil						
M_n	416		422	103	203	191
M_w	629		659	111	420	233
Polydispersity	1.51		1.56	1.08	2.07	1.22
Wax						
M_n	731	556	682	200		191
M_w	1024	959	1067	284		221
Polydispersity	1.40	1.72	1.56	1.41		1.16

M_n = Number average molecular weight (Da)
M_w = Weight average molecular weight (Da)

polydispersity, which reflects the deviation of the molecular weight distribution from the Gaussian distribution of an ideal single compound. A higher polydispersity for a sample indicates a broader range of molecular weight distribution, reflecting a wider range of compounds present in the sample. The data suggest that the oils are all quite complex, containing a complex range of compounds. The polydispersity shown in Table 11.7 for the pyrolysis oil derived from polystyrene indicates that it very high in styrene, since the recorded polydispersity for a single compound is close to 1.0.

Figure 11.10 shows the molecular weight distribution for the oils and Figure 11.11 for the waxes derived from the fluidized-bed pyrolysis of the plastic mixture in relation to pyrolysis temperature. The oils show a higher proportion of low-molecular-weight species compared with the waxes and a clear bimodal distribution for the oils and waxes. The two peaks occur at molecular weights of about 120 and about 1200 Da., depending on whether

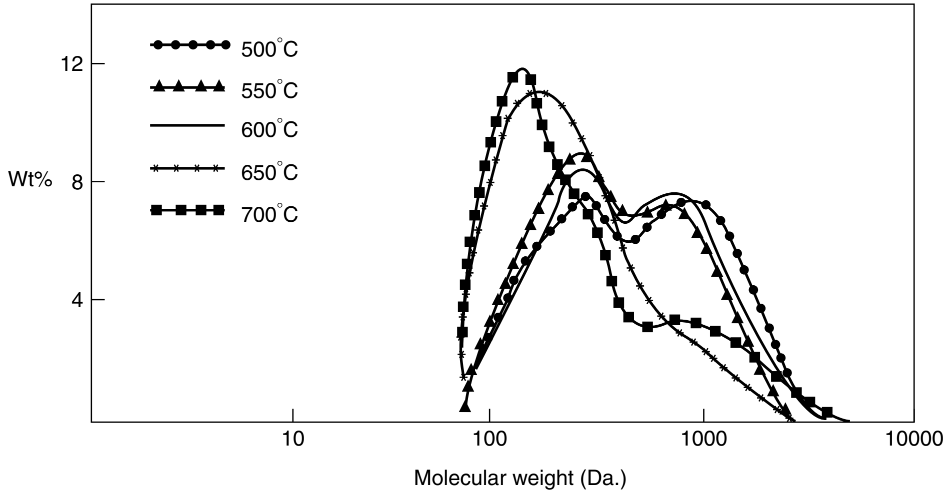


Figure 11.10 Molecular weight distribution of the oils derived from the fluidized-bed pyrolysis of mixed plastics in relation to pyrolysis temperature

the analysis is for oil or wax and also dependent on temperature. At higher temperatures of pyrolysis, the wax breaks down to produce an oil product and gas. The polyalkene plastics, HDPE, LDPE and PP gave peak molecular weights in the higher molecular weight region whereas the other plastics found in the mixture, PS, PVC and PET gave oils and waxes with peaks in the lower molecular weight region. Consequently, the lower fraction of the molecular weight distribution of the mixed plastic product is mainly due to PS, PVC and PET whilst the higher fraction of the molecular weight distribution is due mainly to HDPE, LDPE and PP.

Figure 11.12 shows the molecular weigh distribution of some examples of petroleum-derived fuels for comparison. The molecular weight distribution of the plastics are similar

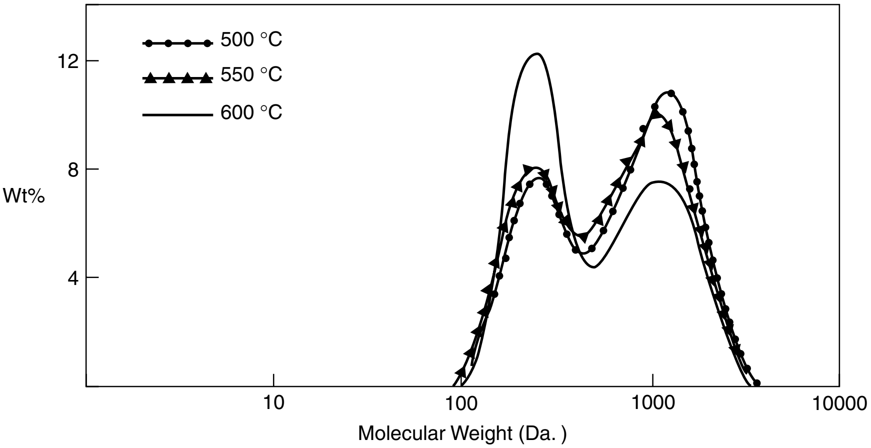


Figure 11.11 Molecular weight distribution of the waxes derived from the fluidized-bed pyrolysis of mixed plastics in relation to pyrolysis temperature

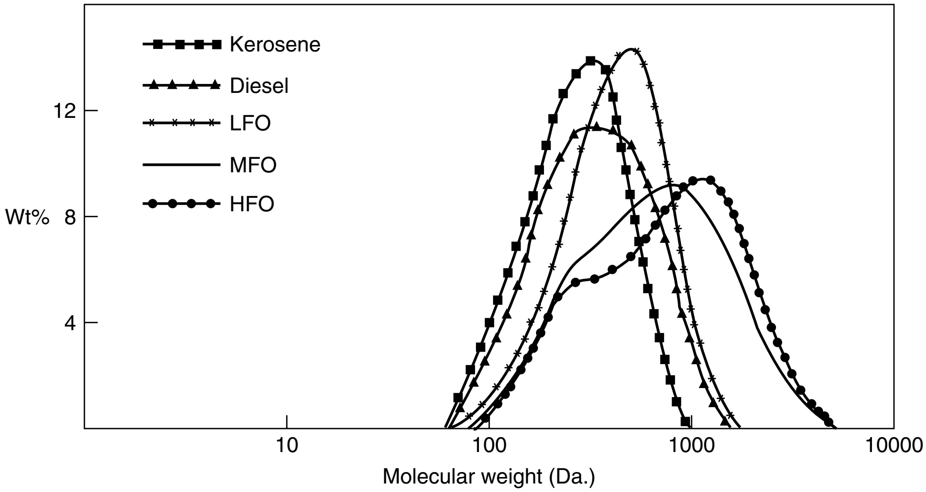


Figure 11.12 Molecular weight distribution of petroleum-derived fuels

to those of the refined petroleum fuels. For example, the oil derived from polystyrene and polyethylene terephthalate are similar to diesel fuel (gas oil) and the oils from the polyalkene plastics (HDPE, LDPE and PP) are similar to medium fuel oil. The waxes from the feedstock recycling of HDPE, LDPE and PP have been refined for use in the petrochemicals industry [45]. The wax produced from the pyrolysis of mixed plastic waste can be mixed with the naphtha fraction of petroleum oil at inputs of up to 20% [45]. The resultant mixture can then be fed to a conventional steam cracker without significantly altering the existing process to produce ethene and other alkenes which are then used to make new plastic polymers. The pyrolysis recycled plastic feedstock replaces naphtha or gas oils used in the conventional process. Alternatively, the oil/wax can be refined in a conventional fluidized catalytic cracker to produce gasoline and thereby replace petroleum gas oils [45]. It was reported that the oil/wax product from plastics pyrolysis was of high purity and would be easily accepted into the refinery process.

2.3.3 Fuel Properties of the Oils/Waxes from the Feedstock Recycling of Plastics

The oils derived from pyrolysis of plastics have the potential to be used directly as fuels. However, to act as direct substitutes for established petroleum-derived fuels requires detailed analysis of their fuel properties in comparison with those of petroleum refined fuels. Table 11.8 shows the fuel properties of oils derived from the pyrolysis of various plastics [46, 47]. Table 11.9 shows comparative data for refined petroleum fuels [48].

The analysis of oils for their fuel properties involves a range of standard ASTM tests. For example, flash point is determined by ASTM D93, calorific value by ASTM 129-64,

Table 11.8 Fuel properties of oils derived from the pyrolysis of various plastics

Property	PE[1]	PP[1]	PS[1]	Nylon[1]	PP 50%[1] PE 43% Nylon 7%	Polyester[2] styrene copolymer
Flash point (°C)	33.6	27.8	26.1	34.8	26.0	26.0
Pour point (°C)	2.7	−39	−67	−28	−5.0	
Water content (ppm)	0.18	0.13	0.67	2500	310	
Ash (wt%)	0.013	0.010	0.006	0.018	0.001	0.53
Viscosity (cst 50°C)	2.19	1.9	1.4	1.8	1.485	3.9[3]
Density (kg/m^3)	0.858	0.792	0.960	0.926	0.799	0.83
Cetane rating		56.8	12.6		54.3	
Carbon (wt%)						86.1
Hydrogen (wt%)						7.2
Sulphur (wt%)	0.01	0.01	0.01	0.01	0.013	0.0
Initial B.Pt (°C)						75
10% B.Pt (°C)						93
50% B.Pt (°C)						189
90% B.Pt. (°C)						354
CV (MJ/Kg)	52.3	53.4	50.4	44.4	46.3	33.6

[1] Reference [46]
[2] Reference [47]
[3] cst at 40°C

Table 11.9 Fuel properties of petroleum-derived fuels [48]

Fuel test	Kerosene	Gas Oil	LFO	HFO
Carbon residue (%)	<0.15	<0.35		
Viscosity				
40°C (cs)	1.2	3.3	21	30
Water content (%)		0.05	0.1	
Density (kg m^{-3})	0.84	0.78	0.89	0.95
Ash content		0.01	0.02	
Flash point (°C)	40	75	79	110
Carbon (%)		87.1	85.5	
Hydrogen (%)	13.6	12.8	12.4	11.8
Sulphur (%)	0.1	0.9	1.4	2.1
Initial boiling point (°C)	140	180	200	252
10% boiling point (°C)				
50% boiling point (°C)	200	300	347	
90% boiling point (°C)	315			
CV (MJ kg^{-3})	46.6	46.0	44.8	44.0

LFO = light fuel oil
HFO = heavy fuel oil

ash content by ASTM D482-74, distillation range by ASTM D86, relative density by ASTM D1298 and viscosity by ASTM D445.

The flash point of the oils derived from the pyrolysis of various plastics was low compared with petroleum-derived fuels, being less than 35°C in all cases. For comparison, diesel fuel has a required minimum flash point of 75°C and light fuel oil 79°C. The flash point of a liquid fuel is the temperature at which the oil begins to evolve vapours in sufficient quantity to form a flammable mixture with air. The temperature is an indirect measure of volatility and serves as an indication of the fire hazards associated with storage and application of the fuel. The low flash points of the oils may be expected since the oils typically represent an unrefined oil with a mixture of components having a wide distillation range. The pour point of a liquid fuel is the lowest temperature at which the oil is seen to flow and as such is an indication of the flow characteristics of the fuel. The viscosity of the plastics pyrolysis oils were similar to that of gas oil (diesel fuel). The viscosity of a fuel is an important property since it affects, for example, the flow of the fuel through pipes and other plant items, the atomization of the fuel in spray combustion systems and the performance and wear of diesel pumps. The density of the plastics pyrolysis oils was high compared with, for example, heavy fuel oils. The sulphur content of the oils was significantly lower than the petroleum refined fuels. The distillation range of the plastics pyrolysis oils reflects the fact that the oils are unrefined and consequently would be expected to have a wide range of boiling points for the components of the oil. This was also shown by the molecular weight distributions of the pyrolysis oils. The petroleum refined fuels have boiling point ranges consistent with their derivation, that is from the fractional distillation of crude petroleum oil.

The calorific value of the plastics pyrolysis oils was between 33.6 and 53.4 MJ kg^{-1} depending on the composition of the original plastic polymer. The calorific value was high apart from the oil derived from the polyester/styrene copolymer resin used in the manufacture of composite. This was attributable to the high oxygen content of the original polyester used in the formulation of the copolymer and which would result in a high oxygen content of the derived pyrolysis oil. The high oxygen content in the oil being responsible for the lowered calorific value.

2.3.4 Chemical Feedstock Potential of the Oils/Waxes from the Feedstock Recycling of Plastics

Feedstock recycling of plastics produces a hydrocarbon oil/wax product which has the potential to be used as a chemical feedstock. The oils and waxes derived from the pyrolysis of the polyalkene plastics, HDPE, LDPE and PP, produce an almost exclusively aliphatic oil and wax. For example, Figure 11.13 shows the gas chromatogram of the wax derived from the fluidized-bed pyrolysis of HDPE. Typically the waxes have a carbon number range up to about C_{60}, whereas the oils would be lower, typically peaking around C_{20}. Figure 11.13 for the wax in fact shows a bimodal distribution of carbon numbers, peaking at C_{14} and C_{30}. Examination of the wax in detail shows that it consists of a series of alkanes, alkenes and alkadienes (Figure 11.14). Gas chromatography has a limited range of resolution and data on the molecular weight distribution would suggest that much higher carbon number aliphatic compounds are present in the waxes. No significant production of aromatic compounds was detected in the waxes derived from the pyrolysis of HDPE, LDPE or PP in a fluidized-bed reactor at 550°C or in a fixed-bed reactor [7, 19]. However, Kaminsky *et al.* [9], using a fluidized-bed reactor at 740°C, reported very high levels of benzene at 19.2 wt% of the original polymer for the pyrolysis of polyethylene. In addition, they reported 18.2 wt% of benzene for polypropylene at 760°C pyrolysis

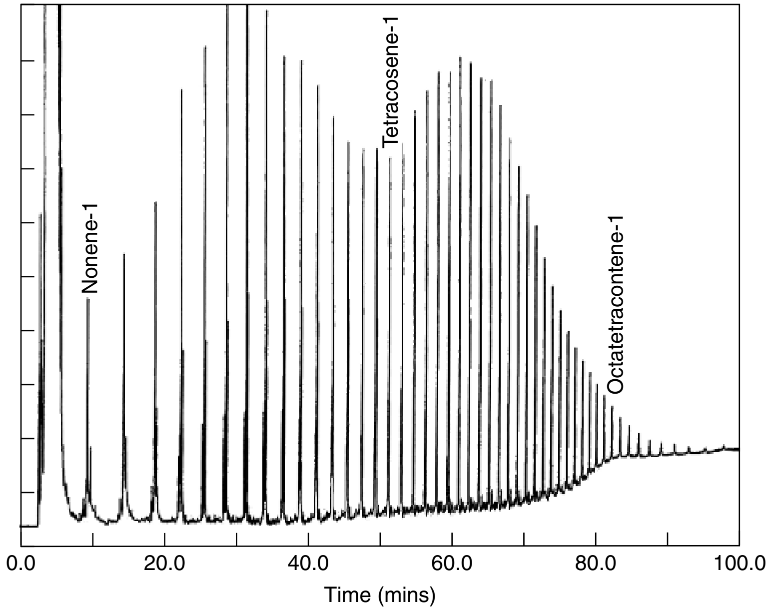


Figure 11.13 Gas chromatographic analysis of the wax material derived from the fluidized-bed pyrolysis of HDPE

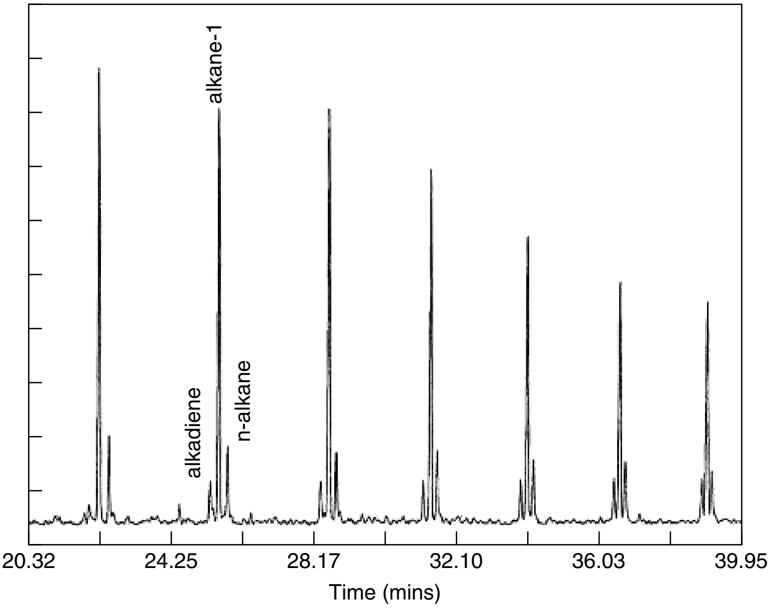


Figure 11.14 Detailed analysis of the gas chromatographic analysis of the wax material derived from the fluidized-bed pyrolysis of HDPE showing the alkadiene, the alkene-1 and the *n*-alkane

temperature. However, Kaminsky *et al.* [9] used a fluidized bed where the pyrolysis gas is partly recycled to provide the gas for fluidization and in addition the temperatures tend to be higher than some other workers. The recycling of the pyrolysis gases at higher temperatures may lead to increased concentrations of certain aromatic compounds, in particular benzene.

The thermal degradation mechanisms of the polyalkene plastics leading to the formation of various reaction products has been investigated by a range of researchers. It is suggested that the thermal degradation of HDPE and LDPE occurs via random scission to yield a wide spectrum of hydrocarbon fragments which may contain any number of carbon atoms [49, 50]. The C–C bond is the weakest in the HDPE and LDPE structure. However, during the degradation process the stabilization of the resultant radical after chain scission leads to the formation of carbon double bonds, $C = C$, in the structure [51]. The large number of compounds with carbon double bonds are shown by the higher concentration of alkenes in the resultant pyrolysis oil/wax. The thermal degradation of polypropylene has also been assigned to a random scission reaction which leads to the formation of a large number of hydrocarbon species. Because the polypropylene is similar in structure to HDPE and LDPE thermal degradation also results in a series of alkanes, alkenes and alkadienes [52]. However, because of the presence of the CH_3 side chain, different hydrocarbons may also form in addition to those outlined for HDPE and LDPE,

Pyrolysis of polystyrene produces an oil very high in concentration of the monomer, styrene and also other aromatic compounds. Figure 11.15 shows a typical gas chromatogram for the pyrolysis oil produced from the pyrolysis of polystyrene, showing

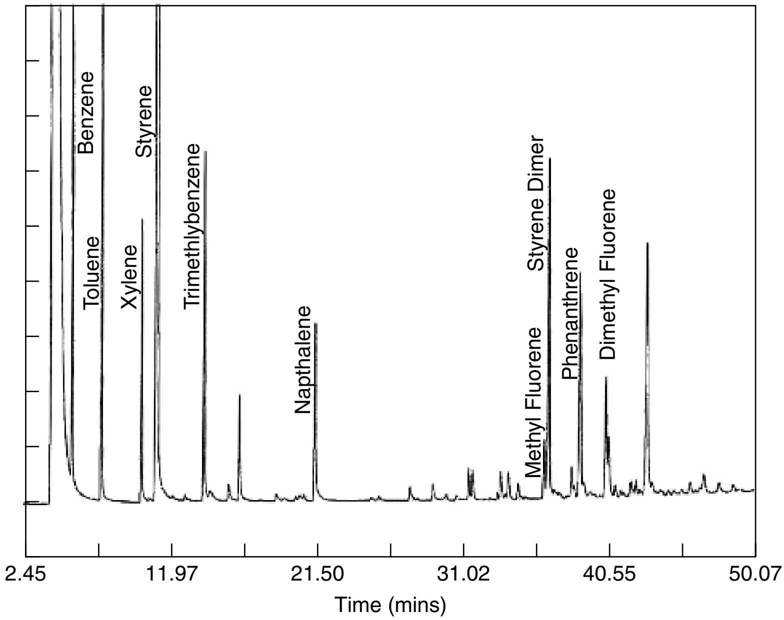


Figure 11.15 Gas chromatographic analysis of the oil material derived from the fluidized-bed pyrolysis of polystyrene

the high concentrations of styrene in the derived oils. For example, Kaminsky *et al.* [9] used a fluidized-bed reactor at 520°C for the pyrolysis of polystyrene and reported a styrene concentration of 76.8 wt% of the original polymer. Other workers have also shown that styrene occurs in very high concentrations in polystyrene-derived pyrolysis oils. For example, Scott *et al.* [8] using fast, fluidized-bed pyrolysis found a higher styrene yield of 76.2 wt% at a pyrolysis temperature of 532°C. Similarly, Buekens and Schoeters [23] also reported a styrene yield of 76 wt% from the fluidized-bed pyrolysis of polystyrene at 600°C. Bouster *et al.* [24] reported high yields of styrene with a maximum of 78.7 wt% for pyrolysis of polystyrene at 800°C. Nishizaki *et al.* [53] showed a lower yield of styrene of 50 wt% for the fast pyrolysis of polystyrene in the temperature range of 450–600°C. Williams *et al.* [16] also reported lower styrene yields of 56.1 wt% in the oil derived from the fluidized-bed pyrolysis of polystyrene at 600°C. Other compounds present in significant concentrations are the styrene dimer and trimer. In addition, the oils contain a significant proportion of toluene, xylene and alkylated benzenes, indene and indane and naphthalene [9, 16]. The thermal degradation mechanism for PS has been shown to be first via chain scission and then random scission [54]. This results in the formation of the styrene monomer and also styrene dimer, trimer and tetramer [55]. Other hydrocarbons formed by the degradation process have been identified as benzene, toluene, ethylbenzene and methylbenzene [54, 55].

The pyrolysis of PVC produces a highly aromatic oil in addition to hydrogen chloride yields of more than 50 wt% [7–9, 14, 19]. The oil contains mainly aromatic compounds. Benzene has been identified as the main aromatic compound at 22.1 wt% in the oil from the fluidized-bed pyrolysis of PVC [19]. Benzene has also been identified as the main product of PVC pyrolysis by Lattimer and Kroenke [32]. Montaudo and Puglisi [39] identified benzene and also naphthalene and some other polycyclic aromatic hydrocarbons in the thermal degradation product of PVC. The thermal degradation mechanism of PVC is initiated by a dechlorination reaction resulting in the formation of hydrogen chloride as was discussed previously. The vinyl structure of the plastic may indicate that aliphatic products may be a consequence of the thermal degradation, however, PVC pyrolysis clearly produces a mainly aromatic oil. The process of the elimination of a chloride atom from the structure results in the formation of a carbon double bond in addition to hydrogen chloride [55]. Further carbon double bonds are formed as more hydrogen chloride is evolved from the resultant chain. Eventually the chain undergoes cyclization to yield aromatic and alkylaromatic compounds [55].

Thermoset plastics have also been pyrolysed with a view to obtain chemicals for recycling into the petrochemical industry. Pyrolysis of a polyester/styrene copolymer resin composite produced a wax which consisted of 96 wt% of phthalic anhydride and an oil composed of 26 wt% styrene. The phthalic anhydride is used as a modifying agent in polyester resin manufacture and can also be used as a cross-linking agent for epoxy resins. Phthalic anhydride is a characteristic early degradation product of unsaturated thermoset polyesters derived from *ortho*-phthalic acid [56, 57]. Kaminsky *et al.* [9] investigated the pyrolysis of polyester at 768°C in a fluidized-bed reactor and reported 18.1 wt% conversion to benzene.

3 CONCLUSIONS

Pyrolysis of plastic waste has the potential to produce an oil or wax with potential uses in the petrochemicals industry. The process also produces a hydrocarbon-rich gas with a high calorific value which may be used to provide the energy requirements for the pyrolysis process. Key process parameters are the composition of the original plastic polymer, the temperature of pyrolysis, the fast removal of products from the hot zone of the reactor to minimize secondary reactions and the design of the reactor. The process may be optimized to produce a high calorific value gas or an oil/wax product. The oil/wax ratio is also dependent on a range of process parameters, including, temperature, condensation system and temperature and type of reactor. Oils from the pyrolysis of plastics have properties which are similar to petroleum-derived fuels. Waxes have a high purity and may be refined at the petroleum refinery to produce high-grade liquid fuels. Depending on polymer type, the oils may also contain valuable feedstock chemicals for use in the petrochemicals industry.

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12

Composition of Liquid Fuels Derived from the Pyrolysis of Plastics

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1 INTRODUCTION

The increasing demand for recycling plastics waste raises the question of how and to what kind of products can be converted. Pyrolysis proved to be a suitable feedstock recycling technique, converting the polymer material of waste into monomers, fuels or other valuable materials by thermal cracking processes. This method can be applied to transform both thermoplastics and thermosets, moreover, it is suitable for the treatment of mixed plastic wastes as well. Depolymerization of condensation polymers (polyester, polyamide, polyurethane) can be carried out through milder chemical pathways (methanolysis, glycolysis, hydrolysis, aminolysis), so pyrolysis is not the best choice for their recycling. Nevertheless, any type of plastic material may be present in plastic fractions of communal and other not thoroughly preselected wastes.

The quality of the product is of primary importance in developing a recycling technology converting plastics into fuels by pyrolysis. Today the characterization of a liquid fuel from any sources is obviously based on the qualification methods and standards of fuels from mineral oil. The properties of the pyrolysis-derived fuels from plastics are expected to be similar to conventional fuels (energy content, viscosity, density, octane and cetane number, flash-point, etc.). However, in addition to the familiar ranking values it is necessary to know more about the chemical composition of the plastic pyrolysis oil, because of the peculiarities as follows:

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- There are a considerably larger variety of compositions of the plastic pyrolysis oil than that of petroleum-related oils because of the diversity of the chemical composition and structure of the source plastics.
- Organic additives (filler, plasticizer, flame retardant, antioxidant, colorant, etc.) or their thermal fragments also appear among the pyrolysis products of plastic wastes.
- Certain components are recognized as responsible for instability or low volatility of pyrolysis oil and for the production of reactive or harmful compounds upon combustion (forming soot, environmentally unfriendly gases).
- In some plastics several kinds of chemical reaction may take place under pyrolysis that could be severely influenced by the reaction conditions, leading to considerably differing pyrolysis oils.

Thus, for the development of polymer waste recycling technologies it is helpful to be aware of the chemical composition of the pyrolysis products of those polymers which are typical components of plastic wastes.

In this chapter it will be demonstrated that there is a strict relation between the chemical composition of plastics and their pyrolysis oil, but the relationship is not well understood in many cases due to the fact that the products are determined by both the source and the pathway of decomposition. The ranking values of pyrolysis oils derived from plastics may be estimated on the basis of the correlation of major oil characteristics and chemical composition and structure of component compounds.

2 EXPERIMENTAL METHODS

Laboratory-scale pyrolysers can be used for producing oils for analytical purposes. Many scientific and technical publications report on the pyrolysis of well-characterized polymers in open or closed reaction vessels, furnace-heated tubes, fixed-bed and fluidized-bed reactors. The pyrolysis products are generally analysed off-line, being condensed in cooled traps.

Chemical analysis of pyrolysis oil can be performed using the same methods as applied to characterize petroleum related oil: various chromatographic tools such as high-resolution gas chromatography (HRGC) [1], high-performance liquid chromatography (HPLC) [2], multidimensional GC and HPLC [3], infra red (IR) and nuclear magnetic resonance (NMR) [4] spectroscopic methods. Mass spectrometry (MS) is the best choice for detecting the components separated by chromatography when qualitative analysis is essential. This option is indispensable for the identification of plastics pyrolysis products because of their variability.

Important properties of the pyrolysis-derived oils may be predicted from the information obtained by fast, hyphenated analytical instruments. Pyrolysis products are analysed on-line in a broad range of volatility from gases to heavy oil components by a micropyrolyser coupled to GC/MS (Py-GC/MS). Such a highly informative examination can be accomplished in less than one hour. The critical temperatures, which should be effective for pyrolysis may be read from the weight loss curve obtained by thermogravimetry (TG) upon gradually heating up the plastic sample. The evolution profile of the volatile thermal decomposition products can be monitored by coupling a thermobalance to a mass spectrometer (TG-MS) or to Fourier transform infra red spectrometer (TG-FTIR). In the followings the optimal temperature range for liquid production obtained in TG will be given for each representative polymer discussed, moreover a pyrolysis gas chromatogram (pyrogram) will be shown which were obtained using the same pyrolysis and GC/MS conditions.

3 CHEMICAL COMPOSITION OF PYROLYSIS LIQUIDS

3.1 RELATION OF MAJOR OIL CHARACTERISTICS AND CHEMICAL FEATURES OF COMPONENT COMPOUNDS

The compositional analysis is an essential part of the quality evaluation of petroleum-derived fuels. The concentration of different compound types such as paraffin, isoparaffin, olefin, naphthene and aromatic are routinely determined by gas chromatography (PIONA analysis), and can be rapidly measured by proton NMR spectroscopy.

Some fuel properties have long been known to be interrelated with chemical composition: density and aromatic content, viscosity and distillation range, cetane number and aromatic content. Correlation studies applying various statistical computational methods revealed the contribution of chemical structural units of organic compounds to the various physical properties of hydrocarbon fluids, such as octane and cetane number, flash point, cloud point, etc.

Octane and cetane number are used to measure fuel performance of gasoline and diesel oil, respectively. The research octane number (RON) is broadly estimated from the chemical composition of the fuels determined with the help of high-resolution GC [5, 6], FTIR spectroscopy [7] and NMR analysis [8, 9]. Cetane number prediction is generally based on the concentration of aromatic compounds and density values of oils. However, the estimation is more reliable – and also applicable to synthetic diesel oils – when a more detailed chemical composition characterization from GC/MS and NMR are taken into account [10, 11]. Structural group contribution methods have been published for predicting the flammability characteristics of pure hydrocarbon fluids as well [12, 13]. Flash point estimated with this method was found to be in better agreement with experimental values than that calculated from boiling point with rough estimation equations. The approach described by Cookson *et al.* [14] for correlating fuel composition and boiling characteristics with fuel properties is based on information readily obtainable from ^{13}C NMR spectroscopy and gas chromatography, and proved to be successful in accounting for changes in fuel properties as a function of boiling range. The abundance of large linear alkanes ($> n$-C_{24}) in paraffinic crude oils increases their tendency to wax crystallization, which can be demonstrated by a linear correlation between the concentration of this hydrocarbon family and the crude oil cloud point [15].

Although these analytical approaches were specially developed for petroleum-derived gasoline and diesel oil, the concept of them is applicable to the same boiling fraction of plastic pyrolysis oil [16, 17]. Unfortunately we have not got enough experimental data for the estimation of usual fuel characterization values when the pyrolysis oil contains not only hydrocarbon components, but also oxygen-, and nitrogen-containing ones. Nevertheless, the suitability of a plastic waste pyrolysate as a fuel is generally predictable on the basis of the knowledge of the chemical composition and structure of the pyrolysis oil at various boiling ranges. Py-GC/MS analysis of a plastic provides fast, one-run information on the chemical composition of pyrolysis products over the whole range of volatility from gases to heavy oils. In the following, results obtained by this method on various plastics will be reported and interpreted from the point of view of possible utilization of the pyrolysis oil.

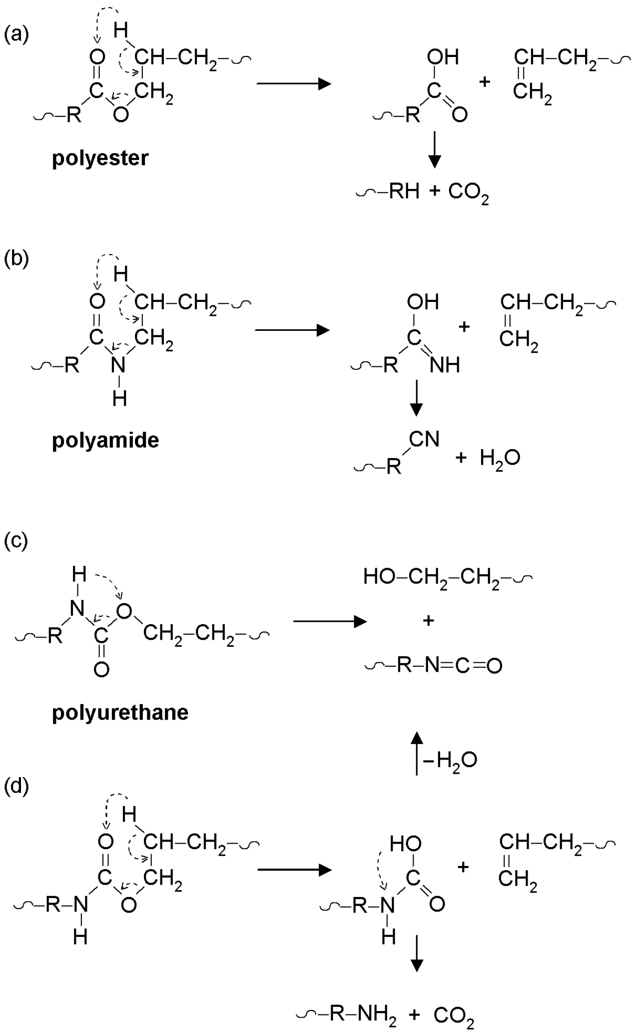
3.2 THERMAL DECOMPOSITION REACTIONS OF POLYMERS

The composition of the pyrolysis products is primarily determined by the means of disintegration of the macromolecule to the molecules of gas, oil, and solid residue. Thus to anticipate the pyrolysis oil composition of a plastic material, the chemical composition and structure of the polymer and its thermal decomposition reactions should be consistently considered. Typical thermal decomposition pathways of the various polymer kinds are abundantly treated in the relevant scientific literature [18–20]. Thermal decomposition of the polymer component of a plastic material is expected to begin at the weakest chemical bonds of the macromolecule. However, there are decomposition pathways which require lower energy than the direct breakage of the bonds, when rearrangement over four or six neighbouring atoms leads to the elimination of a volatile compound or to the scission of the macromolecular chain.

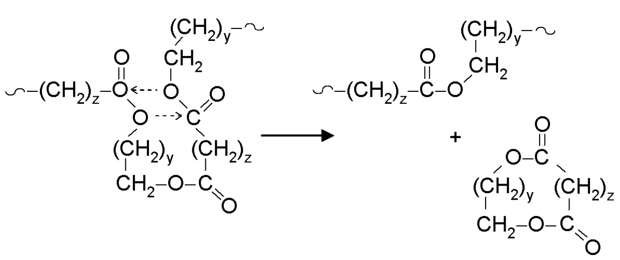
Elimination of carbon dioxide from carboxyl, water from alcoholic hydroxyl, carboxylic acid from alkanoate, and hydrogen chloride from chlorine side groups or chain ends are typical thermal decomposition reactions in the temperature range 250–350°C. Hydrogen chloride is an important product of poly(vinyl chloride) because every second carbon atom of the hydrocarbon polymer chain is chlorine substituted. But hydroxyl, alkanoate and free carboxylic acid groups normally occur only at the ends of the macromolecular chains in customary plastics, thus the contribution of their elimination to the volatile pyrolysis products is negligible.

The relatively low thermal stability of aliphatic polyester, polyamide and polyurethane, decomposing in the temperature range 250–450°C, is due to the *rearrangement* of the ester, amide or urethane linkages along the macromolecular chain, leading to linear fragments when single linking groups are reorganized. One of the newly formed macromolecular ends will be terminated by a carboxylic, imino or isocyanate group, respectively, and the other by a vinyl or a hydroxyl group (Scheme 12.1). The imino group is fast dehydrated to nitrile in polyamide, while decarboxylation of the terminal group leads to an alkyl chain end in polyester, and that of the labile carbamic acidic group to a terminal primary amino group in polyurethane. Cyclic monomer or oligomers may be eliminated by the rearrangement of the atoms of a pair of ester or amide linkages in aliphatic polyester or polyamide, respectively, as indicated in Scheme 12.2 for polyester. Oligomer cycle formation takes place similarly in the aliphatic polyether or polyester soft segments of thermoplastic polyurethane.

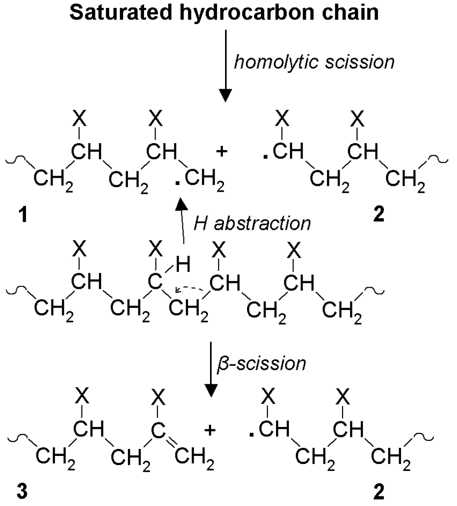
Radical breakage of certain weak chemical bonds may occur already at around 300°C, however, the more typical temperature range is above 400°C for this kind of disintegration of organic compounds. Free radicals formed by thermolysis are unstable fragments of high energy content; their recombination or termination by reaction with another radical or radical trap may stop the process. Alternatively, a radical chain reaction proceeds by the repetition of a reaction in which a free radical attacks a stable molecule causing its decay and producing a new reactive radical. Free radical decomposition is the most frequent reaction type taking place during the pyrolytic recycling of plastic wastes.



Scheme 12.1 Thermal scission of aliphatic polyester, polyamide and polyurethane through rearrangement of six or four atoms



Scheme 12.2 Ester exchange in polyesters through intramolecular rearrangement of two ester groups

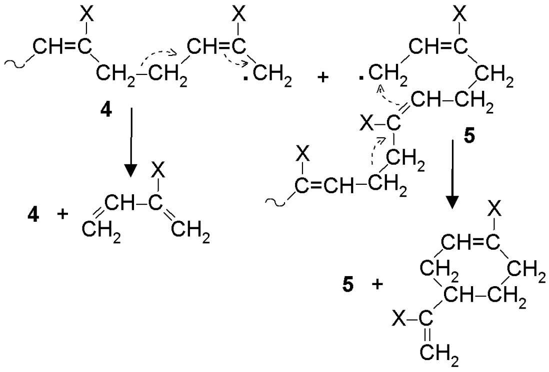


Scheme 12.3 Free radical decomposition of saturated hydrocarbon chain polymers through random cleavage. X=H, methyl, phenyl or chlorine in PE, PP, PS or PVC, respectively, **2-1**, when X=H (in PE)

In saturated hydrocarbon chain polymers homolytic scission of a C–C bond leads to two macroradicals that may be primary (**1**) or secondary (**2**) one shown in Scheme 12.3. A typical free radical attack is the *hydrogen abstraction*, i.e. the transfer of the radical site to another molecule or in to a neighbouring section of the same molecule. Scheme 12.3 illustrates the transfer of a primary radical (**1**) to a tertiary carbon atom of another molecule. The β-*scission* of the mid-chain radical results in a vinyl-group-terminated polymeric chain (**3**) and a new secondary macroradical (**2**). This kind of radical chain reaction cuts the macromolecules randomly in to oligomer chains terminated either by methyl or by vinyl groups. The hydrogen abstraction by a terminal macroradical may be more probable from those carbon atoms of its own coiled chain which are easily approachable due to a favourable conformation. The oligomeric compounds formed through this decomposition route are of smaller molecular mass than the products of the random chain scission. The repetitive β-scission of a terminal radical producing vinyl compounds and reproducing the macroradical represents the radical *depolymerization* of the polymer chain to monomer in vinyl polymers.

The breakage of the polymer chain is the most probable at the allyl position to double bonds, forming primary macroradicals in unsaturated hydrocarbon chain polymers. The deplacement of the primary radical site is carried on through the rearrangement of the C=C double bonds, producing monomer or cyclic dimer and reproducing the primary macroradicals (**4** and **5**) according to Scheme 12.4.

The free radical reactions in aromatic or partly aromatic polymers and phenolic resins are not chain reactions. There is not much opportunity in these macromolecules for rearrangement facilitating a continuing decomposition. In general there are not enough hydrogen atoms available to stabilize the free radicals produced by the cleavage of alkylene, ester, ether or amide linkages connecting the aromatic rings into macromolecules. In this way only a part of the thermal fragments are volatilized, and those radicals that are



Scheme 12.4 Free radical decomposition of unsaturated hydrocarbon chain polymers through rearrangement of bonds at the macroradical end. X=H in BR, X=methyl in NR. **5-4,** when X=H (in BR)

not able to abstract a hydrogen recombine with other radicals, forming a carbonaceous residue. The aromatic rings are generally not cleaved in pyrolysis reactions, however from phenolic moieties carbon monoxide could be split off above 600°C.

As a consequence of the variety of thermal decomposition pathways, the composition of the pyrolysis products may be controlled by the temperature when the plastic is made up of different polymers or when the constituent polymer decomposes through varying routes at different temperatures.

4 PYROLYSIS PRODUCTS OF PACKAGING WASTE PLASTICS

Waste plastics composition varies with collection area, sorting methods and time period, moreover several waste constituent polymer types occur in various waste categories. Nevertheless each customary plastic material will be discussed only in one of the three waste group included in this chapter.

The majority of packaging plastic materials consists of polyolefins and vinyl polymers, namely polyethylene (PE), polypropylene (PP), polystyrene (PS) and poly(vinyl chloride) (PVC). Obviously, these polymers have many other applications not only as packaging materials. Chemically they are all composed of saturated hydrocarbon chains of macromolecular size; their typical thermal decomposition pathway is free radical one initiated by the homolytic scission of a backbone carbon–carbon bond. In spite of the basic similarity of the initial cleavage, the decomposition of the hydrocarbon macroradicals is strongly influenced by the nature of the side groups of the main chain.

The general formula displayed in Scheme 12.3 indicates that the chemical composition of the repeating unit of the polymer (a section of the chain of two carbon atoms) correspond to that of the monomer, where X designates hydrogen and chlorine atom in PE and PVC, methyl and phenyl group in PP and PS, respectively. Since the chemical bond between carbon atoms of the saturated hydrocarbon chain is weaker than that connecting hydrogen, methyl or phenyl group to the chain, PE, PP and PS thermal decomposition begins with homolytic scission of the polymer chain. Cleavage of the X side group occurs only in those vinyl polymers in which the bonding to the substituent is weaker than the backbone C–C bond. In PVC the Cl–$CH(CH_2)_2$–bond strength (356 kJ mol^{-1}) is somewhat lower than that of C–C along the chain (370 kJ mol^{-1}) [21], thus chlorine is cleaved first. Moreover, the breakage of a chlorine bonding to a tertiary carbon, Cl–$C(CH_2)_3$–at an accidental branching point, or at an allyl position to a double bond, Cl–$CH(CH_2)(CH{=}CH)$–representing a defect point of PVC, requires even less energy than the cleavage of the regular chlorine substituents.

4.1 POLYOLEFINS

The reactions of the alkyl macroradicals produced by the scission of the saturated hydrocarbon polymer chain (illustrated in Scheme 12.3) depend on their reactivity and on that of the available reaction partners. It could be expected that radical depolymerization, i.e. β-scission of the primary macroradical will likely take place, however practice contradicts to this expectation in the case of polyolefins. The yields of light olefins evolving by solely thermal decomposition in conventional reactors are rather low compared with those of liquid products. Primary saturated hydrocarbon radicals (**1**) are more reactive than secondary ones (**2**), thus thermal decomposition of PE, in which the polymer chain breakage results in primary radicals only, differs considerably from that of other polyolefins, in which both primary and secondary radicals are formed in the initial breakage, and the mid-chain β-scission leads to secondary radical as illustrated in Scheme 12.3. Any hydrogen atom along the polyethylene chain is equally abstractable by the free radicals, however, in other polyolefins the hydrogen is more easily detached from tertiary carbon atoms than from the secondary ones, because the energy required for the cleavage of a C–H bond in hydrocarbons decreases in the following order [21]:$=CH–H > –CH_2–H > –CH(CH_2)–H > –C(CH_2)_2–H$.

4.1.1 Pyrolysis Products of PE

PE pyrolysis advances at the maximal rate between 420 and 500°C leading to an imposing series of straight-chain hydrocarbons. The yield of hydrocarbon gases and solid residue normally stay low compared with liquids in conventional reactors. In the pyrogram of a HDPE sample displayed in Figure 12.1 the first peak (at 2 min retention time) covers C_1–C_5 hydrocarbons. The next peaks from C_6 to C_{12} include the boiling range of gasoline (in the retention time interval 2–10 min in the pyrogram), then the further peaks corresponding to straight chain hydrocarbons from C_{13} to C_{19} give the boiling range of diesel oil (retention time 10–18 min). The heavy oil and wax components from C_{20} on up to the end of the pyrogram constitute seemingly the major part of PE pyrolysate. Although GC/MS total ion chromatographic peak areas are not truly proportional to the masses of the corresponding compounds, a rough estimation of the contribution of the various boiling ranges to the total pyrolysate can be made based on the relative peak areas of the pyrogram obtained by Py-GC/MS.

In the magnified detail of Figure 12.1 triplets of compounds of the same carbon number are distinguished, the highest of the three GC peaks is 1-alkene and the two smaller peaks of lower and higher retention time correspond to α, ω-alkadiene and *n*-alkane,

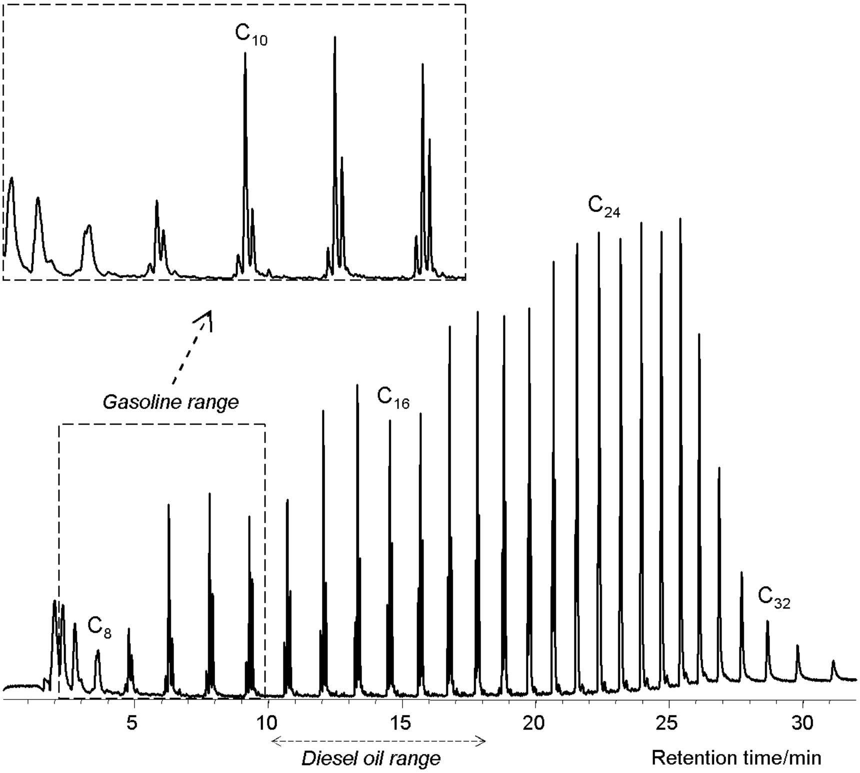


Figure 12.1 Py-GC/MS chromatogram of HDPE at 500°C. C_x denotes 1-alkenes of x carbon atoms

respectively. The formation of these types of compounds from a saturated hydrocarbon chain is well described by a free radical mechanism [22]. Among the thermal decomposition reactions of the primary polyethylene macroradical anticipated [23] only those will be detailed in the followings which contribute to the formation of the generally obtained product distribution. As outlined in the previous part, the primary macroradicals formed by random breakage of the PE chain may abstract hydrogen from any carbon atoms of a macromolecule in sufficient vicinity in the polymer melt. The result of this reaction is a methyl terminal group and a secondary macroradical. The latter decomposes by β-scission, leading to the breakage of the attacked macromolecule, dividing it in to a vinyl-group-terminated and a primary-radical-terminated fragment. Since the initial reactant – the primary radical – is reproduced, the chain reaction will continue and produce equal number of methyl and vinyl terminal groups in the fragments of the gradually decreasing molecular mass, which can be only alkanes, 1-alkenes and α, ω-alkadienes in 1:2:1 relative yields. In principle the process should result in a random distribution of the linear hydrocarbon fragments over a carbon atom range covering volatilizable compounds. The slight positive deviation of peak heights from a statistical distribution of the hydrocarbon homologous series of 1-alkenes at C_6, C_7, C_{10}, C_{11}, C_{14}, C_{15} C_{18}, C_{19} is due to the superposing contribution of backbiting of the primary macroradical in to its own chain at preferred carbon atoms due to the conformation of the polymer coil in the melt [23]. Note that the higher-molecular-mass section of the product distribution is missing in the pyrogram because the given GC conditions are not satisfactory for the analysis of the components over C_{28}. In a mass spectrometer (under vacuum) the distribution has been reported [24] to go up to C_{50}.

The knowledge of the mechanism leads us to the conclusion that from PE we may not expect branched hydrocarbons solely by thermal decomposition, that is why the *octane number* of pyrolysis-derived gasoline from PE is expected to be low (RON value of 20 was reported in a noncatalytic pyrolysate of LDPE [25]). Anyway, the contribution of the gasoline boiling range to the total pyrolysate yield cannot be very high, as pointed out above. The *cetane number* of PE pyrolysis diesel oil should be high due to its composition of exclusively linear chain hydrocarbons. However, the pour point and cloud point will be low because of the high concentration of wax. The yield of isoalkanes is negligible, even from LDPE which contains some short side chains. The production of aromatic and polyaromatic compounds that occur at above 700°C from PE could increase both the relative yield of the gasoline and diesel oil and the *octane number*, while decrease *cetane number*. However, the aromatic and polyaromatic components of fuels are not well tolerated for environmental protection reasons.

The gasoline obtained when pyrolysing 100 g PE waste in a closed autoclave of 1 L volume at 420–450°C for 2 h [26] was reported to give a relatively high research octane number of 80.9, but the aromatic content was also high 16.7 wt% among the pressurized conditions. The diesel oil of the same pyrolysate was characterized by 28.7 wt% aromatic content, 41°C ignition temperature, −11°C cloud point and a cetane index of 32. In a semi-batch reactor HDPE was pyrolysed with a nitrogen flow at 440–460°C for 4 h [27] and the resulting thermolysis products had 2.5 wt% aromatic <22°C flash point, 10°C cloud point, 0°C pour point, and cetane index of 58.2. The product was catalytically hydrogenated in both cases in order to reduce the alkene content responsible for the instability of PE pyrolytic fuels.

4.1.2 Pyrolysis Products of PP

Polypropylene decomposes between 400 and 470°C. The pyrogram of an isotactic PP displayed in Figure 12.2 shows that the most important components of the pyrolysate are trimer, tetramers and pentamers of propene, boiling in the gasoline range. The oligomers of propene are isoalkenes joining the propene units at the second and third carbon atoms similarly to PP. Propene gas and *n*-pentane are eluted under the first and second peak of the pyrogram, the third peak corresponds to the dimer of propene (2-methyl-1-pentene). The second part of the pyrogram (above 13 min) comprising the oil and heavy oil boiling range is populated by the peaks of higher oligomers a series of which are α, ω-isoalkadienes (denoted by asterisk).

The observed pyrolysis product distribution of PP is developed by a free radical mechanism [28, 29] which begins with the homolytic breakage of the polymer chain drawn in Scheme 12.3 where X represent a methyl group in this case. Primary macroradical **1** is formed only in the initial step, thus its decomposition plays a minor role in PP. Secondary macroradicals may decompose to propene by depolymerization reproducing **2**, or

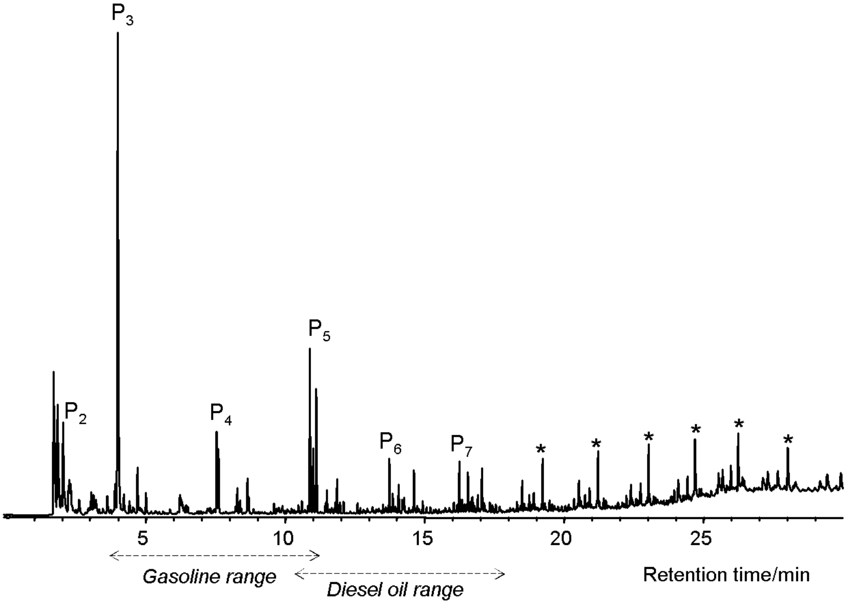
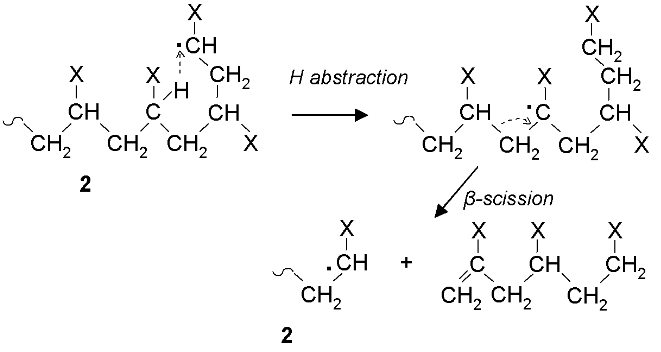


Figure 12.2 Py-GC/MS chromatogram of isotactic PP at 500°C. P_x denotes oligomer of x propene units; peaks labelled* are dienes

abstract hydrogen, transferring the radical site to a tertiary carbon atom of an other macromolecule or that of its own chain. The intermolecular radical transfer of **2** is followed by the β-scission reaction drawn in Scheme 12.3, resulting in a vinyl terminal group **3** and reproducing **2**. This chain reaction produces *n*-propyl and 2-methylvinylene terminal groups in the fragments, which can be isoalkanes, 1-isoalkenes (oligomers) and α, ω-isoalkadienes. The series of peaks above pentamer represent these fragment compounds in the pyrogram of PP in Figure 12.2. The considerably superior yield of trimer, tetramers and pentamers to that of the larger oligomers indicates the contribution of another reaction. Intramolecular radical transfer of a secondary macroradical to a tertiary carbon atom of its own chain leads to these oligomers, drawn in Scheme 12.5. The two possible directions of β-scission explain the occurrence of *n*-pentane among the wholly isoalkanoic products of PP.

In the pyrolysis process of PP the intramolecular radical transfer is preferred to the intermolecular one, thus the low oligomer formation predominates. Consequently the pyrolysis oil of PP is much more volatile than that of PE, decomposing mainly through intermolecular radical transfer. The difference of the backbone structure of the products of these polymers is more important from the point of view of fuel properties. The isoalkanoic structure of PP is held in the thermal decomposition products, in this way the octane number of the pyrolysis oil might be high. In a batch reactor [26] the gasoline fraction (44–220°C) of the pyrolysis oil obtained from 100 g PE and PP mixture at 440°C has an octane number of 88.6 with 5.6 wt% aromatic content, and the diesel oil (151–347°C boiling point range) had 56°C ignition temperature, −4°C cloud point and a cetane index of 59.5. Pyrolysing waste PP in an 1 L autoclave at 430°C for 20 min



Scheme 12.5 Intramolecular radical transfer and oligomer formation in vinyl polymers

under nitrogen atmosphere of 3.5 MPa [30], the RON value of the liquid boiling <150°C was found to be 53. When mixed with 16% of PE and PS the observed RON was 56 for this fraction, and for an oil boiling <270°C it was 45. A mixture of 1:1:1 of the three polymers under similar conditions gave a liquid boiling <150°C of 58 RON, and an oil boiling <270°C of 40 RON. When PE was the major component of the mixture (70%) the two fractions of the pyrolysate have got as low a RON value as 24 and 20, respectively.

4.2 VINYL POLYMERS

In the general formula of the hydrocarbon chain polymers in Scheme 12.3 the vinyl polymers contain a nonalkyl X substituent. The size and the chemical composition of the substituent influence the reactions of the secondary macroradical, the main reactive competitor of the thermal decomposition process in vinyl polymers. A bulky substituent such as the phenyl group in PS may hinder the intermolecular radical transfer by shielding the easily abstractable hydrogen atoms [31] while at the same time a phenyl group is able to give a higher stability to the secondary macroradicals by resonance over the aromatic ring. The secondary macroradical plays the main role in the pyrolysis process of several vinyl polymers [19, 28] which is either depolymerized to monomer or transferred to the third and fifth carbon atom from the radical end of the macromolecule evolving dimer and trimer after β-scission, respectively, reproducing the secondary macroradical in a chain reaction as drawn in Scheme 12.4. The β-scission may also proceed in the other direction along the macroradicals, leading to small radicals and vinyl-terminated macromolecules in this case. The volatile radicals abstract hydrogen atoms, and the radical site is transferred to another macromolecule continuing the chain reaction.

Division of the side groups from the main chain occurs only in those vinyl polymers in which the bonding of the substituent to the chain is weaker than the backbone C–C bond. The radical of the cleaved substituent draws hydrogen from the neighbouring carbon atom and is eliminated, for example as acetic acid from poly(vinyl acetate), or as hydrogen chloride from PVC.

4.2.1 Pyrolysis Products of PS

Polystyrene (PS) has somewhat lower thermal stability than the polyolefins, its pyrolysis goes on between 380 and 450°C without producing gases or leaving a remarkable amount of residue after total conversion. In spite of the fact that the majority of the carbon atoms are assembled in phenyl side groups in this polymer, a negligible amount of benzene is formed at that temperatures, because the $C_{aryl}-C_{alkyl}$ bond connecting the phenyl group to the polymer chain is stronger than the bond of alkyl carbons along the chain. The pyrogram of PS contains three dominant components, styrene (bp 145°C) in the gasoline boiling range, styrene dimer in the diesel oil range, and styrene trimer boiling at 400°C. This pyrolysis product distribution suggests that the intermolecular radical transfer is negligible in PS. Among the decomposition pathways of the free radical mechanism in hydrocarbon chain polymers, the intramolecular processes dominate. The lack of those products, which were originating from the β-scission in the direction of volatile radical formation, confirms the supposition that intermolecular hydrogen abstraction is obstructed in PS.

The pyrolysate of PS could be better used as feedstock than as fuel, because of its high aromatic content and low storage stability. The high aromatic content of PS pyrolysis oil helps to compensate the low octane number of PE oil. Pyrolysing waste PS in an autoclave at 430°C [30], the light liquid fraction boiling <150°C and the oil <270°C had 98 and 89 RON, respectively. When PS was only 70% in a waste mixture containing PE and PP as well, RON values were decreased to 80 and 66, respectively. From a mixture of PE and PS at 440°C gasoline of 95.8 octane number was obtained in a batch reactor [26], however, the aromatic content was 56.7 wt%. The diesel oil fraction (170–360°C boiling point range) contained nearly as much aromatics and had ignition temperature 58°C, cloud point −8°C and a cetane index of 50. From a plastics-derived liquid produced by the pyrolysis of a mixed plastics feed consisting of HDPE, PP and PS the naphtha fraction (boiling range up to 205°C) had a RON of 84.8 with a composition of 25% aromatics, 54% paraffin and 21% olefin [16].

4.2.2 Pyrolysis Products of PVC

TG analysis of poly(vinyl chloride) indicate that thermal decomposition is carried out in two distinct decomposition steps between 280 and 350°C, then 410 and 490°C. In the first step dehydrochlorination and benzene formation goes on simultaneously. In a second step of decomposition alkylaromatic and polyaromatic compounds are produced through aromatic ring formation [32] and around 8–15% carbonized solid residue remains after pyrolysis. Figure 12.3 shows the pyrogram of PVC, where the two main peaks are hydrogen chloride and benzene that originate from the dehydrochlorination step. The other peaks all correspond to aromatic compounds, one- and two-ring alkylaromatic ones in the gasoline boiling range, with two- and three-ring alkylaromatic ones in the diesel oil boiling range.

PVC is a vinyl polymer where X is a chlorine atom in the general formula of Scheme 12.3, but its thermal decomposition follows a quite different pathway from that of PS, starting with division of the side groups from the main chain. When a chlorine atom is cut off from a defect point (tertiary carbon atom or allyl bond), it abstracts the hydrogen atom from the next carbon atom, then hydrogen chloride is eliminated, together with the

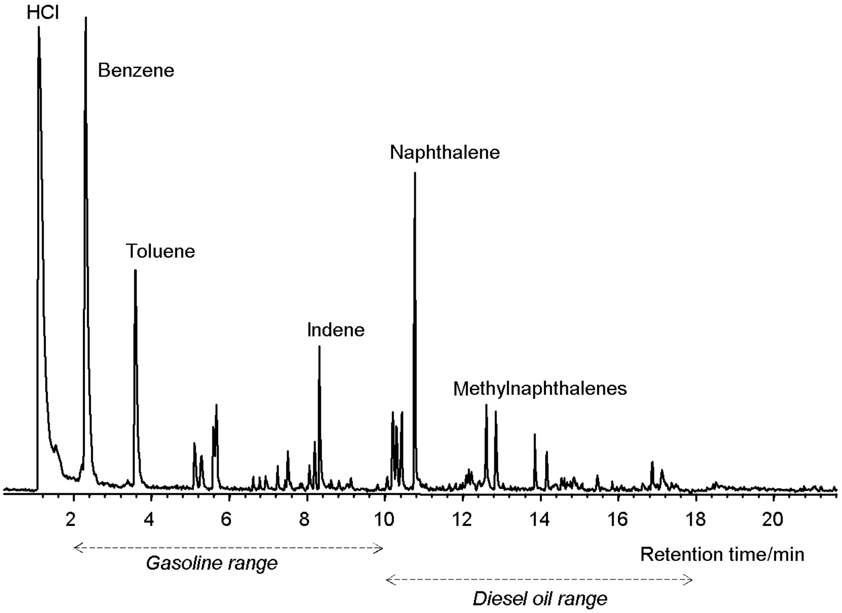
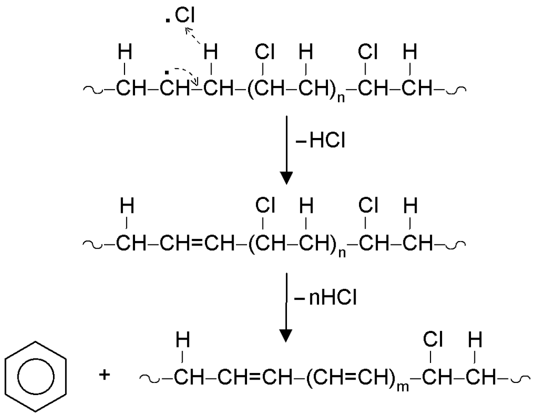


Figure 12.3 Py-GC/MS chromatogram of PVC at 500°C



Scheme 12.6 Thermal decomposition reactions in PVC

formation of a double bond along the polymer chain, as shown in Scheme 12.6. The next chlorine atom, being at an allyl position to the newly formed double bond, will be split easily and hydrogen chloride elimination continues in a chain reaction, leaving a series of conjugated double bonds behind, transforming the saturated hydrocarbon chain of the polymer to a conjugated polyene. Through this process the polymer can be nearly quantitatively dechlorinated at as low temperature as around 300°C.

Plasticizer is added to PVC in many applications. Most frequently di(2-ethylhexyl phthalate) is used, boiling at 230°C, thus it may be evaporated from the molten PVC at the dehydrochlorination stage, if the pyrolysis is carried out first at a lower temperature in order to get rid of the chlorine prior to higher temperature pyrolysis. At above 600°C the phthalic ester decomposes and its fragments, phthalic acid anhydride, 2-ethylhexanol and 3-methylheptene are condensed in the gasoline boiling range of the PVC pyrolysate. Thus concentration of oxygenates and aliphatics in the pyrolysis oil of plasticized PVC can be considerably increased due to high plasticizer content.

4.3 POLYESTERS

Among polyesters synthesized from 1,4-benzenedicarboxylic acid and aliphatic diols, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) are the most frequently applied ones. Hydrolysis is evidently the easiest chemical recycling technique of polyesters, however they may be mixed with other waste plastics, thus it is useful to know the properties of their pyrolysis product.

4.3.1 Pyrolysis Products of PET

Thermal decomposition of polyesters of terephthalic acid proceeds between 380 and 450°C, leaving about 20% of carbonized residue. In the pyrogram of PET displayed in Figure 12.4, in addition to the carbon dioxide peak there are sharp peaks corresponding to esters and broad peaks of aromatic carboxylic acids. The thermal fragments seen in the chromatogram are all derived from a reaction involving six-atom rearrangement of the ester linkage and the ethylene unit, analogous to that drawn in Scheme 12.1a. In PET the successive formation of a free carboxylic acid and an ethenyl ester-group-terminated macromolecular fragment leads finally to mono- and diethenyl terephthalate (denoted as ET and ETE in Figure 12.4), which are the main components in the diesel oil boiling range of the pyrolysate. Partially decarboxylated carboxylic acid products of the same reaction are benzoic acid and ethenyl benzoate (EB), which boil in the gasoline range. The two-aromatic-ring fragments of PET, ethylenedibenzoate (BEB) and benzoyoxylethylethenyl terephthalate (BETE) are already heavy oil components.

The main inconvenience of PET pyrolysate is related to the aromatic carboxylic acid components having high melting points (i.e. benzoic acid melts at 122.4°C, much higher than n-C_{24} at 54°C).

5 PYROLYSIS PRODUCTS OF AUTOMOTIVE WASTE PLASTICS

Automotive plastic waste components are, in addition to PP and PVC, styrene copolymers, rubber, polyamides and polyurethanes.

5.1 STYRENE COPOLYMERS

Plastics copolymerized from styrene, butadiene and acrylonitrile offer a wide application scope, thus high-impact polystyrene (HIPS, styrene–butadiene copolymer), styrene–

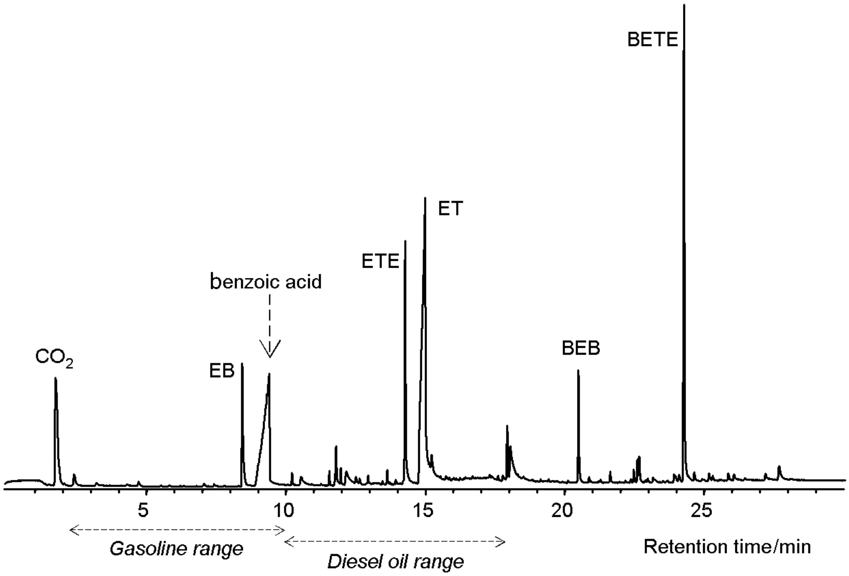


Figure 12.4 Py-GC/MS chromatogram of PET at 500°C. B, E and T denote benzoate, ethylene and terephthalate units, respectively, in ester-type compounds

butadiene rubber (SBR), poly(acrylonitrile-*co*-styrene) (SAN), and poly(acrylonitrile-*co*-styrene-*co*-butadiene) (ABS) may be present in municipal, automotive and electronic plastic wastes as well.

In HIPS the butadiene content is in general low, the chemical structure of the polymer kept of vinyl type, thus the pyrolysis product distribution is very much like that of PS. However, some negligible components of PS pyrolysate such as toluene, α-methylstyrene, and 1,3-diphenylpropane are markedly produced from HIPS. These compounds originate directly from those volatile radicals which have been produced by the β-scission of the PS chain end. Presumably the intramolecular radical transfer necessary for the stabilization of the volatile radicals is facilitated due to the presence of butadiene segments in the copolymer.

5.1.1 Pyrolysis Products of ABS

The pyrolysis liquid production range of ABS extends from 380 to 470°C similarly to that of PS, and the decomposition goes on in a single step with 1–2% solid residue. According to the pyrogram of ABS displayed in Figure 12.5 the pyrolysate contains monomers, dimers and trimers, as expected from a vinyl polymer. Since the copolymer is composed of acrylonitrile and styrene segments, the main components of the pyrolysate are acrylonitrile in the gaseous phase, styrene in the gasoline boiling range, dimers and those trimers which are composed of two acrylonitrile and one styrene units in the diesel oil boiling range, styrene trimer and the other set of trimers which are composed of one

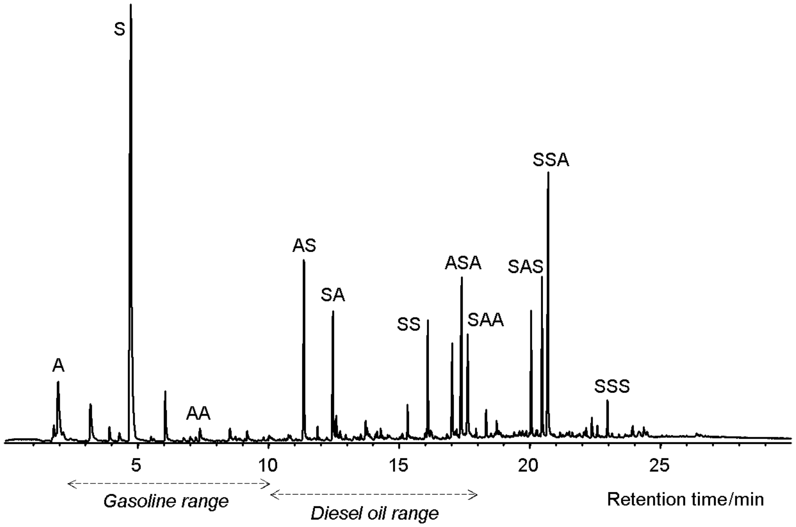


Figure 12.5 Py-GC/MS chromatogram of ABS at 500°C. A and S denote acrylonitrile and styrene, and these units in dimers and trimers

acrylonitrile and two styrene units in the heavy oil range. The same slight differences can be observed in the composition of the pyrolysate of SAN and ABS as in that of PS and HIPS described above. The pyrolysis product distribution is consistent with the same free radical decomposition mechanism that has been described for PS. Although the presumption explaining the minimal contribution of intermolecular radical transfer by the hindrance of the bulky phenyl group [31] is not confirmed. The nitrile group is not as large as phenyl, and about the half the substituents are nitriles in ABS. Even so the same extent of hindrance is reflected in the product distribution of ABS as in that of PS.

The hybrid dimers and trimers of ABS all contain nitrile groups, thus their robust contribution to diesel oil and heavy oil boiling range may be strongly disadvantageous for the utilization of oil products as fuels, because of NO_x formation under combustion. At the same time the gasoline with boiling range beginning at above the boiling point of acrylonitrile (77.3°C) contains only a low concentration of acrylonitrile dimer as nitrogen-containing component.

5.2 RUBBER PLASTICS

The polymers of rubber plastics have unsaturated hydrocarbon chain structure, since they are polymerized from alkadienes. The general formula of poly(1,3-butadiene) or butadiene rubber (BR) and polyisoprene or natural rubber (NR) is drawn in Scheme 12.5, where X is hydrogen in BR and methyl group in synthetic polyisoprene or NR. The free radical mechanism of thermal decomposition starts by homolytic scission of the alkyl C–C bonds. Two primary macroradicals (**4** and **5**) are formed for which the rearrangement of the nearest double bond is an easy way of stabilization, splitting off a monomer and reproducing **4** which continues the chain reaction. Interaction of the macroradical with the second-nearest double bond, resulting in its rearrangement also takes place, forming a ring of six atoms (see Scheme 12.5) producing cyclic dimer and reproducing **5**. Through the interaction of the macroradical with further double bonds of its own chain, higher oligomers are also formed similarly.

5.2.1 Pyrolysis Products of NR

Polyisoprene, either synthetic polymer or natural rubber, decomposes to liquids between 340 and 430°C. The pyrogram of NR displayed in Figure 12.6 shows that there are two major individual components in the gasoline boiling range, isoprene, the monomer and limonene, the cyclic dimer. The relative contribution of the higher oligomers to the pyrolysis oil should not be underestimated [33]. Humps of trimers and tetramers in the diesel oil boiling range, and even pentamers and hexamers in the heavy oil range, are observed in the pyrogram under which a group of oligomer isomers of the same molecular mass are eluted in the pyrogram. The higher oligomers are not totally separated by GC, most probably because of the occurrence of several conformational isomers. The product distribution in the pyrogram indicates that NR pyrolysis reactions conform with the decomposition mechanism of the polymer chain outlined above.

The isoalkene structure of the majority of the oil components confirms the good gasoline quality of pyrolytic fuel from NR. Nevertheless, from tyre waste other components are also evolved related to the vulcanizing agent and additives.

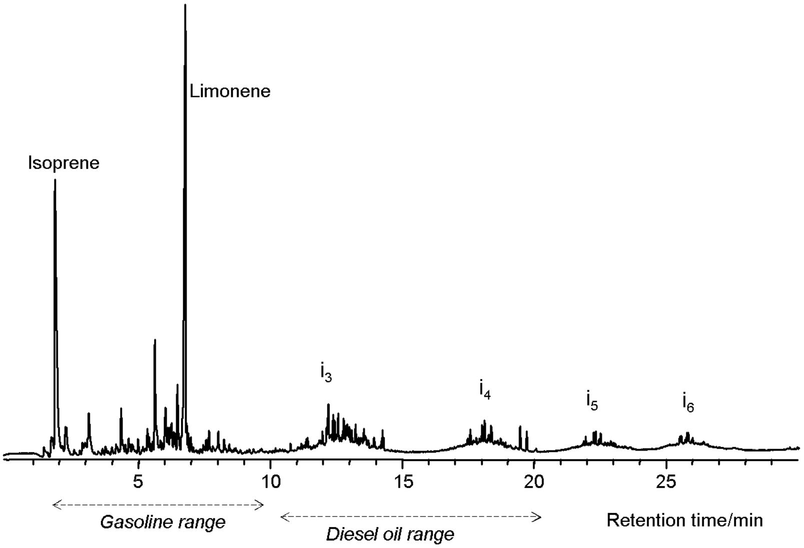


Figure 12.6 Py-GC/MS chromatogram of natural rubber at 500°C. i_x denotes oligomers of x isoprene units

5.2.2 Pyrolysis Products of BR and SBR

Polybutadiene has a considerably higher thermal stability than polyisobutylene. BR is pyrolysed between 370 and 480°C in TG, and only 3% residue is left. The pyrogram of BR is analogous to that of NR, in addition to the important peaks of monomer (butadiene) and cyclic dimer (dipentene, i.e. 4-ethenylcyclohexene), groups of higher oligomers appear at higher retention times. The decomposition temperature range of poly styrene–butadiene rubber (SBR) is roughly the same as that of BR. In the pyrogram of SBR styrene is also an important component besides BR oligomers, but the other aromatic compounds such as benzene, toluene, xylenes occur in similarly small concentrations in the pyrolysis liquids, as in that of BR and NR. The concentration of aromatic compounds in the pyrolysis oil increases with pyrolysis temperature, at the same time hydrogen evolves at above 600°C from tyre waste.

The important contribution of styrene makes the gasoline of SBR pyrolysate, rather aromatic while the oil boiling range is like that of BR.

Pyrolysing waste tyres in TG, three weight loss stages are reported [34]: 200–330°C, 330–400°C and 400–500°C. The first step corresponds to the thermal decomposition of the mixture of oils, moisture, plasticizers and other additives, the second one to that of NR and the third one to the decomposition of BR and SBR content of the tyre. The pyrolysis conditions influence strongly the resulting oil [35].

An oil of low flash point in the range 14–18°C, and of 41–43 MJ Kg^{-1} gross calorific value has been obtained in batch pyrolysis [36] of automobile tyre waste. In a pilot plant with semi-continuous feeding [37] the liquid yield of tyre waste decreased seriously with increasing temperature, and it was always lower in an atmosphere containing oxygen that in nitrogen.

5.3 POLYAMIDES

Among the several kinds of polyamides composed of the large variety of acyclic and aromatic amino carboxylic acids or diamines and dicarboxylic acids, two Nylons are the most extensively applied in many fields. Nylon 6 and Nylon 6,6 are found in various waste streams, they may be present in pyrolysis recycling feeds as well.

Amide group scission (termed as *cis*-elimination mechanism) and intramolecular rearrangement of two amide groups, leading to cyclic compounds [20] are the main pyrolysis reactions in acyclic polyamides. The former reaction is outlined in Scheme 12.1b and the ester exchange drawn in Scheme 12.2 is analogous to the latter one.

5.3.1 Pyrolysis Products of Nylon 6

Polyamide-6 (PA-6 or Nylon 6) decomposes between 410 and 490°C predominantly to ε-caprolactam which is its cyclic monomer. The intramolecular rearrangement of a pair of amide groups separated by five methylene units is geometrically favoured in the coiled polymer chain of PA-6, thus the seven atomic monomer ring is easily formed. Cyclic dimer and its dehydrated derivatives are also produced through a rearrangement reaction analogous to ester exchange shown in Scheme 12.2. Amide group cleavage by *cis*-elimination, resulting in 5-hexene nitrile makes only a minor contribution to the pyrolysis of Nylon 6.

The pyrolytic recycling of Nylon 6 is attractive for recovering the valuable monomer from a waste consisting only of this polymer, although catalytic recovery of caprolactam seems to be a more suitable process [38]. When this polymer is present as only one of the components of a mixed waste it should be taken into consideration that the constituents of Nylon 6 pyrolysis liquid are nearly all nitrogen-containing compounds, namely small amounts of alkane and alkene nitriles boiling in the gasoline range, ε-caprolactam in the diesel oil boiling range, and cyclodiamides in the heavy oil range.

5.3.2 Pyrolysis Products of Nylon 6,6

The pyrolysis temperature range of PA-6,6 is essentially the same as that of PA-6. However, the thermal decomposition product distribution of the two Nylons are quite dissimilar. There are several peaks in the pyrogram Pa-6,6 displayed in Figure 12.7. Two important peaks correspond to compounds formed through the rearrangement of amide groups according to the reaction in Scheme 12.1b, i.e. hexanedinitrile and *N*-5-hexenyl-1-cyanopentanamide. Cyclic diamide (1,8-diaza-2,9-diketocyclotetradecane) and its dehydrated derivative are the products of the rearrangement of two amide groups (similar to Scheme 12.2). Cyclopentanone is known as a characteristic pyrolysis derivative of the adipic (hexanedioic) acid moiety of polyamides [39], moreover, some ε-caprolactam has been generally reported as a minor side product of the thermal decomposition of various aliphatic polyamides.

The pyrolysis liquid of Nylon 6,6 contains alkadienes and cycloalkenes in addition to cyclopentanone in the gasoline boiling range, furthermore this fraction also involves hexanedinitrile and even alkylamines. The components of the diesel oil boiling range

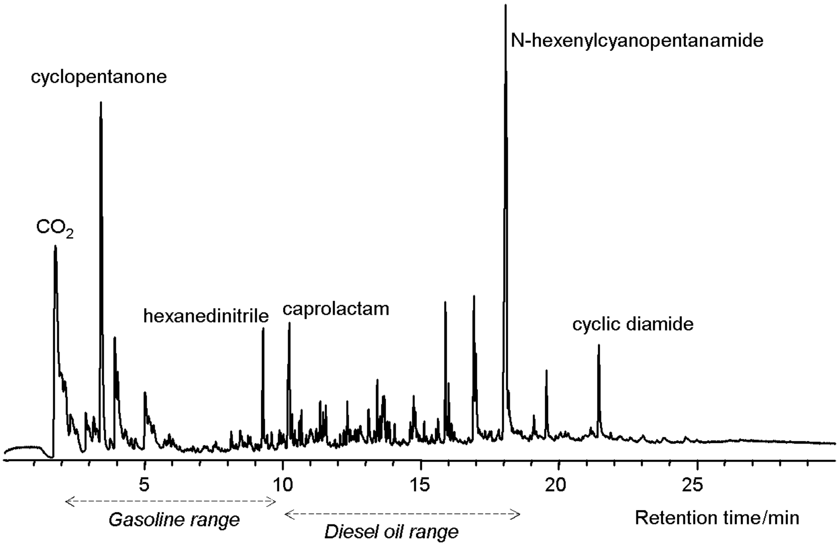


Figure 12.7 Py-GC/MS chromatogram of Nylon 6,6 at 500°C

are all amide compounds, the majority of which contain a vinyl group. The heavy oil components are cyclic amides. In spite of the various nitrile and amino-group-containing pyrolysis products, relatively low hydrogen cyanide and ammonia emissions have been reported from Nylons in pyrolytic processes [40].

5.4 POLYURETHANES (PU)

Pyrolysis could be considered as an unsuitable way of recycling for polyurethanes because the liquid product is extremely viscous and can solidify over time [41]. The main reason of the severe instability of polyurethane pyrolysate is the reactivity of the diisocyanate component, the regained polyurethane-forming reactant. The other component of thermoplastic polyurethanes is either a polyether or a polyester which could lead to stable pyrolysis liquid if the reactive diisocyanate is eliminated from it.

The thermal decomposition of polyurethanes can be explained by two principal mechanisms [42] as shown in Scheme 12.1c and d. The dissociation of the urethane linkage yields products with isocyanato and hydroxyl end groups. The latter groups are dehydrated at higher temperatures to yield compounds with vinyl groups. Through the rearrangement of the bonds of the urethane linkage a carbamic acid group and a vinyl group are produced, the former one decomposes to amine end group and carbon dioxide. Cyclic polyester or polyether oligomers are formed by intramolecular exchange reactions in the soft segments (analogously to the reaction drawn in Scheme 12.2).

5.4.1 Pyrolysis Products of Polyester-segmented Polyurethane

Polyester-segmented PU undergoes decomposition to volatiles in two steps from 280 to 340°C and to 420°C. The nitrogen content of the polymer diminishes in the first step [43] because diisocyanate, the main nitrogen-containing thermal decomposition product is evolving at around 300°C. The thermal decomposition of the flexible polyester segment takes place in the second step at higher temperature. The pyrogram of a PU composed of diphenylmethane diisocyanate (MDI), 1,4-butanediol and poly(butylene adipate), is displayed in Figure 12.8. The components of the gasoline and diesel oil boiling range are various oxygenated hydrocarbons, the fragments of the polyester. The only nitrogen-containing product compound is the isocyanate component of PU, which is MDI in the heavy oil range of the presented pyrogram. The lowest temperature decomposition products of PU (MDI and some cyclic ester dimer) are derived from the breakage reaction of the urethane linkage drawn in Scheme 12.1c; MDI with two isocyanate groups and cyclic dimeric ester, which is cleaved from the hydroxyl group terminated polyester segment by intramolecular ester exchange. The other mechanism supported by pyrolysis-MS experiments [42] leading to aromatic amine (shown in Scheme 12.1d) does not contribute to the volatile products of fast pyrolysis displayed in the pyrogram of Figure 12.8. Pyrolysis of the ester segment of PU is fragmented to vinyl-group-containing esters by reaction (a) in Scheme 12.1 (butadiene, butenyl hydrogen adipate, dibutenyl adipate) and cyclic esters by ester exchange reaction (Scheme 12.2). Tetrahydrofuran and cyclopentanone are the products of cyclic decomposition of the butanediol and adipic acid moieties of the polyester, accompanied by decarbonylation and decarboxylation, respectively.

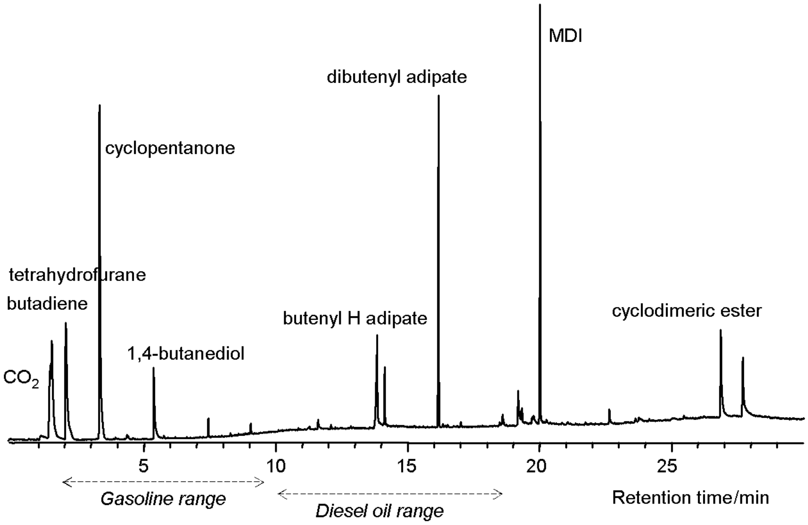


Figure 12.8 Py-GC/MS chromatogram of polyester-segmented PU at 500°C

When PU is based on more volatile diisocyanates than MDI, such as HDI (hexamethylene diisocyanate) or TDI (toluene diisocyanate), these compounds spoil the gasoline or diesel oil boiling fraction of the pyrolysis oil, respectively. It is possible to eliminate the reactive and toxic diisocyanate products from the pyrolysis oil, either in a lower-temperature pyrolysis step or with the help of an adsorbent [41].

The octane number of the gasoline fraction composed of the aliphatic polyester fragments could be predicted by taking into account the linear and cyclic oxygenated saturated hydrocarbon nature of the components.

5.4.2 Pyrolysis Products of Polyether-segmented Polyurethane

Thermal decomposition of PU with polyether soft segments produces volatiles in two steps similarly to that of polyester-segmented PU from 280 to 350°C and to 430°C, however the second step covers a slightly higher temperature range. Only diisocyanate is formed in the first step, aliphatic polyether decomposition products are accumulated in the pyrolysate above 400°C. The pyrogram of a PU composed of diphenylmethane diisocyanate (MDI), 1,4-butanediol and poly(tetrahydrofuran) is displayed in Figure 12.9. The peak of MDI is more dominant in the pyrogram of polyether-segmented PU than in that of polyester-segmented one, because polyether is fragmented in to more compounds. In addition to the series of cyclic oligotetrahydrofurans (the corresponding peaks are indicated in the pyrogram) several other types of oligoether components are present in each boiling fractions of the pyrolysis oil. The gasoline boiling range contains more alcoholic compounds (butanol, butanediol and tetrahydrofuranol) than the higher boiling fractions.

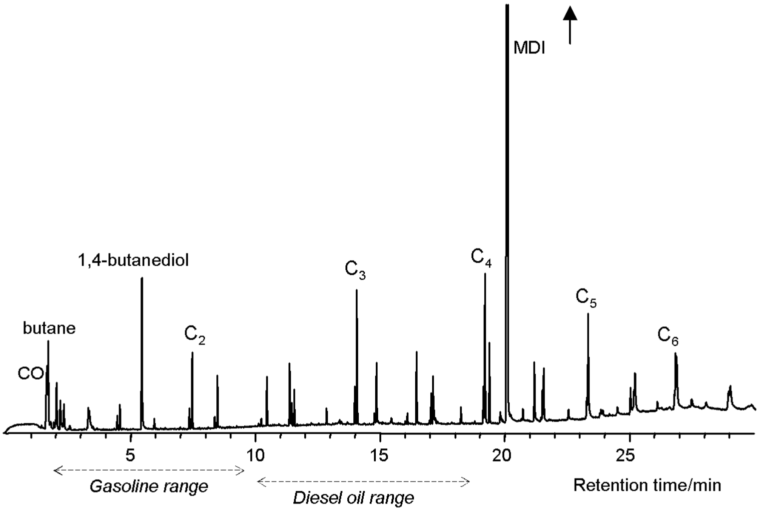


Figure 12.9 Py-GC/MS chromatogram of polyether-segmented PU at 500°C. C_x denotes cyclic oligotetrahydrofuran of x tetrahydrofuran units

MDI is derived from the breakage reaction of the urethane linkage drawn in Scheme 12.1c, the polyester product are formed by intramolecular rearrangement of ether bonds, eliminating cyclic oligomers, and by radical breakage of the polyester chain to partly unsaturated linear oligoethers.

The fuel properties of the pyrolysis oil of an aliphatic polyether-segmented PU could be predicted by taking into account the linear and cyclic oxygenated saturated and olefinic hydrocarbon nature of the components. Elimination of the reactive and toxic diisocyanate from the pyrolysis oil of PU in a lower temperature pyrolysis step is easier in the case of polyether soft segment, because of the larger temperature difference of decomposition steps compared to that of polyester-segmented PU.

6 PYROLYSIS PRODUCTS OF ELECTRONIC WASTE PLASTICS

Electrical and electronic devices are made utilizing several various types of plastic materials, thus when discarded their waste is difficult to recycle. The plastics employed in housing and other appliances are more or less homogeneous materials (among others PP, PVC, PS, HIPS, ABS, SAN, Nylon 6,6, the pyrolysis liquids of which have been discussed above). However, metals are embedded in printed circuit boards, switches, junctions and insulated wires, moreover these parts contain fire retardants in addition to support and filler materials. Pyrolysis is a suitable way to remove plastics smoothly from embedded metals in electrical and electronic waste (EEW), in addition the thermal decomposition products of the plastics may serve as feedstock or fuel. PVC, PBT, Nylon 6,6, polycarbonate (PC), polyphenylene ether (PPO), epoxy and phenolic resins occur in these metal-containing parts of EEW.

There is a common feature of the polymer composition in PC, PPO, epoxy and phenol–formaldehyde resin, all contain phenoxy moieties in their repeating unit. Hence, it is not unexpected that the major pyrolysis products of these plastics are phenols. The reason of the production of phenolic compounds is the higher bonding energy of the C–O linkage in the phenoxy moiety related to that of other bonds along the polymer chain.

6.1 POLYCARBONATE

Aromatic moieties and carbonate groups alternate in the chain of this type of polymer. The oxygen atom is more strongly linked to the aromatic ring than to the carbonyl carbon in the carbonate group [21], thus the thermal cleavage of the weaker C–O bond results in phenoxy radicals and carbon dioxide [44]. The phenoxy radical either becomes a phenolic chain end or a phenolic compound by abstracting a hydrogen atom. If the aromatic moiety of the macromolecule has not enough available hydrogen for abstraction, the combination of the free radicals leads to polyaromatization and yields carbonaceous residue.

6.1.1 Pyrolysis Products of PC

Volatile production occurs from polycarbonate by entirely thermal decomposition between 450 and 550°C yielding about 25% solid residue as well. The pyrogram of the most common aromatic polycarbonate, poly(bisphenol A carbonate) is displayed in Figure 12.10. Alkylphenols and phenol are the main constituents of the boiling range 180–250°C and

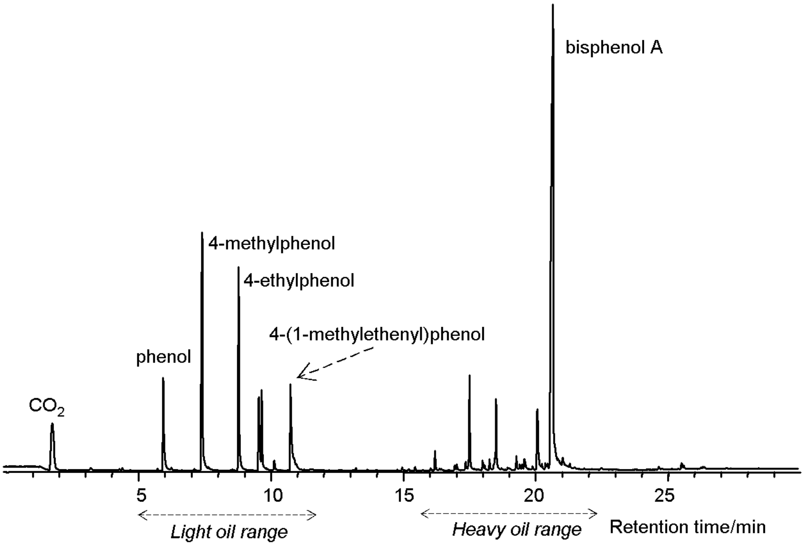


Figure 12.10 Py-GC/MS chromatogram of bisphenol A polycarbonate at 600°C

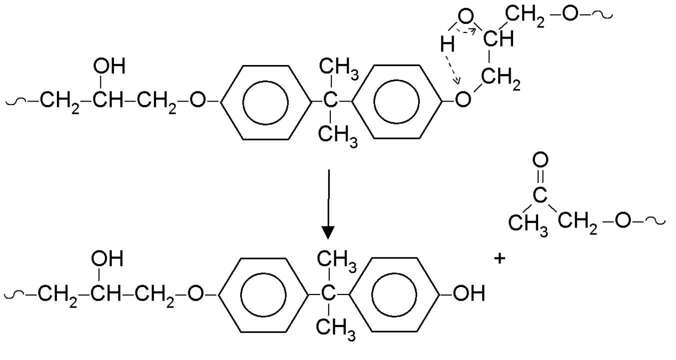
bisphenol A and phenylalkylphenols from 300 to 380°C from this PC in which the aromatic constituent is composed of two phenylene ring linked with an isopropylidene group. There is not enough available hydrogen in this polymer to stabilize all radicals, and so a considerable proportion of the polymer is carbonized.

6.2 EPOXY RESIN

Diglycidylether bisphenol A (DGEBA)-type epoxy resin is generally used in printed circuit boards, and is easily made flame retardant by involving brominated bisphenol A segments as well in the polymer chain. These thermosetting polymers have low thermal stability in spite of their aromatic structural building elements and their network macromolecular structure. The cleavage of the ether link connecting the diglycidyl segments to the aromatic rings is facilitated by a geometrically favoured intramolecular interaction and yields phenol and methyl ketone ends at the scission of the macromolecule shown in Scheme 12.7. The breakage of the C–C bond between the phenol ring and the tertiary carbon of isopropylidene group leads to phenol and isopropenylphenol by disproportion.

6.2.1 Pyrolysis Products of Flame-retarded Epoxy Resin

Volatilization of epoxy resin by thermal decomposition occurs between 330 and 390°C, and a residue of 10% is left. The pyrogram of an epoxy resin flame retarded by incorporation of tetrabromobisphenol A segments is displayed in Figure 12.11. Phenol and isopropenylphenols are the main components of the boiling range 180–280°C, and bisphenol A compounds between 300 and 420°C. The tetrabromobisphenol A segments are decomposed similarly to the regular epoxy ones, yielding brominated bisphenol A compounds, although bromine is also partially cleaved from the phenol rings, leading mostly to mono- and dibrominated compounds. The breakage of the bisphenol segments results not only in phenol and isopropenylphenol, but also to the corresponding brominated compounds, the GC peaks of which are indicated in Figure 12.11 by asterisks. The relative yield of the lower boiling range to the higher one can be considerably increased by



Scheme 12.7 Epoxy chain cleavage through intramolecular rearrangement

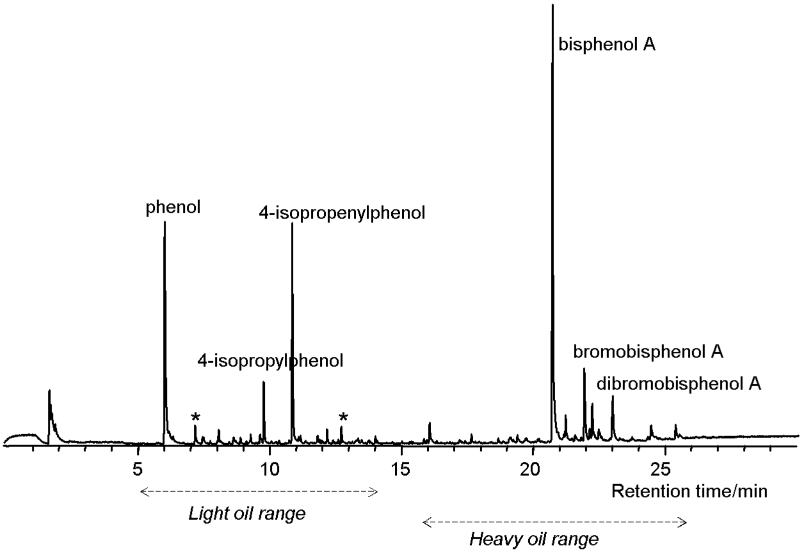


Figure 12.11 Py-GC/MS chromatogram of brominated epoxy resin at 450°C. Peaks labelled* are 2-bromophenol and 2-bromo-4-isopropenylphenol, respectively

increasing the pyrolysis temperature, which promotes the breakage of the bisphenol segments. It must be taken into consideration that the brominated phenols are precursors of polybrominated dibenzodioxins (PBDD), thus dehalogenation is essential before using this pyrolysis oil as a fuel.

6.3 PHENOL–FORMALDEHYDE RESIN

In this polymer phenolic rings are linked through methylene bridges at ortho (2 and 6) or para (4) positions. Branching points are those phenol units which are linked to other phenoic moieties at three carbon atoms, namely at 2, 4 and 6 positions. In a resin where no reactive methylol groups have been left after curing the only possibility for intramolecular interaction requiring relatively low energy is the condensation of two phenolic rings of two phenols connected at ortho–ortho positions. Apart from some water elimination occurring throughout the thermal decomposition of phenol–formaldehyde resin [45] the disintegration of the macromolecule is a free radical process. The scission of the methylene bridges produces aryl and phenylmethyl radicals, both require hydrogen for stabilization and evolution of volatile molecules. Neither phenolic hydroxyl nor the original alkyl substituent groups are cleaved by pyrolysis below 600°C, thus the pyrolysis product compounds are all phenols and similarly substituted as the starting material of the resin [46]. In the pyrolysis oils of phenol–formaldehyde novolacs having no branching points bisphenol compounds are also present.

6.3.1 Pyrolysis Products of Cured Phenol–Formaldehyde Resin

The thermal production of volatile compounds progresses in the temperature range 450–620°C in phenol–formaldehyde resin. From novolacs about 20%, while from cured

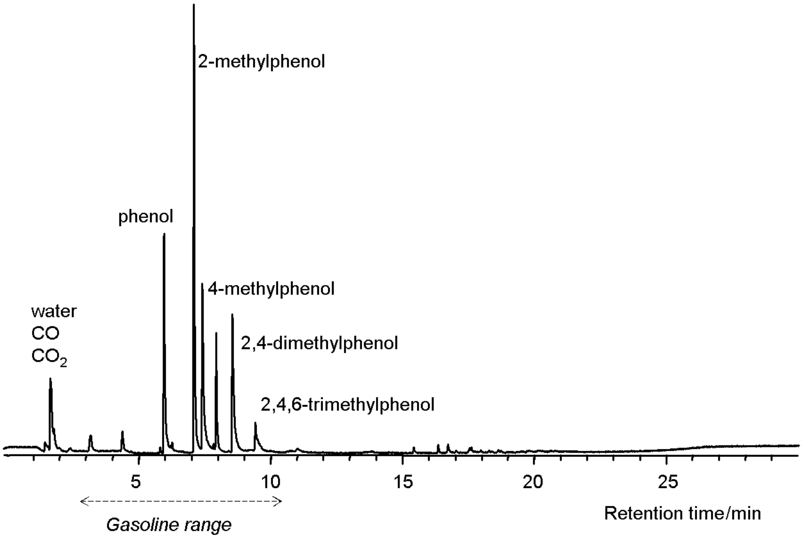


Figure 12.12 Py-GC/MS chromatogram of cured phenol–formaldehyde resin at 600°C

resins 30–50% carbonized residue is also formed. The pyrogram of a cured resin is shown in Figure 12.12. As expected from a free radical scission at the methylene bridges, only 2-, 4-, and 6-methylphenols are components of the liquid, which has a boiling range between 180 and 220°C. From phenol–formaldehyde novolac higher boiling products are also expected in the range 180–220°C. Benzene, toluene and xylenes could be produced at higher temperatures, but at the same time polyaromatic hydrocarbons (PAHs) are also formed.

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13

Production of Premium Oil Products from Waste Plastic by Pyrolysis and Hydroprocessing

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1 BACKGROUND

In the US, plastics is the largest growing waste stream, rising from less than 5 wt% of total municipal solid waste (MSW) in 1980 to over 11 wt% today. In 2001, of approximately 25 million tons of waste plastic, only about 1 million tons were recycled [1]. In California and elsewhere, waste plastic is a major issue due to the growing cost of landfilling. Even plastic which is collected and separated often gets sent to landfills due to lack of a sufficient market [2]. While state law in California has set a recycle rate at 25%, the rate has actually been declining in recent years, from 24.6% in 1995 to only 17.9% in 1999 [3].

Of the waste plastic not recycled, about 43% (or about 11 MM ton/yr) is polyethylene (Figure 13.1), with most of this in containers and packaging [1]. Polyethylene plastic is found in two main forms: high-density (HPDE) and low-density (LDPE). Major uses for HDPE include rigid containers such as bottles, as well as agricultural film. Major uses for LDPE include flexible films such as grocery and dry cleaning bags.

This chapter presents a summary of research on the conversion of waste plastics to premium oil products performed in the United States in the period from approximately 1993 through 2000.

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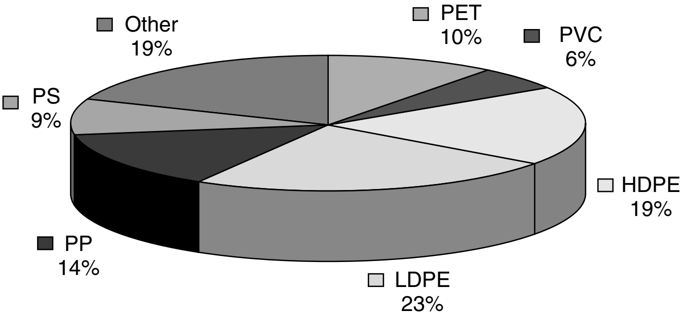

Figure 13.1 Plastics in municipal solid waste

2 CONVERSION OF WASTE PLASTICS TO TRANSPORTATION FUELS

A multi-year research program on the production of liquid transportation fuels from waste polymers and the co-processing of waste polymers with coal to produce liquid fuels was carried out by a group of academic, industrial and government scientists under the sponsorship of the US Department of Energy, Office of Fossil Energy. Much of the laboratory research was conducted by the Consortium for Fossil Fuel Science (CFFS), a five-university research consortium with participants from the University of Kentucky, Auburn University, the University of Pittsburgh, the University of Utah and West Virginia University. Industrial participation was provided by Hydrocarbon Technologies, Inc. (HTI), where pilot-scale and continuous tests were conducted; Consol, where specialized analytical techniques were employed; and Mitretek Corporation, where economic analyses were performed. Research conducted at the US DOE National Energy Technology Laboratory (NETL, Pittsburgh) complemented work in the academic and industrial sectors.

Subsequent to the research performed under sponsorship of DOE, ChevronTexaco sponsored research at the University of Kentucky and at their corporate laboratories that was focused on the conversion of waste plastic (principally polyethylene) into lubricating oil. This chapter presents a summary of the DOE-sponsored research conducted by the University of Kentucky and of the research conducted jointly by ChevronTexaco and the University of Kentucky.

3 DIRECT LIQUEFACTION AND CO-PROCESSING OF WASTE PLASTIC

Much of the research in the US was based on direct liquefaction technology to convert waste plastic into oil products. This work has been summarized in several symposia of the Division of Fuel Chemistry of the American Chemical Society [4–6], a special issue of *Fuel Processing Technology* [7], and an IEA review of research on the co-processing of wastes with coal by a variety of processes prepared by Davidson [8]. A significant amount of research and development has also taken place in Germany [9, 10]. In Germany, a liquefaction plant capable of converting 80 000 tons of waste plastic per year into oil products was developed by Kohleöl-Anlage Bottrop, GmbH (KAB), a subsidiary of Veba Oil. This facility was operated for several years with support from the Duales System

Deutschland, or DSD, which is the organization established by the German packaging industry to deal with the strict recycling laws in that country.

The liquefaction of commingled waste plastic typically yields 70–90% oil, 5–20% gas, and 5–10% solid residue. A significant amount of research has been conducted on the catalytic direct liquefaction of plastic [11–16]. Extensive work has been done using solid acid catalysts and metal-promoted solid acid catalysts, which generally improve oil yields and oil quality. At temperatures above 440°C, however, thermal and catalytic oil yields are comparable. No solvent is required, but good results have been obtained using mixtures of waste oil and petroleum resid with plastic. The reactions can be carried out at low hydrogen pressures (∼100–500 psig) and with low hydrogen consumption (∼1%).

4 PYROLYSIS AND HYDROPROCESSING

Although direct liquefaction of waste plastic looked promising, problems associated with impurities (paper, aluminum, etc.) and chlorine derived from PVC caused operational difficulties. Consequently, it currently appears that the first step of any feedstock recycling process for waste plastics or tires should be pyrolysis, which allows much easier separation of solid impurities and chlorine. Research on pyrolysis of post-consumer plastic has been carried out by Kaminsky and co-workers [17, 18], Conrad Industries [19, 20], and Shah *et al.* [21]. Shah *et al.* [21] conducted pyrolysis experiments on relatively dirty post-consumer waste plastic obtained from the DSD. The pyrolysis oils were then subjected to hydroprocessing to convert them into high-quality transportation fuels (gasoline, kerosene, diesel).

As discussed in detail elsewhere [22], the waste plastic collected by the DSD is subjected to several dry shredding and cleaning steps that reduce the nonplastic residue to typically 4–5 wt%. The cleaned waste plastic is then processed into a pelletized form. The pyrolysis treatments on the DSD waste plastic pellets were performed as a function of temperature in a batch mode reactor (Figure 13.2) [21]. After placing the waste plastic in the reactor and flushing the system with an inert gas, the reactor was lowered into the floor furnace. The furnace was then heated from room temperature to the pyrolysis temperature in 15–20 min and held at that temperature for 1 h before cooling back to room temperature. The yields of oil, gas, and solid residue are shown as a function of the pyrolysis temperature in Figure 13.3. Oil yields approaching 80% were obtained at a pyrolysis temperature of 600°C.

Hydroprocessing of these pyrolysis liquids was carried out at 450°C (200 psig H_2 pressure, cold, 60 min), both thermally and catalytically (1 wt% HZSM-5). The results obtained by simulated distillation (simdist) analysis of the resulting liquids are illustrated in Figure 13.4, which shows the percentages of liquid product in the gasoline (IBP-200°C), kerosene (200–275°C), and heavier oil fractions (275°C-FBP) in the pyrolysis oils before and after thermal and catalytic hydrotreatment of the pyrolysis liquids derived from DSD plastic; the pyrolysis temperatures are indicated along the x-axis. These results show that the lighter boiling point fractions are increased significantly by hydrotreatment at 450°C. The percentage of heavier pyrolysis liquids increases with increasing pyrolysis temperature due to the fact that higher-boiling oils are more quickly volatized at higher temperatures and therefore have less chance to undergo further cracking in the pyrolysis

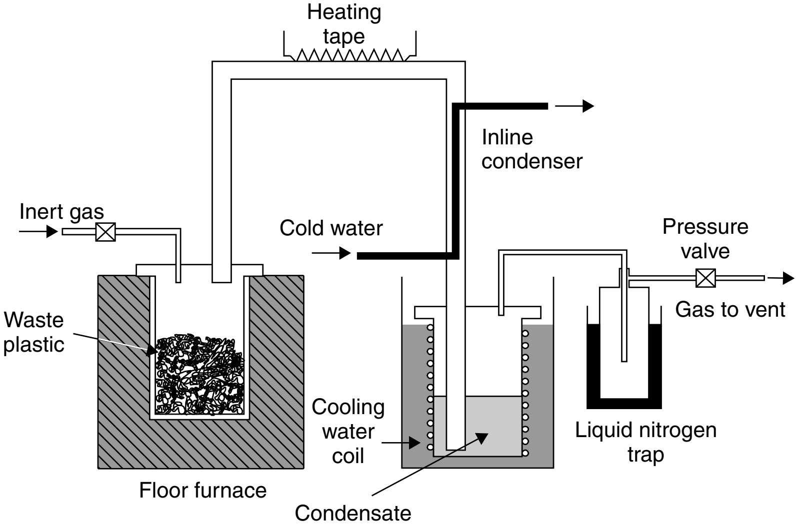

Figure 13.2 Schematic of batch mode laboratory plastic pyrolysis reactor

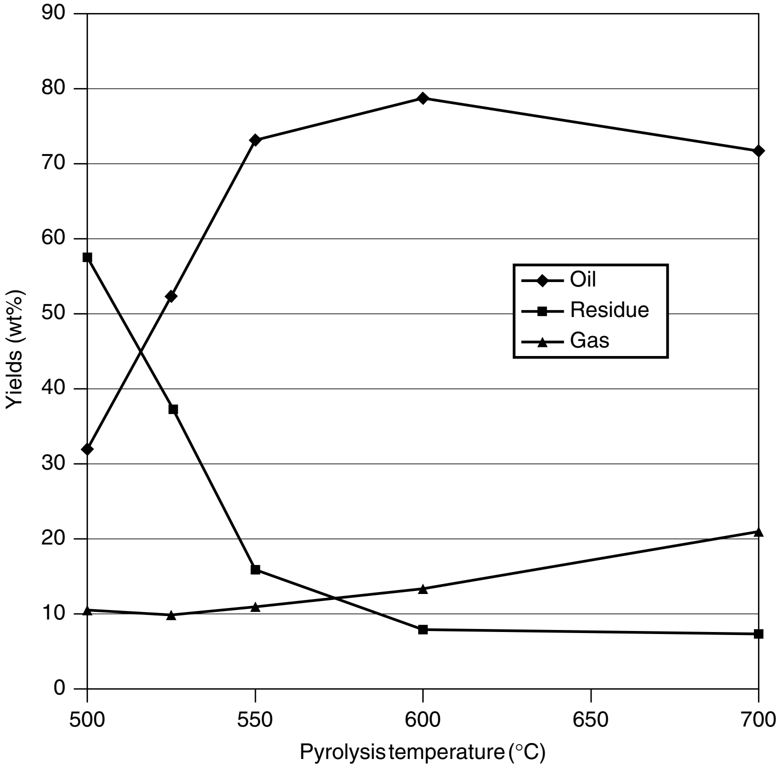

Figure 13.3 Oil, gas, and residue yields from DSD plastic as a function of pyrolysis temperature. (Reproduced by permission of the American Chemical Society)

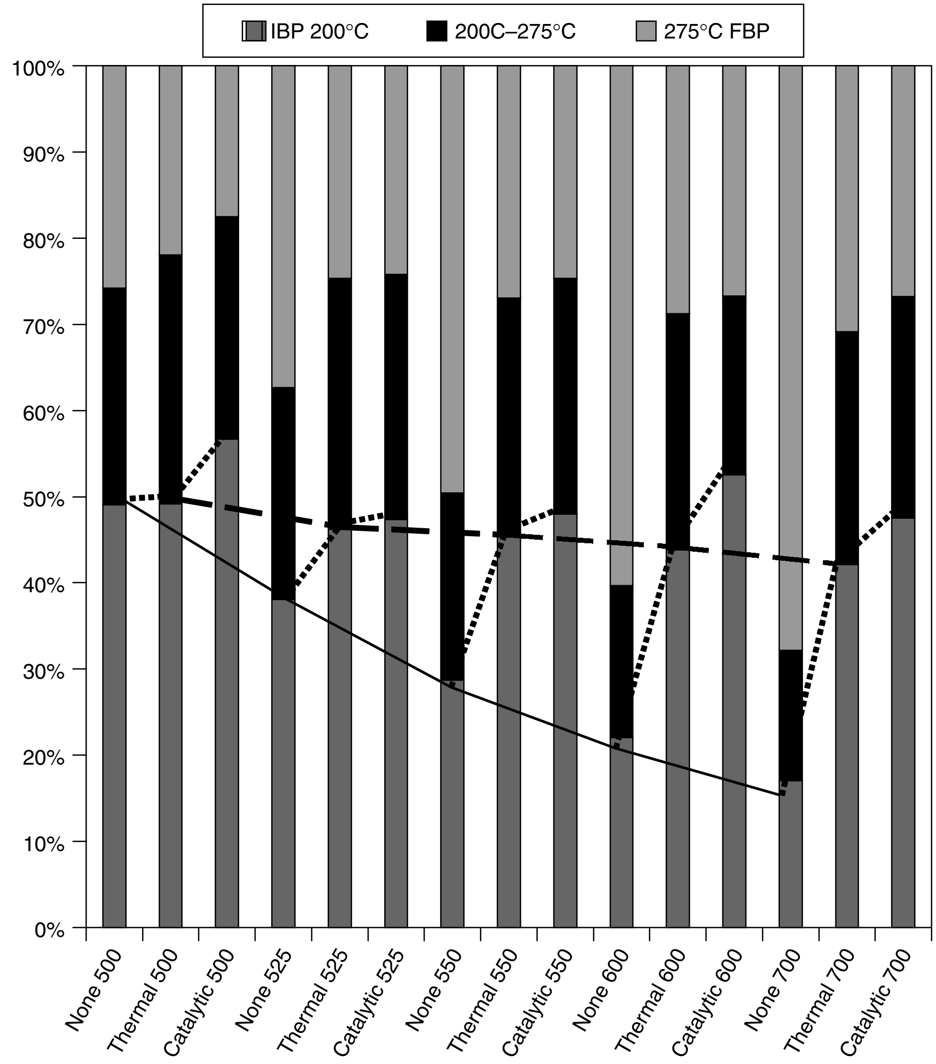

Figure 13.4 Simdist analysis of pyrolysis oil from DSD waste plastic before and after thermal or catalytic hydroprocessing. (Reproduced by permission of the American Chemical Society)

zone. Thermal or catalytic hydroprocessing of the pyrolysis liquids improves the yield of lighter fractions, yielding about 50% of product in the gasoline range and 25–30% in the kerosene or jet fuel range. Catalytic hydroprocessing using 1 wt% of HZSM-5 catalyst gave somewhat better yields of light products than thermal hydroprocessing (Figure 13.4).

Chlorine derived from PVC is the impurity of most concern in oil produced from waste plastic. Because the DSD plastic contained 1.26 wt% Cl, measures were required to remove it in these experiments. To lower the chlorine content of the oil products, small additions (2–3 wt%) of sodium carbonate were made to both the pyrolysis and hydroprocessing reactors to react with HCl released at elevated temperatures. The pyrolysis oils had chlorine contents of approximately 50–70 ppm, while the hydroprocessed oil products exhibited chlorine contents of only 2–8 ppm.

5 FEASIBILITY STUDY

On the basis of promising laboratory and pilot-scale results, DOE commissioned a feasibility study for a 300 ton per day (t/d) plant to convert waste plastic and/or waste tires into transportation fuel and to co-process coal with these waste polymers as required [23]. The principal results of this study were published in Chemtech [22]. Here we present only a brief summary of the feasibility study results for a 300 t/d plant converting waste plastic into oil.

A conceptual design for the plant is shown in Figure 13.5. Detailed information on the estimated capital cost of a 300 t/d plant with this design and its estimated annual operating costs are available [22]. The experimental results indicate that a conservative estimate of the oil yield per ton of waste plastic is about 5 bbl/t. Assuming a plant operating at 90% capacity, this would yield 495,000 bbl/yr.

As part of the feasibility study [22], an economic analysis was performed that was based on oil prices of $15–25 per bbl, which seemed like a reasonable range at that time. On the assumption that the 300 t/d plant would receive tipping fees of $20–40 per ton for accepting the waste plastic, returns on investment (ROI) of 5–20% were predicted. Currently, oil prices are about $50/bbl. If one assumes oil prices of $30–50/bbl, our earlier economic analysis would predict ROI of approximately 20–40%, even with zero tipping fees for waste plastic. However, this is a topic that clearly needs to be revisited using updated capital and operating costs. Moreover, as discussed in the next section, it now appears that lubricating oil would be the product of choice from feedstock recycling of waste plastic and this should have a significant positive impact on the economics.

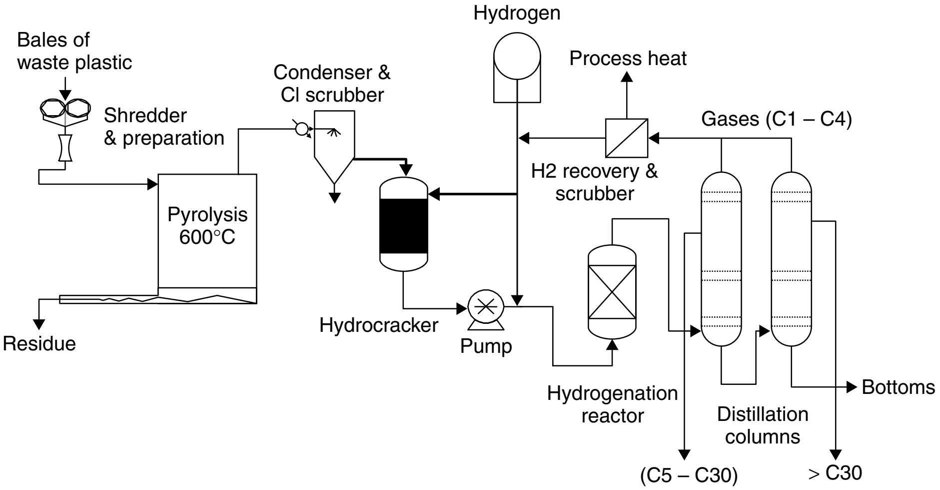

Figure 13.5 Conceptual design for a plant converting waste plastic to oil products

6 CONVERSION OF WASTE PLASTIC TO LUBRICATING BASE OIL

Most of the work on feedstock recycling of plastic has focused on conversion of plastic to transportation fuels. Little has been reported on conversion of waste plastic to higher-valued products. In this section, research on the conversion of waste polymers such as polyethylene to high-quality lubricant oils is summarized. A more detailed account of this research is available elsewhere [24].

There is currently a shift to oils of lower viscosity that reduce engine friction and thereby improve fuel economy. These oils will be in increasing demand by automakers to meet government-mandated minimum miles-per-gallon requirements. A second change is a reduction in oil volatility, which reduces oil consumption and evaporative emissions into the environment. A strong dependence of diesel particulate emissions on engine oil volatility has been shown [25].

EPA statistics show that each year in the US, approximately 200 million gallons of used oil is dumped into the environment [26]. This problem can be largely addressed by producing oils which are more stable, thereby extending the interval between oil drains and reducing the amount of used oil which would need disposal. A high viscosity index (VI) signifies high stability to change in viscosity over a wide temperature range. Oil having a high VI resists excessive thickening when the engine is cold and, consequently, promotes rapid starting and prompt circulation; it resists excessive thinning when the motor is hot and thus provides full lubrication and prevents excessive oil consumption. Most lubricating base oils produced today have a VI of 95–105 and are called conventional base oil (CBO). The term ‘base oil’ refers to the lubricating oil before the addition of additives. Base oils required to meet the future needs discussed above will have to have a VI >115 and are called unconventional base oil (UCBO).

Since paraffins have low volatility for their viscosity, high thermal and oxidative stability, and high VI, these new requirements could be met by using oils that are highly paraffinic. To meet mandated fuel economy and emissions standards plus customer demands will require large quantities of these advanced oils within the next few years.

One technology for preparing the high-VI UCBOs uses a highly selective molecular sieve catalyst to isomerize waxy feeds to allow the oil to flow at low temperature, where that ability is measured by the lowest temperature at which the oil will pour, or its pour point. This technology, first commercialized in the US in the early 1990s [27, 28], converts wax to oil, allowing production of oils at high yield with high paraffinicity, and therefore high VI and low viscosity.

7 LUBRICATING BASE OILS FROM FISCHER–TROPSCH WAX AND WASTE PLASTIC

Fischer–Tropsch (FT) technology converts synthesis gas produced by reforming of methane or coal gasification into waxy products. Long alkanes ($-CH_2-$chains) produced by using FT synthesis are chemically similar to polyethylene. Lubricating oils derived from isomerization of FT waxes are gaining interest due to increased demand for lubricants with the advanced performance and environmental benefits described earlier.

Although FT waxes are high in quality, their availability over the next decade is expected to be limited. Therefore, there is an effort to find other sources of feedstocks of equal quality to co-process along with FT waxes, both to meet the demand and decrease the cost of lubricant products. Waste plastic is a potentially significant new source for such waxy feed. We have performed combined pyrolysis–hydroisomerization experiments, looking at the following feedstock options:

1. Polyethylene
2. Polyethylene + polyethylene terephthalate (PET), where PET (e.g. soft-drink bottles) is one of the major non-PE plastics in municipal waste
3. Polyethylene + FT wax
4. FT wax

HDPE and LDPE were obtained from Chevron Phillips Chemical Company. PET was obtained by cutting up soft-drink bottles. FT wax was obtained from Moore & Munger.

Laboratory pyrolysis of HDPE was first carried out using the batch mode reactor (Figure 13.2). After flushing the system with an inert gas, the reactor was lowered into the floor furnace. The furnace was heated from room temperature to the pyrolysis temperature in 15–20 min and held at that temperature for 1 h before cooling back to room temperature. There was complete conversion of the HDPE in all runs and the reactor was clean at the end of the run. Several runs were carried out to optimize the temperature and pressure conditions.

Because there is no control on the residence time in the batch pyrolysis set-up, pyrolysis at higher temperature allows larger molecular weight species to leave quickly. At lower furnace temperature, the larger molecules are not vaporized, but spend longer times in the furnace to undergo further cracking. This is shown by Figure 13.6, which shows the simulated distillation analysis of HDPE pyrolysis products at 0.1 atmosphere reactor pressure for various furnace temperatures. It is evident that higher boiling point products desired

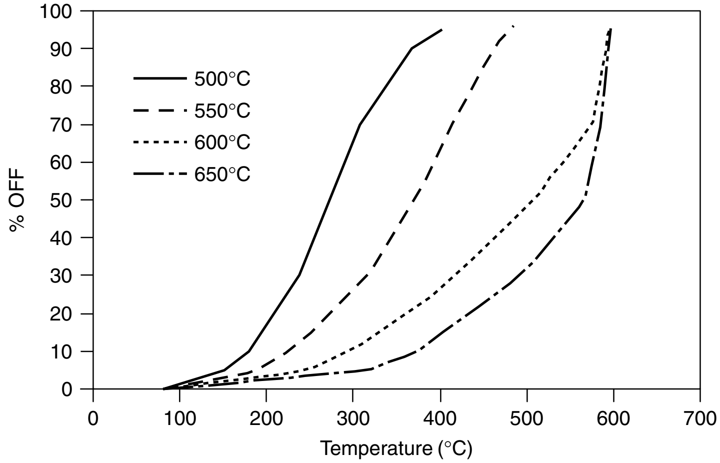

Figure 13.6 Simulated distillation boiling point distributions of HDPE pyrolysis condensates

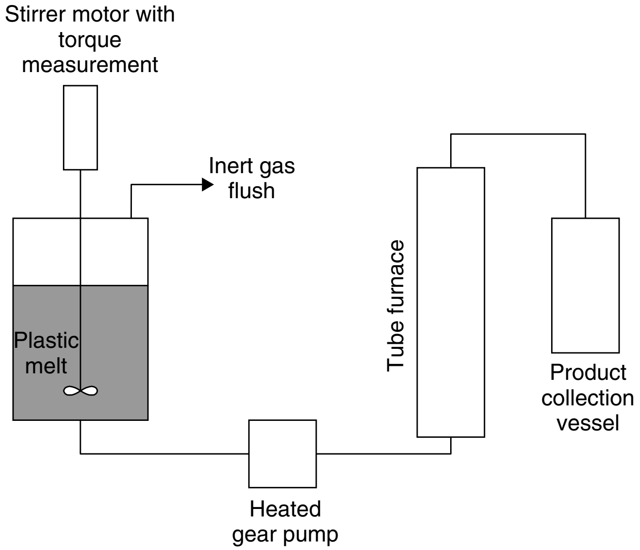

Figure 13.7 Schematic of continuous laboratory pyrolysis reactor

for lube base oil are produced in greater abundance at the higher pyrolysis temperatures (600–650°C). At higher (atmospheric) reactor pressure, the difference between boiling point distributions narrows.

To make the process continuous and to achieve better control of residence time (space velocity) of the process, a second laboratory pyrolysis unit was designed (Figure 13.7). The feed (approximately 500 g) was placed in a melter vessel equipped with a stirrer motor with torque measurement and heated under a 4 psig argon blanket. Melted feed was conveyed by $\frac{1}{2}$-inch (1.25 cm) OD stainless steel tubing to a heated Parker Hannifin Zenith gear pump. This pump could deliver metered feeds at temperatures as high as 450°C with little dead volume. The feed then went by way of $\frac{1}{4}$-inch (0.625 cm) stainless steel tubing to a 25 cc, $\frac{1}{2}$-inch (1.25 cm) OD, upflow stainless steel reactor in a tube furnace. Products were collected downstream in a water-cooled collection vessel.

Kinetics were determined using the laboratory pyrolysis unit with the melter/feed vessel temperature set at about 325°C and the pump temperature set at about 300°C. By varying the speed on the gear pump, residence times in the furnace were set. Residence times used ranged from 1 to 12 min, yielding a HDPE throughput of about 100 to 1200 g/h.

In all cases, gas make was low, not more than a few percent for the 600–650°C pyrolysis runs. Simulated distillation results (by thermogravimetric analysis) on the collected products were used to calculate the wt% conversion to products with boiling points below 538°C (1000°F). These showed the conversion to follow close to first order kinetics (Figure 13.8). The apparent activation energy for the process was 42 kcal/mole ±20 kcal/mole (Figure 13.9), which is within the range of values reported in the literature [29]. These results indicate that it should be possible to get substantial conversion to lube oil feedstock at temperatures (500–550°C) and residence times (30 min to 1 h.) similar to conventional refining processes, but at atmospheric pressure and without co-feeding hydrogen.

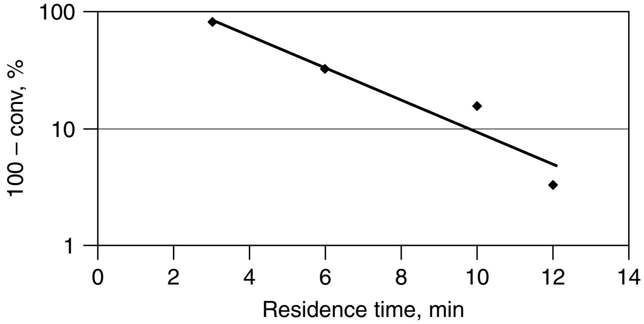

Figure 13.8 Conversion of HDPE pyrolyzed at 650°C at atmospheric pressure to < 538°C boiling fraction as a function of residence time

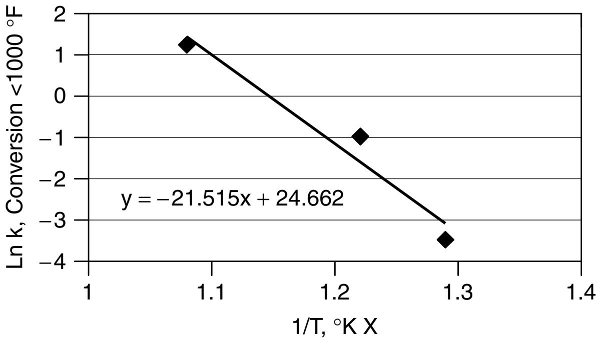

Figure 13.9 Ln *k* versus 1/*T* determined the activation energy for the process

8 ONE-GALLON-PER-DAY PILOT PLANT

A diagram of the one-gallon-per-day pyrolysis pilot plant is shown in Figure 13.10. Feedstock was melted at 260°C in a 30-liter feed pot equipped with an air-driven stirrer, and which had a 10 psi nitrogen blanket. Using a Parker Hannifin Zenith gear pump, the feed was pumped through a stainless steel preheat coil at 370°C and then up-flowed through a 2.5-cm diameter stainless steel reactor that contained pre-heat and after-heat steel bars to reduce the reactor volume to 140 cm^3. When plastic without Fischer–Tropsch wax was run, the feed was diluted 50/50 by weight with a 290–370°C hydrocracked diesel to lower the viscosity to a point at which the feed could be pumped. All pyrolysis runs were at atmospheric pressure and approximately 1 h residence time (based on plastic and/or wax), with no added gases.

Product from the reactor was sent to a still, set at about 230°C, with nitrogen stripping gas to cut the effluent stream at about 340°C. Both overhead and bottoms liquids were collected in cans on scales. Gas went through a gas meter and gas sampler for analysis.

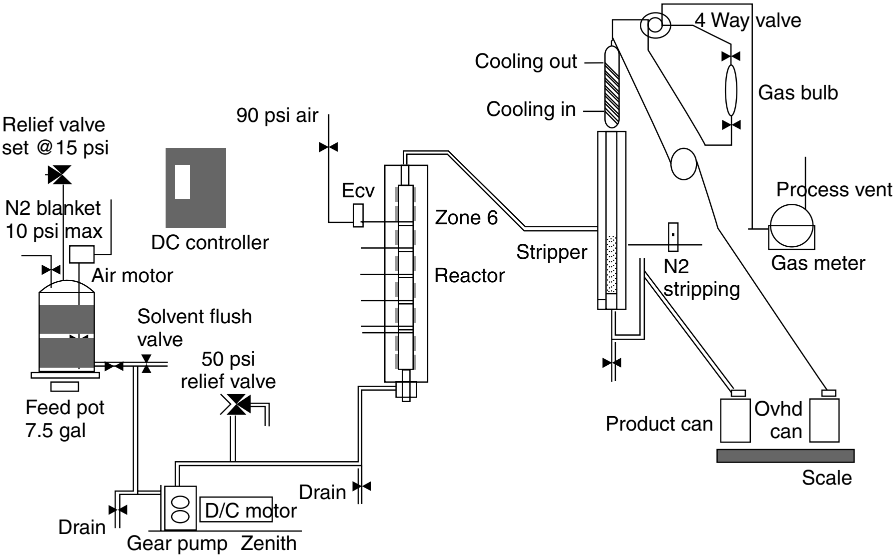

Figure 13.10 One-gallon-per-day pyrolysis pilot plant

8.1 HYDROPROCESSING

8.1.1 Hydrotreating

Hydrotreating of the pyrolyzer stripper bottoms was carried out over a commercial nickel–tungsten on silica–alumina hydrotreating catalyst at 300°C, a liquid hourly space velocity of 1.5 h^{-1}, 13.4 MPa total pressure, and 880 standard cubic meters once-through H_2 per cubic meter of feed. At these conditions, cracking of the feed was minimal.

8.1.2 Hydroisomerization

Isomerization of the waxy pyrolyzer stripper bottoms was carried out over a proprietary wax hydroisomerization catalyst. A commercial Pt–Pd on silica–alumina hydrofinishing catalyst was used in a second reactor downstream from the first to hydrogenate any unsaturated compounds to improve thermal and oxidative stability.

8.2 PYROLYSIS PILOT PLANT RESULTS FOR VARIOUS FEEDSTOCKS

Table 13.1 shows the yields and inspections from the pyrolysis run in the one gallon per day pilot plant with HDPE. The yield of 385°C+ product, with an endpoint of about 593°C, suitable for lubricating base oil, was 51.4 wt% based on plastic in the feed. At the conditions of the run, there was only 6 wt% 538°C+ in the product, yet only about 5 wt% of the low valued C4- light ends. Minimizing both might be possible through further optimization.

Table 13.1 Pyrolysis of 50/50 by weight plastic/diesel at atmospheric pressure, and 1 h residence time

Plastic	HDPE	HDPE	96/4 HDPE/PET
Temperature (°C)	552	524	524
Yield (wt%)			
C1	0.8	0.5	0.2
C2 =	1.8	0.8	0.5
C2	0.9	0.6	0.4
C3 =	2.4	1.2	0.6
C3	0.8	0.5	0.4
C4 =	2.2	0.8	0.6
C4	0.4	0.5	0.2
C1–C4	9.3	4.9	2.9
C5–385°C	69.6	69.4	75.9
385°C+	21.1	25.7	21.2
385°C+, based on plastic	42.2	51.4	42.4

8.2.1 Polyethylene + PET

The price of baled HDPE with up to 2% impurities has fluctuated from 7–10 cents/lb two years ago to about 30 cents/lb recently. If the plastic used in the pyrolysis process did not require this limit, the cost could be considerably lower. (Unseparated waste plastic can be valued as low as negative 2 cents/lb, which accounts for landfilling cost or tipping fee.) Consequently, the run with HDPE was repeated, except the plastic was 96 wt% HDPE and 4 wt% waste polyethylene terephthalate from soft-drink bottles. Pyrolysis yields are given in Table 13.1, showing a 385°C+ yield, based on plastic, of 42.4 wt%.

In the pyrolysis run, C4– was again quite low (about 3 wt%), and the product contained no 538°C+ in the bottoms. Assuming all the C4- came from the plastic would indicate about 6 wt% of the plastic was converted to gas.

8.2.2 Polyethylene + FT Wax

Pyrolysis was carried out on a feed composed of a 50/50 mixture by weight of low-density polyethylene (LDPE) and hydrotreated FT wax. Yields are given in Table 13.2, showing a 385°C+ yield of 57.5 wt%. The yield for a broader lube feed, 343°C+, was 66.0 wt%. While there was considerable 538°C+ in the feed to the pyrolyzer, there was little 538°C+ in the product, which is believed here to be advantageous for low cloud point. Olefinicity in the pyrolysis overhead was 76 wt% by PONA analysis. The olefinic overhead liquids from the pyrolysis of both FT wax and LDPE/FT wax were analyzed using gas chromatography. This showed the cracked product to be almost entirely 1-normal olefins and normal paraffins.

The pyrolysis bottoms were then hydroisomerized to give a –22°C pour point, 4.4 cSt oil of 154 VI (Table 13.3). The overall 343°C+ yield, based on feed to the pyrolyzer, was 44 wt%. Adding the potential lube from oligomerizing the lighter olefinic product from the pyrolyzer would increase the 343°C+ yield to about 59 wt%. However, in this run, a significant amount of 343°C– was in the feed to the hydroisomerization step (10 wt% based on feed to the pyrolyzer). Had this been sent to oligomerization, the potential 343°C+ would be at 67 wt% (Figure 13.11), based on the PONA olefin analysis.

Table 13.2 Pyrolysis of FT wax feeds at 524°C, atmospheric pressure, and 1 h residence time

Feed	50/50 LDPE/FT wax	FT wax
Yield (wt%)		
C1	0.2	1.0
C2=	0.6	0.6
C2	0.4	2.4
C3=	0.9	0.8
C3	0.7	1.8
C4=	0.9	1.6
C4	0.4	1.3
C1–C4	4.1	9.5
C5–177°C	9.9	8.4
177–343°C	20.0	21.4
343–385°C	8.5	9.6
385°C+	57.5	51.1

Table 13.3 Hydroisomerization of pyrolyzed product from FT wax feeds

Feed	Pyr. 50/50 LDPE/FT wax	Pyr. 50/50 LDPE/FT wax	Pyr. FT wax
Hydrotreated	No	Yes	No
Yield (wt%)			
C1–C2	0	0.1	0
C3	0.5	0.8	0.5
C4	0.9	1.7	1.0
C1–C4	1.4	2.6	1.5
C5–177°C	8.7	13.7	10.2
177–343°C	32.6	31.7	37.4
343–385°C	11.5	11.0	12.4
385°C+	45.8	41.0	38.5
Bottoms			
Feed (wt%)	60.9	61.6	64.7
Pour point (°C)	−22	−15	−14
Cloud point (°C)	−2	−2	−1
Viscosity, 40°C (cSt)	18.70	15.23	12.56
Viscosity, 100°C (cSt)	4.416	3.829	3.380
VI	154	150	150
Simulated distillation, °C (wt%)			
10	353	329	319
30	396	377	363
50	437	426	407
70	474	470	449
90	516	517	491
Overall 385°C+ (wt%)	34.8	31.2	27.6
Overall 343°C+ (wt%)	43.7	39.7	36.5
Total 343°C+, (including Oligomers) (wt%)	59	55	52

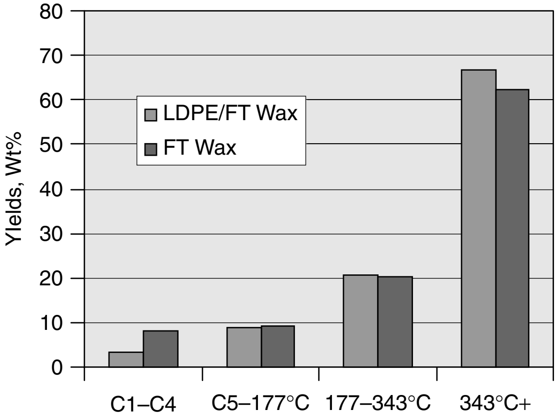

Figure 13.11 Potential yields with isomerization/oligomerization

A portion of the pyrolysis bottoms was hydrotreated to reduce the nitrogen from 8 ppm to less than 1 ppm. This was then hydroisomerized to give a −15°C pour point 3.8 cSt oil with a 150 VI (Table 13.3). The overall 343°C+ yield was 40 wt%, close to that estimated for unhydrotreated feed at the same pour point.

8.23 FT Wax

FT wax was next run without plastic. Yields through the pyrolyzer are given in Table 13.2, showing a surprisingly similar product distribution and olefinicity to the run with a 50/50 LDPE/FT wax mix. Again, there was little 538°C+ in the product, which was mostly in the neutral oil boiling range, as shown in Figure 13.12. Hydroisomerization of the pyrolysis bottoms gave a −14°C pour 3.4 cSt oil of 150 VI (Table 13.3). The overall 343°C+ yield was 37 wt%. Adding the potential lube from oligomerizing the lighter olefinic product from the pyrolyzer would increase the 343°C+ yield to about 52 wt%. Had all the 343°C− from the pyrolyzer been sent to oligomerization, the potential 343°C+ would be about 62 wt% (Figure 13.11). Note that the product distribution in Figure 13.11 is about the same for either FT wax alone or FT wax plus plastic. This suggests, along with the similar properties found in the isomerized products, that a pyrolysis process could be developed with a wide flexibility in choice of feedstock mix.

9 SUMMARY AND CONCLUSIONS

This chapter has summarized research conducted on feedstock recycling of waste plastic into light oil products ($\sim C_5$–C_{20}) suitable for transportation fuels (gasoline, jet fuel, and diesel fuel) and a high value product, lubricating oil. The principal results are summarized below.

Transportation fuel. For mixed post-consumer plastic (PCP) that contains significant amounts of paper, inorganics, and chlorine, the best approach appears to be pyrolysis followed by hydroprocessing. Batch mode pyrolysis at 600°C, followed by thermal or

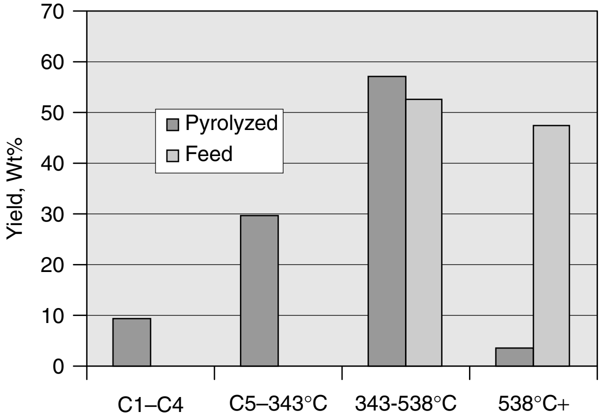

Figure 13.12 Pyrolysis of FT wax at 524°C and 1 h residence time

catalytic hydroprocessing at approximately 450°C under low hydrogen pressures gave oil yields of approximately 80%, of which 50–55% was in the gasoline boiling point range, and 20–30% in the kerosene range. Catalytic hydroprocessing using 1 wt% HZSM-5 improved the yields of the lighter products by about 5–10%. The results of a feasibility study for a plant converting 300 t/d of waste plastics into oil for the transportation fuel market were briefly reviewed. If oil prices in the range $30–50/bbl are assumed and waste plastic is available at no cost and without any tipping fees, it appears that such a plant could achieve returns on investment (ROI) of 20–40%.

Lubricating oil. A new process has been developed for the conversion of waste plastic and Fischer–Tropsch (FT) wax to lube range molecules that can be hydroisomerized to low pour point lube base oils of unconventional base oil (UCBO) quality. The process employs pyrolysis, a thermal, noncatalytic, low-pressure reaction where high-molecular-weight molecules are cracked to ones of lower molecular weight. The major by-product is diesel, with little production of C_4- gas. The by-product liquids are highly olefinic and could be oligomerized to provide additional base oil.

Laboratory experiments were first conducted using a continuous pyrolysis reactor to establish optimal conditions for lube base oil production from polyethylene (PE). A pilot plant study was then carried out in a 1-gallon-per-day unit. The main findings included:

1. Potential lube yields were in the 60–70 wt% range, assuming all the olefins (almost all 1-olefins) could be upgraded to lube. About half this yield would come from hydroisomerization and half from oligomerization.
2. The product distribution and lube oil quality surprisingly showed little variation, whether the feed was PE, FT wax, or a combination of the two. Therefore, waste PE could be *co-processed* in the same plant as FT wax, increasing product volume and improving the economics of the process.
3. The pyrolysis process could be carried out at atmospheric pressure, and at a temperature and residence time typical of refinery operations, i.e. 524°C for 1 h, with total conversion of plastic to lube range and lighter product, almost all of which was 538°C−.

4. Hydrotreating the feed prior to the hydroisomerization step did not significantly affect lube oil yield or quality. Eliminating this step could benefit the overall process economics.
5. When 4 wt% polyethylene terephthalate (PET), derived from used soft-drink bottles, was added to the PE, no decline in lube quality was observed, with hydroisomerization giving a 160 VI 5 cSt oil. This indicates that a high degree of separation of the waste plastic may not be necessary, which would lower the cost of feedstock to the process.

In summary, we have shown that by pyrolyzing waste polymers such as polyethylene, waxy products similar to those from Fischer–Tropsch processing can be made, which can then be converted to high-quality lubricant oils via wax hydroisomerization. While a detailed economic analysis has not yet been carried out, the much higher value of lube oil relative to transportation fuels suggests that this may be a more viable and profitable way of disposing of waste plastic, a growing waste stream problem.

ACKNOWLEDGEMENTS

The research on conversion of waste plastic to oil products suitable for transportation fuels was supported by the US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, under DOE research contract no. DE-FC22-93PC93053. The post-consumer waste plastic used for this part of the research was provided by Gerhard Fahrbach and Sabine Melichar of the DSD. Funding for the research on conversion of waste plastic and Fischer–Tropsch wax into lubricating oil was provided by ChevronTexaco Energy Technology Company.

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14

The Conversion of Waste Plastics/Petroleum Residue Mixtures to Transportation Fuels

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1 INTRODUCTION

Plastics have become the material of choice in the modern world and their applications in the industrial field are continually increasing. Presently plastics are manufactured for various uses such as: consumer packaging, wires, pipes, containers, bottles, appliances, electrical/electronic parts, computers and automotive parts. Most post-consumer plastic products are discarded and end up as mixed plastic municipal waste. The disposal of this waste has become a major social concern.

Mixed plastic waste (MPW) recycling is still very much in its infancy. Approximately 20 million tons of plastic waste is generated in the United States of America, while about 15 million tons is generated throughout the Europe. With existing recycle efforts, only 7% of the MPW are recycled to produce low-grade plastic products such as plastic sacks, pipes, plastic fencing, and garden furniture. The current plastic reclamation technology options are generally grouped into the following four types:

- primary – the processing of plastic for use comparable to the original application;
- secondary – the processing of plastics waste into new products of a lower quality level;
- tertiary – the chemical or thermal processing of plastic waste to their basic hydrocarbon feedstock. The resulting raw materials are then reprocessed into plastic material or other products of the oil refining process;
- quaternary – the incineration of plastics waste to recover energy.

This chapter deals exclusively with tertiary recycling by pyrolysis and catalytic cracking of plastics waste alone and by coprocessing with petroleum residue or heavy oils to

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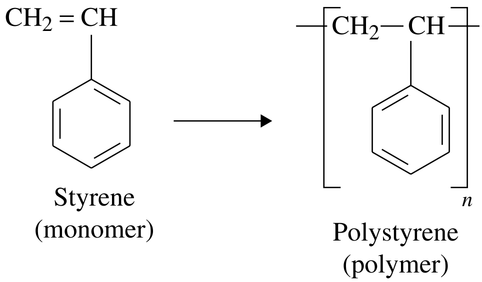
fuels and petrochemical feedstock for further processing in existing refinery and petrochemical units.

2 THE CHARACTERISTICS AND CHEMICAL STRUCTURE OF PLASTICS

Plastics are organic polymers consisting of giant molecules made up of a large number of repeating units known as monomers. Polymer molecules have molecular weight in the range of several thousand or more, and therefore, are also referred to as *macromolecules*. This is illustrated by the following equation, which shows the formation of the polymer polystyrene.



Polymers are classified according to their structure and degree of polymerization such as:

(a) Linear polymers – a single linear chain of monomers.
(b) Branched polymers – linear chain with side chains.
(c) Cross-linked polymers – two or more chains joined by side chains (Figure 14.1).

All polymers can be divided into two major groups (*thermoplastics* and *thermosets*) based on their thermal processing behavior. Thermoplastics soften and flow when heated. Upon cooling, thermoplastic polymers harden and assume the shape of the mold. Examples of commercial thermoplastics include polystyrene, polyolefins (e.g. polyethylene and polypropylene), nylon, poly(vinyl) chloride (PVC), and poly(ethylene) terephthalate (PET). Thermoplastics make up 80% of the plastic produced today and these polymers are linear or branched in their structure.

Thermosets are polymers whose individual chains have been joined by side chains (cross-linked). These polymers usually exist initially as liquids; they can be shaped into

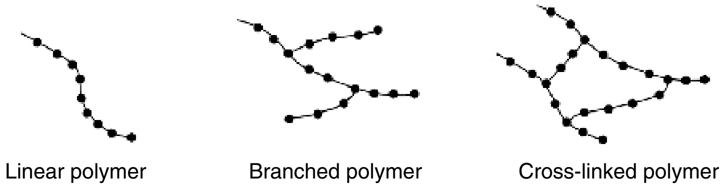


Figure 14.1 Different types of polymer structure

desired forms by the application of heat and pressure. Once formed, they harden and cannot be thermally processed or mechanically recycled. Principal examples of thermosets include epoxies, phenol–formaldehyde resins, polyurethanes (PUR), and unsaturated polyesters. Vulcanized rubber used in industry is also an example of a thermosetting polymer. Thermosets make up the remaining 20% of plastic produced today. Presently, all plastics are produced from petrochemicals derived from petroleum.

3 THE CHARACTERISTICS AND CHEMICAL PROPERTIES OF PETROLEUM RESIDUE

Petroleum is a complex mixture of various aliphatic and aromatic compounds, including sulfur, nitrogen and organometallic compounds. Petroleum residue constitute mostly of the nonvolatile, high-molecular-weight fractions of petroleum, that remain after the removal of the distillate fractions with boiling points up to 500°C. These compounds may differ from one another greatly in both polarity and molecular size. The more polar compounds interact with one another to form molecular associations of varying strengths and sizes. These polar compounds are insoluble in *n*-alkanes and are known as *asphaltenes*. The asphaltenes contain very high concentration of the detrimental heteroelements (S, N, O and metals). Structurally, asphaltenes are condensed polynuclear aromatic ring systems bearing mainly alkyl side chains. The number of these rings in petroleum asphaltenes can vary from 6 to 15. Because of their condensed structure, asphaltenes tend to be extremely refractory during processing operations. They are heat labile and are gradually deposited as coke on the walls of a reactor vessel and also are adsorbed onto the surface of catalysts. Metals present in asphaltenes also fill up the pores of the supported catalyst within a short period. These characteristics of the petroleum vacuum residue prevent its use as a feedstock to fluid catalytic cracking (FCC) or hydrocracking (HC) units.

Table 14.1 illustrates the more important properties of vacuum residues from Saudi crude oils [1]. The three most important properties from the upgrading standpoint are sulfur, metals and asphaltenes contents. Sulfur continues to be a problem chiefly because of environmental objections to sulfur dioxide emissions. Therefore, a primary requirement is the removal of at least a major portion of the sulfur in the vacuum residue.

4 TECHNOLOGIES FOR PETROLEUM RESIDUE UPGRADING

A number of technologies are available to upgrade distillation residues [2]. Thermal processing is the traditional way to treat residues. Examples include visbreaking, flexicoking,

Table 14.1 Typical vacuum residue properties of Saudi Arabian crude oils (~538°C+)

Properties	Arabian light	Arabian medium	Arabian heavy
Gravity (° API)	8.53	6.15	5.60
Sulfur (wt %)	4.16	5.31	5.50
Carbon residue (wt%)	15.2	19.8	22.4
Vanadium + nickel (ppm)	76	92	194
Asphaltene (wt%)	11.5	16.0	19.5
Nitrogen (wt%)	0.29	0.24	0.37

delayed coking, etc. These processes remove carbon as coke, thus increasing the H/C ratio.

$$2\text{–}(\mathrm{CH}_{1.4})_n\text{–} \xrightarrow{\Delta} \mathrm{C} + \text{–}(\mathrm{CH}_{2.2})_n\ \text{–}$$

If cracking catalysts are used to support the cracking process, the sulfur and metal contaminants must be removed upstream since they poison the catalyst, such as in the residue FCC process [3].

The deasphalting process is also based on carbon removal [4]. However, it uses a completely different technology. Here, asphaltenes are extracted by solvents from the heavy ends. Light hydrocarbon (e.g. propane) or supercritical gases are used as solvents. The resulting deasphalted oil is essentially free of metallic contaminants. The carbon removal processes yield large amounts of low-value coke or asphalt beside the desired hydrocarbon products.

None of the different processes has decisive economic advantage over the others. They are economically feasible only in special situations, when an outlet for the low-value products is available.

$$\mathrm{R\text{–}CH_2\text{–}CH_2\text{–}R'} \longrightarrow \mathrm{R\text{–}CH_2} + \mathrm{R'\text{–}CH_2} \xrightarrow[\text{catalyst}]{+\mathrm{H}_2} \mathrm{R\text{–}CH_3} + \mathrm{R'\text{–}CH_3}$$

Addition of hydrogen for improving the H/C ratio leads to better yields of high value products. Hydrocracking is the process of choice to upgrade crude oils [5]. It breaks down high-molecular compounds in a cracking step and the fragments are saturated *in situ*by addition of hydrogen to the points of scission. However, as a catalytic process hydrocracking is sensitive to catalyst poisons. Therefore the sulfur, nitrogen and metal contaminant of the feed must be removed upstream in a separate reactor [6]. Although hydrocracking is well suited for crude oils, it is much less advantageous for upgrading distillation residues. The highly condensed aromatic compounds in residues do not undergo hydrogenation easily and even under severe conditions the conversion is only of the order of 75%. This leads to very short catalyst lifetimes, especially when zeolite based catalysts are used. Because of the required high investment costs and other disadvantages, the overall economics of the hydrocracking of residues are not much better than those of the thermal cracking processes [7, 8].

In conclusion, most of the available technologies to upgrade oil residues are not free of major disadvantages. Hydrocracking of residues is hampered by short lifetimes of the zeolite catalysts and increasingly high cost of hydrogen. The carbon removal processes such as coking, cracking or deasphalting, yield large amounts of low calorie gas, coke or asphalt, which are difficult to market.

5 TECHNOLOGIES FOR TERTIARY RECYCLING OF MIXED PLASTIC WASTE (MPW)

Tertiary recycling of MPW is getting a lot of attention as an alternative method to landfill disposal and mechanical recycling. Tertiary recycling includes both *chemical recycling* and *feedstock recycling*. Chemical recycling implies a change of the chemical structure of the material, but in such a way that the resulting chemicals can be used to produce the original material again. Feedstock recycling implies a change of the chemical structure of the material, where the resulting chemicals are used for another purpose than producing original material. Various technologies for tertiary recycling, therefore, include all those processes which attempt to convert MPW to basic chemicals by the use of chemical reactions such as hydrolysis, methanolysis and ammonolysis for condensation polymers and to fuels with conventional refinery processes such as pyrolysis, gasification, hydrocracking, catalytic cracking, coking, and visbreaking for addition polymers. However, some of these options are not suitable for MPW containing a high amount of PVC due to corrosion problems arising from chlorine and hydrogen chloride. For this reason the feedstock recycling technology is grouped into the following three main categories:

1. MPW with a limited chlorine (i.e. PVC content)
2. PVC-rich MPW
3. Specific plastic waste such as PET, PUR and Nylon

The available technology options for these three classes are discussed in the following sections:

5.1 FEEDSTOCK RECYCLING OF MPW WITH LOW PVC CONTENT

The following technologies have been reported as most promising options for feedstock recycling of MPW [9].

5.1.1 Texaco Gasification Process (Netherlands, Pilot in the US)

Gasification is a thermal process which uses high temperatures to break down any waste containing carbon. This technology uses less oxygen than traditional mass-burn incineration. The pyrolysis process degrades waste to produce char (or ash), pyrolysis oil and synthetic gas (called syngas). The gasification process then breaks down the hydrocarbons left into a syngas using a controlled amount of oxygen.

Texaco gasification, based on a combination of two processes, liquefaction and an entrained bed gasifier, is summarized in the Figure 14.2.

In the liquefaction step the plastic waste is cracked under relatively mild thermal conditions. This depolymerization results in a synthetic heavy oil and a gas fraction, which in part is condensable. The noncondensable fraction is used as a fuel in the process. The process is very comparable to the cracking of vacuum residues that originate from oil recycling process.

5.1.2 Polymer Cracking Process (Consortium Project, Pilot)

This is a fluid-bed cracking process. It was first tested in 1990s. This pilot plant has a 400 tonne per year feed capacity, but runs continuously on a 50 Kg/h scale as it has limited product storage. The next steps in the development process to follow are optimization and scale-up.

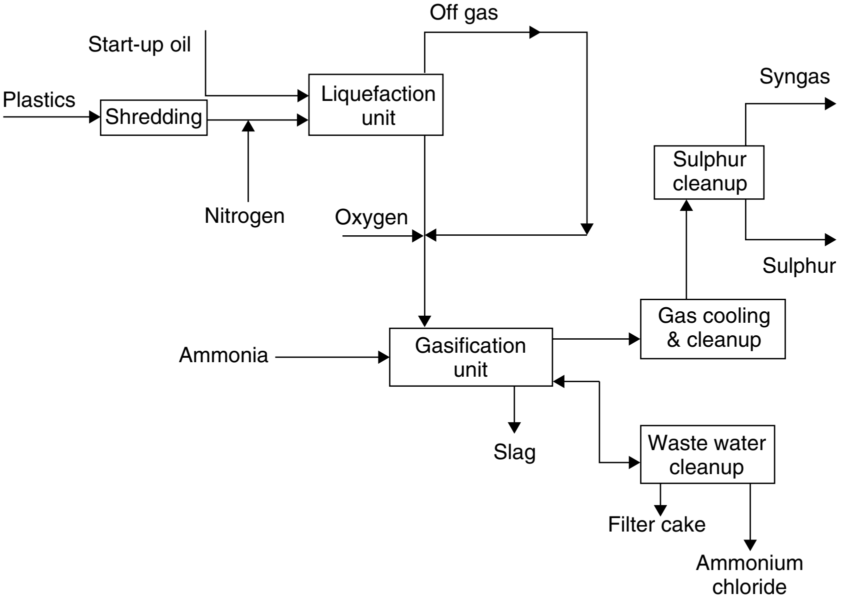


Figure 14.2 Schematic representation of the Texaco process

The decomposition of PVC leads to the formation of HCl, which is neutralized by bringing the hot gases into contact with a solid absorbent. This results in a $CaCl_2$-fraction that has to be landfilled. The purified gas is cooled, most of the hydrocarbon condensed as distillate feedstock. The remaining light hydrocarbon gas is compressed, reheated and returned to the reactor as fluidizing gas. Part of the stream could be used as fuel gas for heating the reactor, but as it is olefin-rich, recovery options are underway.

The process shows good removal of elements such as chlorine. With an input of 10 000 ppm Cl, the products will contain around 10 ppm. This is somewhat higher than 5 ppm requirements for refinery use. Also metals like Pb, Cd and Sb can be removed to very low levels in the products. All hydrocarbon products can be used for further treatment in refineries.

5.1.3 BASF Conversion Process (Germany, Pilot but on Hold)

A 15 000 tone per year pilot plant was set up in Ludwigshafen, Germany, in 1994. Due to the uncertainty of the feedstock waste supply, the pilot plant was closed in 1996. The BASF process is shown in Figure 14.3. The products of this process are HCl, naphtha, ethylene, propylene and heavy oils.

5.1.4 Use of Mixed Plastic Waste in Blast Furnaces

In this process MPW is used as a reducing agent, and hence this is generally seen as a form of feedstock recycling. Recently, the reduction of iron ore has been started with

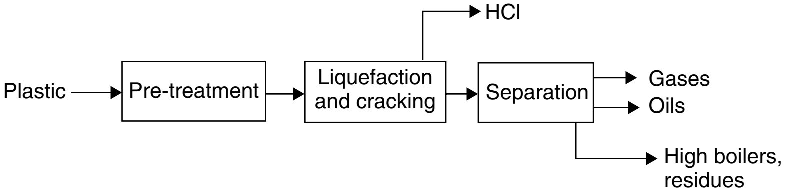


Figure 14.3 Schematic representation of the BASF pyrolysis process

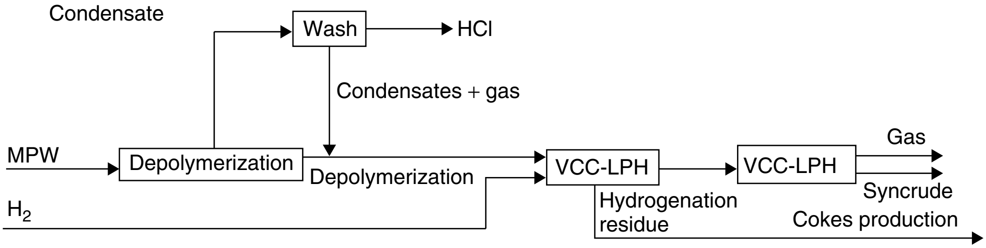


Figure 14.4 Schematic representation of the Veba Oel process

plastic waste. This new idea of reduction is replacing the old reducing agents such as coke, coal and heavy oil. An advantage of plastic waste is its low sulfur content compared with coal. However, plastic waste has relatively high chlorine content due to the presence of PVC. The main part of the chlorine forms HCl going into solution in the washer. Any additional metals present in PVC end up either in the product (steel), or in one of the residue flows from Blast furnaces [10].

5.1.5 Veba Combi Cracking Process (Germany, Operational until 2000)

Veba Combi Cracking (VCC) is a modified process technology of Veba Oel AG which was first used for coal liquefaction. Coal was converted by hydrogenation into naphtha and gas oil. The modified VCC process was used to convert vacuum distillation residues of crude oil into fuel oils containing naphtha, gas oil and heavy distillates. Since 1988 Veba have started to substitute the petroleum residue feedstock by chlorine-containing waste. The plant configuration was changed to include a depolymerization section. In the depolymerization section the plastic waste is heated to 350–400°C to effect depolymerization and dechlorination. The products of this process are HCl, syncrude free of chlorine and low in oxygen and nitrogen, gases and hydrogenated solid residue. Schematic representation of Veba Oel process is shown in Figure 14.4.

6 COPROCESSING FOR FUEL FROM MIXED PLASTIC WASTE

Coprocessing refers to the combined processing of petroleum residue with other hydrocarbon feedstocks. The petroleum residue contains chiefly 75 wt% materials boiling above

500°C. The waste plastics are petroleum derived and therefore, provide a hydrocarbon source that can be used for chemical feedstocks. The feedstocks are mixed and processed simultaneously with the dual objective of liquefying the solid waste and upgrading the heavy residue from either the liquefied solid wastes or petroleum oil to the premium fuel oils boiling lower than 500°C.

The coprocessing of waste plastics with coal and other hydrocarbon sources such as heavy oils, tar mats, and petroleum residue has been reported [11–13]. The results have shown that adding heavy petroleum residue as a solvent in coprocessing reactions with waste plastics and coal has some beneficial effect on the reactivity of the system. The petroleum resid acts as an effective bridging solvent that, when added to coal and waste plastics, provides a medium for their mutual dissolution. The processing of waste plastics with coal, however, was found to be problematic, requiring multifunctional catalysts due to the compositionally diverse nature of the two materials. The petroleum residue, however, having a composition that includes both aromatic and aliphatic compounds, was found to be a more compatible material for processing with waste plastics [14, 15].

Catalytic processing of model and waste plastics with light Arabian crude oil residue was investigated using NiMo/Al_2O_3, ZSM-5, FCC, and hydrocracking catalysts. Reaction systems that were studied included low-density polyethylene (LDPE), high-density polyethylene (HDPE), polystyrene (PS), and polypropylene (PP). A series of single (plastic/catalyst) and binary (plastic/residue/catalyst) reactions were carried out in a 25 cm^3 microautoclave reactor under different conditions of weight and type of catalyst, duration, pressure, and temperature. The optimum conditions selected were: 1% catalyst by weight of total feedstock weight, 60 min reaction time, 8.3 MPa of H_2, and 430°C [14].

The coprocessing reactions of plastics with residues were followed by the quantitative measurement of masses of the products that included gas, oil, preasphaltene, asphaltene, and insolubles. Figure 14.5 shows the schematic representation of coprocessing method and products separation [15].

The effects of catalyst on the product distribution for selected plastic/residue double-component systems are shown in Table 14.2. The results show that the presence of residue increased the overall conversion in the double-component coprocessing reactions compared to the single-component reactions except in the case of polystyrene [14].

The effect of different temperatures and time durations on the product distribution of LDPE, residue and LDPE/residue are given in Table 14.3. The conversions from LDPE ranged from 50.0 to 57.3% at 430°C, 60 min and from 11.5 to 17.0% at 400°C 60 min. When the time was reduced to 30 min the conversions were 21.5–23.7% at 430°C. At the higher reaction temperature (430°C) the amount of hexane solubles (HXs) was high and the THFs were low. At 400°C the amount of HXs produced from the LDPE reaction was very low and recovery was high, indicating that low-boiling compounds were not formed. The LDPE/resid system also produced less HXs at 400°C than at 430°C.

The effect of different catalysts on the conversions and product distribution showed a significant improvement when the temperature was increased from 400 to 430°C. The catalysts showed greater reactivity at 430°C, as indicated by the higher conversion percent. The LDPE reaction with ZSM-5 (Z) and NiMo (N), were most effective for increasing LDPE conversion and HXs yields at 430°C [14].

The product distribution for the catalytic coprocessing of waste plastics with petroleum was also reported by our group [14]. High yields of liquid fuels in the boiling range

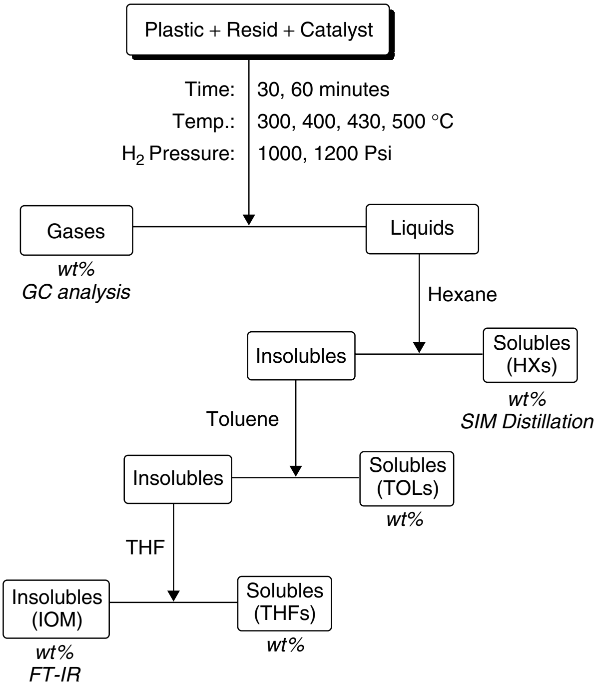


Figure 14.5 Schematic representation of coprocessing method and products separation

Table 14.2 Effect of catalyst on the product distribution for selected plastic/resid double-component systems

Reactants	*Catalyst H,Z,F or N	Product distribution (%)						
		Gas	HXs	TOLs	THFs	IOM	Conversion (%)	Recovery (%)
LDPE/resid	H	7.4	65.5	3.2	3.0	20.5	79.1	99.6
	Z	8.7	62.5	6.2	3.9	18.0	81.3	99.3
	F	5.2	60.2	11.6	4.5	18.0	81.5	99.5
	N	3.5	70.7	8.8	1.4	14.6	86.9	97.7
HDPE/residue	H	9.2	57.2	10.5	2.8	19.8	79.7	99.5
	Z	10.5	55.7	8.9	3.2	21.4	78.4	99.8
	F	7.2	63.5	10.5	3.8	14.5	85.0	99.5
	N	5.2	65.5	11.8	2.1	13.1	86.9	97.7
PS/resid	H	6.5	82.5	4.0	3.0	3.8	96.0	99.8
	Z	7.3	80.7	3.5	3.8	4.5	95.3	99.8
	F	5.2	84.2	3.0	3.9	3.5	96.3	99.8
	N	5.1	83.3	4.8	2.3	2.6	97.4	98.1
PP/resid	H	6.5	69.5	6.0	3.4	14.4	85.4	99.8
	Z	7.5	70.2	5.7	3.9	12.5	87.3	99.8
	F	5.0	64.5	10.3	8.2	10.2	88.0	98.2
	N	4.2	66.8	8.9	7.8	10.2	89.8	97.7

* H hydrocracking catalyst DHC-32; Z ZSM-5; F FCC catalyst; N NiMo catalyst
Reaction conditions: 430°C, 60 min, and 8.3 MPa H_2 introduced at ambient temperature

Table 14.3 Effect of reaction temperature and time on the product distribution for reactions with different catalysts

Reactants	Catalyst H,Z,F or N	Product distribution (%)						
		Gas	HXs	TOLs	THFs	IOM	Conversion (%)	Recovery (%)
430°C, 60 min								
LDPE	Z	7.2	36.7	8.2	5.5	42.1	57.3	99.7
	N	9.6	30.7	6.5	4.0	49.6	50.0	99.6
Residue	Z	16.0	71.2	3.8	3.5	5.2	94.5	99.7
	N	10.3	71.5	10.2	2.5	5.0	94.5	99.5
LDPE/residue	Z	8.7	62.5	6.2	3.9	18.0	81.3	99.3
	N	3.5	70.7	8.8	1.4	14.6	86.9	97.7
430°C, 30 min								
LDPE	Z	4.0	16.2	2.0	2.5	74.3	23.7	99.0
	N	4.5	12.5	1.5	3.0	78.0	21.6	99.5
Residue	Z	9.2	61.5			29.0	70.7	99.7
	N	6.5	59.3			34.0	65.8	99.8
LDPE/Residue	Z	4.5	31.0			64.0	35.5	99.5
	N	2.0	28.9			69.0	30.9	99.9
400°C, 60 min								
LDPE	Z	6.5	10.5			83.0	17.0	100.0
	N	2.0	9.5			88.5	11.5	100.0
Resid	Z	10.5	52.0			37.5	62.5	100.0
	N	7.2	48.7			44.1	55.9	100.0
LDPE/resid	Z	3.9	20.4			75.7	24.3	100.0
	N	2.0	15.6			82.4	17.6	100.0

100–400°C and gases were obtained along with a small amount of heavy oils and insoluble material [14].

Post-consumer plastic samples consisting of soft-drink bottles, water bottles, water cups, water bottle caps and yogurt pots were collected. The thermal and catalytic coprocessing of these materials was also studied over NiMo catalysts. The reaction products were analyzed and are given in Table 14.4. The product distributions of these plastic types were found to have a very high conversion reaction (79.2–95.8%) affording higher amount of hexane solubles (46–68%). However, when the other three types of catalysts (ZSM-5, FCC and HC) were used the boiling point distribution of reaction products was fairly well representative. The boiling point distribution of reactions for LDPE/residue and HDPE/residue mixtures are shown in Table 14.5. The proportion of material that boiled in the ranges 300–400°C and 400–500°C was found to be relatively larger.

In another study, we carried out coprocessing of model and waste PVC using petroleum residue and VGO using two different reaction processes [16]. In a single-stage pyrolysis reaction, PVC was processed with petroleum residue at 150 and 430°C, under N_2 gas for 1 h at each temperature in a glass reactor. The model PVC and waste PVC showed slight variations in the product distribution obtained from the glass reactor. In the two-stage

Table 14.4 Summary of resid/waste plastic conversion and product distributions

Reactants	Catalyst	Gas	Product distribution (wt%)						
			HX-S		TOL-S	THF-S	IOM	Conversion	Recovery
			Actual	Calculated					
Resid/soft-drink bottle-PET	NiMo	19.1	45.9	47.9	8.6	9.2	15.2	84.8	98.0
Residue/yogurt pot-HDPE	NiMo	12.1	66.5	67.9	11.6	4.3	4.1	95.9	98.6
Resid/cap of water bottle-HDPE	NiMo	17.6	67.9	69.3	5.7	3.2	4.2	95.8	98.6
Resid/water bottle-PET	NiMo	21.9	50.6	51.8	8.1	6.0	12.2	87.8	98.8
Resid/water cup from Arabian Gulf-PS	NiMo	21.78	54.15	55.05	10.10	8.12	4.95	95.05	99.1
Resid/water cup from Al-Watania-PS	NiMo	20.2	57.53	58.23	9.50	7.52	4.55	95.45	99.7

Reaction conditions: 430°C, 60 min, and 8.3 MPa H_2 introduced at ambient temperature.

Table 14.5 Boiling point distribution of reaction products for polyethylenes

System	Product distribution (wt %) in terms of boiling point						
	IBP–100°C	100–200°C	200–300°C	300–400°C	400–500°C	>500°C	IOM
LDPE/RESIDUE	4.3	12.8	26	25	17.3	14.6	
HDPE/RESIDUE	2.8	19	26	18	21.1	13.1	

IBP = Initial Boiling Point; IOM = Insoluble Organic Materials

process, model PVC, vacuum gas oil (VGO) and a number of different catalysts were used in a stainless steel autoclave microtubular reactor at 350°C under a stream of N_2 gas for 1 h and at 430°C under 950 psi (6.5 MPa) H_2 pressure for a duration of 2 h. Significantly different products distributions were obtained. Among the catalysts used, fluid catalytic cracking (FCC) and hydrocracking catalysts (HC-1) were most effective in producing liquid fuel (hexane soluble) materials. The study shows that the catalytic coprocessing of PVC with VGO is a feasible process by which PVC and VGO materials can be converted into transportation fuels. The reaction products obtained from the coprocessing of PVC and VGO using different catalysts were analyzed and are given in Table 14.6.

These studies concluded that the coprocessing of waste plastics with petroleum resid is a feasible process by which plastics and resid materials can be converted to liquid fuels. Reaction temperature and reaction time were found to affect the conversion rate and the production of hexane-soluble material. The hexane-soluble materials from this initial conversion can be further upgraded to gasoline and other high-value diesel fuels or chemical feedstock. The rate of conversion in the coprocessing system depended upon the chemistry and composition of the particular plastic material and resid. In general, these studies help to demonstrate the technical feasibility for upgrading both waste plastics and petroleum residue and alternative approach to feedstock recycling.

Table 14.6 Product distribution from two-stage pyrolysis of PVC and VGO mixture

Experiment[a]	Reactants	HXNs	TOLs	THFs	IOM	*HCl	Gas
1	PVC + iron oxide catalyst	6.8	4.3	0.0	36.6	50.6	1.6
2	VGO + ZSM-5	70.5	4.2	0.0	9.5	0.0	15.8
3	VGO + PVC + ZSM-5	61.3	6.5	1.3	10.8	8.3 (54)	11.8
4	VGO + PVC + NiMo	61.5	6.2	1.8	9.8	7.9 (51.3)	12.8
5	VGO + PVC + FCC	65.9	7.1	1.8	10.2	8.1 (52.6)	6.9
6	VGO + PVC + HC-1	65.2	7.9	1.7	10.7	7.8 (50.7)	6.7
7	VGO + PVC + iron oxide catalyst	55.0	8.5	2.6	16.0	7.7 (50)	10.2
8	VGO + PVC + HC-2	59.0	7.1	2.1	13.0	7.8 (50.7)	11.0
9	VGO + PVC + HC-3	60.1	6.7	1.9	14.1	7.6 (49.4)	9.6

1. PVC 10 g, catalyst 0.5 g; 2. VGO 12.5 g, catalyst 1.25 g; 3–9. VGO 12.5 g, PVC 2.5 g, catalyst 1.25 g
Figures in parenthesis under *HCl are % HCl content of PVC
Yield calculation basis wt%
Gas = 100 − (HXs + TOLs + THFs + residue + HCl)
HCl = NaOH titration
Reaction conditions: 1 h at 350°C under N_2 gas +2 h at 430°C under 6.5 MPa H_2 gas

7 PYROLYSIS

The chemical decomposition of organic materials by heat in the absence of oxygen is called *pyrolysis*, and when these reactions takes place under the hydrogen gas pressure is some times also referred as *hydropyrolysis*. Pyrolysis/hydropyrolysis typically takes place in the temperature range 400–800°C and under 500–1500 psi hydrogen gas pressure. Pyrolysis transforms organic materials into carbonaceous char, a small quantity of oils, gases and ash. The combustible gases produced during the pyrolysis of organic material include carbon monoxide, hydrogen, methane, carbon dioxide, water, and more complex hydrocarbons, such as ethane, ethene, propane, propene, butane, butene and other hydrocarbons.

The temperature and heating rates have considerable influence in the pyrolysis process and can be controlled to produce desired solid, gas and liquid products. Pyrolysis mechanisms for municipal solid waste, tires, plastics sewage sludge and biomass have been reported by many workers [17–20]. A series of pyrolytic reactions producing varying amounts of products at different temperatures and heating rates have been reported [21, 22]. Pyrolysis at very slow heating rates coupled with a low final maximum temperature maximizes the yield of solid (char). A slow or conventional pyrolysis takes place at moderate heating rates in the range of 20–100°C/min and at a maximum temperature of 600°C which produces almost equal amounts of solids, liquids and gases. Whereas a fast or flash pyrolysis takes place at very high heating rates of about 100–1000°C/s at temperatures below 650°C and with fast quenching that leads to the formation of mainly liquid product. At high heating rates and high temperatures, the oil products quickly break down to yield a mainly gas product, but this process is totally different from gasification. Pyrolysis process conditions can be optimized to produce either solid char and gas or a liquid/oil product [23, 24].

7.1 REACTOR TYPES USED FOR PYROLYSIS

Different types of reactors are utilized for a wide variety of pyrolysis applications, including processing of waste plastics. The worldwide waste plastic pyrolysis systems utilize the fixed-bed designs of vertical shaft reactors and dual fluidized-bed, rotary kiln and multiple hearth reactor systems. The type of reactor used is chiefly based on material to be pyrolyzed and expected products from the pyrolysis. Stainless steel shaking type batch autoclave and stainless steel micro tubular reactors have also been used extensively [14]. Fluidized-bed reactors have been extensively used in producing raw petrochemicals from the pyrolysis of waste plastics [22, 24].

Due to high viscosity of plastics material the continuous feeding to conventional reactor systems such as a fixed-bed reactor is problematic. Waste lubricating oils are used as carriers. Content of plastics above 10 wt% increases viscosity hugely, requiring large amount of oils. A screw kiln reactor was designed and used in order to overcome these problems. The residence time can be modified just by varying the screw rate. The reactor system has been found to be useful for both the thermal and catalytic cracking of waste plastics [25].

The semi-continuous type of reactor with the large capacity was comprised of a pyrolysis chamber, a catalytic cracking chamber and a separation and purifying section. The feed plastic material was melted and decomposed in the pyrolysis chamber held at the ambient pressure and at the temperature 723–783 K, and fed to the catalytic cracking chamber. A reflux condenser was used to separate and purify the products formed in the chamber and individual factors were obtained using fractional distillation apparatus [26]. Different types of reactors are being utilized depending on the type of feed and the expected products from the pyrolysis.

7.2 CHEMICAL PRODUCTS OF PYROLYSIS

Pyrolysis of waste plastics with petroleum residue produces varying proportion of solid, liquid and gas products under different conditions [23, 27]. The product gas from pyrolysis is usually a fuel with a medium to low heating value. The product gas contains carbon monoxide, which varies from 15 to 30% by volume. Hydrogen is also a part of the product gas and varies from 10 to 20% by volume. Methane constitutes 2–4% by volume and adds to the heating value. Noncombustible gases, such as carbon dioxide and nitrogen, constitute a large part of the product gas. Carbon dioxide varies from 5 to 15% and nitrogen from 45 to 60% by volume. Higher percentages of carbon dioxide indicate incomplete reduction of the waste material [27]

The pyrolysis liquids consist mainly of tar, light oil, and liquor. The tar contains 16–25% olefins, 62–80% aromatics, and 3–14.5% paraffins and naphthenes, and the remainder is organic compounds that have been identified as acids, bases, ketones, and aldehydes containing from one to eight carbon atoms. The major components of light oil are benzene and toluene. The boiling point curves obtained from the simulated distillation (SIM) of oil, hexane soluble, fractions ranged from 70 to 550°C, showing the recovery temperatures at initial boiling point (IBP) 10%, 50%, 90% and final boiling point (FBP). These distillation cut-off points were used as base line in assessing the extent of conversion of plastic–resid mixture into the transportation fuels [14]. Pyrolysis of PVC in a technical-scale fluidized-bed reactor yielded aromatic oils and heating gas [28]. The most important products were benzene, toluene, xylene and styrene, with a total yield of 31.4% by weight (referring to the total organic input). Additionally, pyrolysis gas with a high calorific value of 50 MJ/Kg was obtained.

8 ENVIRONMENTAL IMPACTS OF RECYCLING OF WASTE PLASTICS

The production and disposal of waste plastic products contributes significantly to their environmental impact. Most plastics are nondegradable and take longer time to break down when landfilled. With the increased use of plastics in modern life, the landfill space required by plastics waste is a matter of serious concern. Furthermore, plastic production requires significant quantities of primarily fossil fuels for both as a raw material and to deliver energy for the manufacturing process. It is estimated that 4% of the world's annual oil production is used as a feedstock for plastics production and an additional 3–4% during manufacture. The overall environmental impact of waste plastics varies according to the type of plastic used and the production method employed [29].

The production of plastics also involves the use of potentially harmful chemicals under the name of stabilizers or colorants. Many of these stabilizers/additives have not undergone environmental risk assessment and their impact on human health and the environment is currently uncertain and doubtful. Phthalates, as additives, are widely used in the manufacturing of PVC products, and risk assessments of the effects of phthalates on the environment are currently being carried out. Recent research for the Community Recycling Network casts doubt on whether pyrolysis and gasification are the right processes for dealing with the residual municipal waste.

Waste disposal contributes towards climate change, for example through the release of methane from landfill sites or the burning of fossil-fuel-based plastics. Human toxicity is a measure of the potential risk to health from a plant. Like incineration, pyrolysis and gasification produce emissions: Air emissions include acid gases, dioxins and furans, nitrogen oxides, sulfur dioxide, particulates, cadmium, mercury, lead and hydrogen sulfide; solid residues include inert mineral ash, inorganic compounds, and any remaining unreformed carbon [30].

9 ECONOMIC EVALUATION

The research on the liquefaction of waste polymers and the coprocessing of waste plastics with vacuum residue or coal has been a subject of study by many groups at universities and environmental agencies. A significant amount of effort and funds are being diverted to develop process technology in order to convert mixed plastics waste from municipal and industrial waste into a heavy liquid, suitable for use either as petroleum feedstock or in producing ethylene and propylene, the building blocks of much plastics production.

This section deals with the economic evaluation of the conversion of mixed plastics waste (MPW) into synthetic crude (syncrude) oil and coprocessing of MWP with vacuum residue into syncrude. In their feasibility study, Ali and co-workers considered the process technology developed by Veba Oel AG of Germany the Veba Combi-Cracking (VCC) option for the processing of MPW [31]. The process data and economic data were taken mainly from Dijkema and Stougie [32] and Huffman and Shah [33] for this study. All the cost data were translated to represent the economic analysis for Saudi Arabian conditions.

It is estimated that solid wastes in cities of Saudi Arabia constitute approximately 15 wt% of total solid wastes. It is estimated that around 600 000 ton/yr of plastics are being consumed in Saudi Arabia. This gives an estimated amount of 90 000 ton/yr of plastic waste.

The plant configuration developed by Veba includes a depolymerization section to allow MPW processing in two downstream sections: a condensate processing section which comprises an alkaline wash and a hydrotreater to obtain a light syncrude of good quality, and a VCC section where the depolymerizate produced is processed together with an appropriate amount of vacuum residue (VR) into syncrude, E-gas and hydrogenation residue. A simplified block flow diagram of the process is shown in Figure 14.6.

The depolymerization section is required to allow continuous MPW feed to the VCC section. MPW itself cannot dissolve in VR, so direct feeding of MPW to a VCC is impossible. In the depolymerization section, MPW is broken down into smaller chains, thereby lowering its viscosity by applying a mild cracking process. The viscosity of the depolymerized MPW is about the same as the viscosity of VR; hence intimate mixing with VR becomes easy. A substantial amount of MPW (about 70%) is converted into condensate; the remaining material is a heavy bottom product that has to be dechlorinated both for economic as well as environmental reasons. The dechlorination is very effective; over 99 wt % of chlorine present in MPW is liberated as HCl, which is removed by alkaline washing.

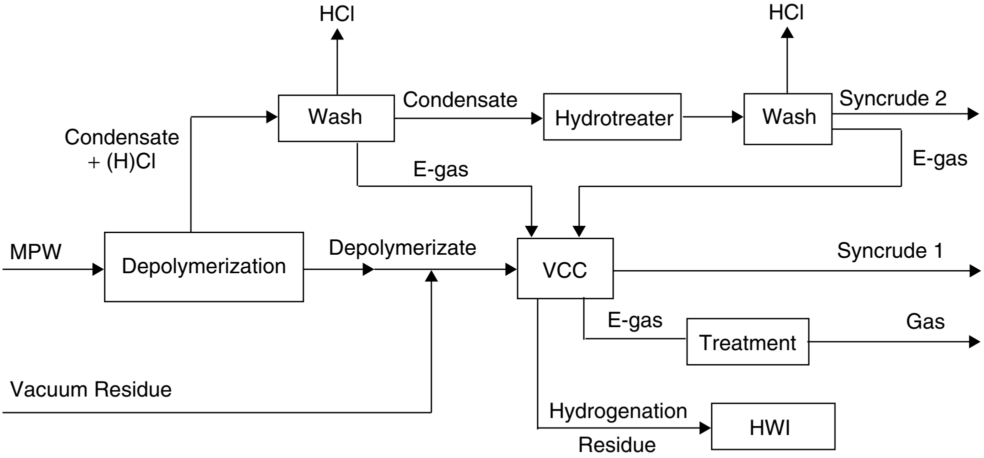


Figure 14.6 Block diagram of Veba option for the processing of MWP

The estimated cost of erecting a MPW processing facility in Saudi Arabia is estimated to be US$47 790 000 to process 100 000 ton/yr MPW or to produce 73 600 ton/yr of synthetic crude oil. The price of syncrude oil is taken as $155 per ton.

The production cost of syncrude oil is estimated to be $179 per ton from a 100 000 ton/yr MPW (only) processing facility. An additional cost of $24 per ton is required to process MPW in a 100 000 ton/yr facility. However, if the capacity of the plant is increased to 200 000 ton/yr, the production cost decreases to $125 per ton thereby making the project slightly profitable with a return on investments (ROI) of 5.4% per year.

If the MPW is coprocessed with VR, the production cost of syncrude oil is estimated to be $133.7/ton from a 100 000 ton/yr (40 000 ton/yr MPW + 60 000 ton/yr VR) processing facility. The ROI is positive with 3.24% per year, indicating that additional cost is not required to process these waste materials. Increasing plant capacity to 200 000 ton/yr in the ratio of MPW : VR as 2:3, the production cost further decreases to $108.2 per ton.

This study concluded that processing of MPW with VR at a capacity of 200 000 ton/yr (80 000 ton/yr MPW and 120 000 ton/yr VR), is economically feasible for Saudi Arabian conditions. This capacity is adequate in view of the amount of MPW generated in Saudi Arabia. The internal rate of return (IRR) is about 14.6% with a payback period of 6.4 years and break-even capacity of 47.6%. Although profitability is not very attractive, the project is recommended to solve the waste disposal problem of both MPW and VR. Some assistance should be provided to operate these plants through environmental protection agencies.

10 CONCLUSIONS

Coprocessing of waste plastics with petroleum residue is a feasible process by which waste plastics and resid materials can be converted to liquid fuels. Reaction temperature and reaction time strongly affect the conversion and the production of hexane-soluble material. The hexane soluble materials from the initial conversion can be further upgraded to gasoline and other high-value diesel fuels or chemical feedstock. The rate of conversion in the coprocessing system depends upon the chemistry and composition of the particular plastic material and petroleum residue. Finally, these studies help to demonstrate the technical feasibility for upgrading both waste plastics and petroleum residue and alternative approach to feedstock recycling.

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PART IV

Reactor Types

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15

Overview of Commercial Pyrolysis Processes for Waste Plastics

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1 INTRODUCTION

The production of gasoline, kerosene and diesel from waste plastics is an emerging technological solution to the vast amount of plastics that cannot be economically recovered by conventional mechanical recycling operations.

Plastic pyrolysis involves the thermal degradation of the wastes in the absence of oxygen/air. It provides for the disposal of plastic wastes with recovery of valuable gasoline and diesel-range hydrocarbons. During pyrolysis, the polymeric materials are heated to high temperatures, such that their macromolecular structures are broken down into smaller molecules, resulting in a wide range of hydrocarbons being formed. These pyrolytic products can be divided into a noncondensable gas fraction, a liquid fraction (consisting of paraffins, olefins, naphthenes and aromatics), and solid residues (i.e. char).

Pyrolysis of waste plastics appears simple in concept. However, thermal cracking often yields low-value mixtures (cocktails) of hydrocarbons having very broad compositional range, sometimes extending from light alkane gases to coke (Figure 15.1). It is therefore necessary to find the optimal pyrolysis conditions and/or the most advantageous catalyst to obtain marketable products (e.g. diesel fuel or gasoline) from plastic wastes. Catalytic degradation yields a much narrower product distribution of carbon atom number and reduces the reaction temperature. Such a mixture of hydrocarbons may be used as transportation fuels.

Pyrolysis recycling of mixed waste plastics into generator and transportation fuels is seen by many as the answer for deriving value from unwashed, commingled plastics as well as managing their desired diversion from landfill.

Pyrolytic recycling of plastic wastes has already been achieved on a commercial scale, albeit to a limited extent. Nevertheless, the development and improvement of pyrolysis plastics recycling technologies in recent years has shown great commercial

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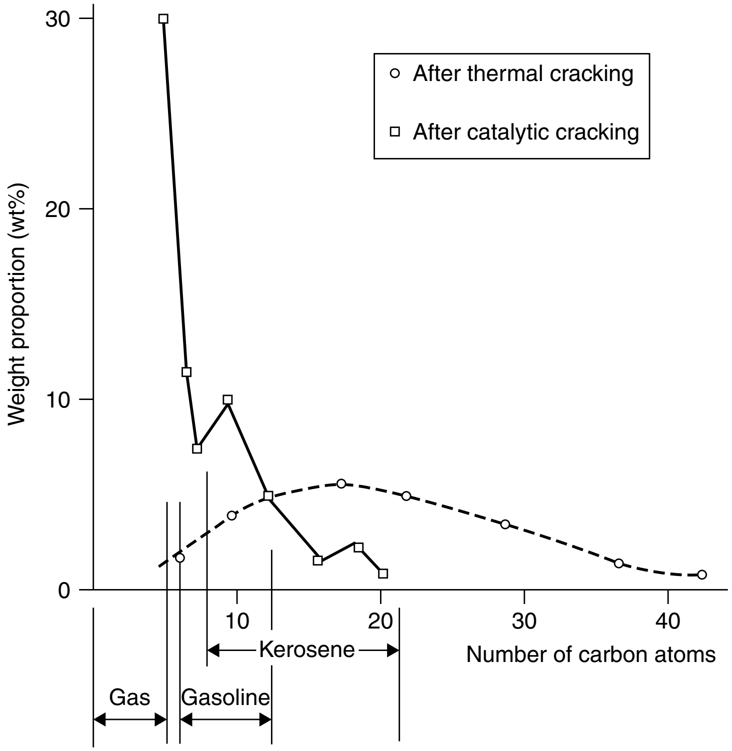


Figure 15.1 Schematic showing difference in yields and carbon length distribution for thermal cracking and catalytic cracking. Note different distribution of carbon atoms in liquid fuels made by thermal cracking and catalytic cracking of polyethylene

potential. The development of bench-scale experiments carried out in laboratories, through to full-scale pyrolysis processes, have now resulted in a number of technically mature processes.

Through the use of low-temperature vacuum pyrolysis and cracking catalysts, liquid fuel yields of up to 80–85% are possible, with the resultant product resembling diesel fuel, kerosene, gasoline or other useful hydrocarbon liquids. There are now emerging a number of processes that will take post-consumer plastics and catalytically convert them into gasoline and low-sulfur diesel fuel. This diesel fuel meets or exceeds both European and Federal EPA standards for emissions and is designed specifically for the solid waste disposal industry that has significant investment in diesel-powered equipment. The types of plastic targeted as feedstock for this project have no commercial value and would otherwise be landfilled.

A distinct advantage of plastic pyrolysis into fuels as a means of recycling is its ability to handle mixed and unwashed plastics. Post-consumer plastics are often commingled and contaminated with extraneous materials such as soil, dirt, aluminium foils, paper labels and food remnants. While soil, dirt and glue can be removed from post-consumer plastics by washing, this is a fairly expensive operation and it leads to secondary waste streams such as waste-water. Pyrolysis recycling of mixed plastics thus has great potential for heterogenous plastic waste that cannot be economically separated.

1.1 ADVANTAGES OF PYROLYSIS

The advantages of pyrolysis of waste plastics into liquid fuels include:

- it allows the recycling of waste mixed plastics that cannot be efficiently recycled by alternative means;
- it permits the recycling of unwashed and soiled plastics (e.g. agricultural plastics, mulch/silage/greenhouse films and dripper/irrigation tube);
- it enables recycling of plastic laminates, coextrusions and multilayer packaging films, particularly those with aluminium foil layers that are difficult to recycle using traditional reprocessing technologies.

Most commodity hydrocarbon plastics are suitable for pyrolysis. Generally the larger the substituent in the side chain, the easier the plastic can be degraded. The order of increasing side chain size is polyethylene<polypropylene<polyvinyl chloride<polystyrene.

Problems with many pre-existing plastic cracking technologies include:

- noncontinuous (batch) processes (not commercially viable);
- coking and carbon deposits on heat exchanging surfaces;
- stickiness of sand particles in fluidized-bed processes;
- unsatisfactory fuel quality;
- relatively high sulphur levels (100–700 ppm) in end product.

In the last five years however, a limited number of plastic pyrolysis processes have been developed to overcome these limitations.

1.2 THERMAL CRACKING

Thermal cracking often yields a low-value mixture of hydrocarbons with a very broad volatility range that can extend from hydrogen to coke. It is therefore important to determine the optimal pyrolysis conditions and/or the most advantageous catalyst to obtain marketable products (e.g. diesel fuel) from mixed plastic wastes.

The pyrolysis product yield and composition are controlled not only by the temperature, but also by the duration of the residence time. As a general rule of thumb the higher the pyrolysis temperature, the higher the yield of noncondensable gaseous products and the lower the yield of liquid fuels such as diesel. The optimum temperature range for the production of diesel products from waste plastics is 390–425°C. Studies in a tubular reactor have highlighted the importance of short residence time with high-temperature pyrolysis for obtaining a high yield of light olefins.

There is a dramatic increase in gas yield with increasing temperature of pyrolysis. While the hydrocarbon pyrolysis product yield increases with pyrolysis temperature, the yield of the oil fraction is higher at the lower pyrolysis temperatures. The composition of the pyrolysis oil also changes with pyrolysis temperature, generally containing larger quantities of aliphatic compounds at the lower temperatures than at higher temperatures where aromatics are the dominant compounds.

1.3 CATALYTIC CRACKING

The poor selectivity of the thermal decomposition of polyolefins has promoted the development of catalytic cracking. Catalytic cracking lowers the pyrolysis process temperature and lowers the boiling temperature range of the resultant liquid products. The use of molecular sieves and amorphous silica–alumina catalysts for the cracking of waste polymers into a range of hydrocarbons has been widely studied (see Chapters 3–5, 7, 8).

Catalytic cracking has some distinct advantages over thermal cracking, such as, lowering the cracking temperature, increasing the reaction rate and increasing the production of iso-alkanes and aromatics which are desirable for diesel fuel. Suitable cracking catalysts have the ability to both substantially reduce the pyrolysis temperature and control the pyrolysis products.

Using catalysts does not only lower the activation energy, reduce the energy consumption and improve the process efficiency, but can also improve the selectivity and quality of the products produced.

Catalysts with acidic surface sites and hydrogen ion donating ability enhance the isomerization of products and thereby increase the yield of isomeric hydrocarbons that have a beneficial effect on the cetane rating and fuel quality. Catalysts having stronger acid sites of higher density are thus more effective in cracking polyolefins. However, strong acidity and large pore size both lead to faster deactivation of the catalyst. Pyrolyzing with catalysts having mild acidity and long life are preferred for the cracking of polyolefins. A major problem with using catalysts in the pyrolysis of mixed plastics is that of coke formation deactivating the catalyst over time. The cost of these catalysts also influences their selection and commercial viability.

The amount of the catalyst to be added to the waste plastic for catalytic cracking is at least 5% by weight (typically 5–10% by weight).

The problems associated with the use of a catalyst in the pyrolysis vessel are:

- the catalyst is a consumable and therefore adds to the running cost;
- the catalyst can have a short life-cycle due to poisoning/deactivation;
- the catalyst leads to increased levels of solid residue that requires disposal.

Figure 15.1 highlights the differences between thermal and catalytic cracking in terms of the breath and distribution of carbon chain lengths of the products.

2 FEEDSTOCK OPTIONS

The composition of the plastic feedstock for pyrolysis processes has a direct bearing on the quality of the resultant fuel products, especially flash point, cetane index, low-temperature properties and heteroatom content (e.g. sulphur, chlorine and nitrogen).

While condensation polymers such as PET and polyamides can be broken down into their monomer units by thermal depolymerization processes, vinyl (addition) polymers such as polyethylene and polypropylene are very difficult to decompose to monomers. This is because of random scission of the carbon–carbon bonds of the polymer chains during thermal degradation, which produces a broad product range.

2.1 POLYETHYLENE (PE)

There have been many reports on the thermal and catalytic degradation of high-density polyethylene (HDPE), as it is one of the main polymers in municipal solid wastes [1].

PE-derived fuel has a very low cetane rating and is very high in linear paraffins and 1-olefins. Paraffins are straight-chain hydrocarbons that are normally present in diesel. They are the first components to come out of solution as diesel cools. The tendency of paraffin crystals to aggregate up at low temperatures to form sheets can result in fuel-filter blockages, ultimately leading to interruption of the fuel flow. Paraffin crystals form in the fuel, making the gelled suspension appear cloudy. As these suspended flakes pass through the filter, they gum up its microporous surface.

Due to the high concentration of linear *n*-paraffin hydrocarbons in fuel derived from PE, it is desirable to isomerize them in order to lower the cloud point and the freezing point of the fuel. The branched isomers do not exhibit the same tendency to crystallize as linear paraffins, so that wax crystals do not form until lower temperatures are reached.

2.2 POLYPROPYLENE (PP)

The liquid products of the pyrolysis of PP contain primarily olefins that resemble the molecular skeleton of PP (i.e. branched hydrocarbons). A distinguishing feature of PP pyrolysis is the predominant formation of a particular C_9 olefin in the pyrolysis product. The level of this C_9 compound identified as 2,4-dimethylhept-1-ene can be as high as 25%. Also present are C_5 olefin, C_6 olefin, several C_{15} olefins and some C_{21} olefins [2]. The tertiary carbon sites in PP allows for the facile chain cleavage and rearrangements according to the Rice–Kossiakoff cracking mechanism shown in Figure 15.2. The non-condensable gas from PP pyrolysis contains elevated levels of propylene, isobutylene and *n*-pentane.

Compared with PE, PP produces less coke residue and more liquid products, but with a higher content of ‘lights’. In the pyrolysis process of PP the intramolecular radical transfer is preferred to the intermolecular one, thus the low oligomer formation predominates, skewing the carbon number distribution towards the light end of the distillate spectrum. Consequently the pyrolysis oil of PP is much more volatile than that of PE, decomposing mainly through intermolecular radical transfer. The difference in the backbone structure of the products of these polymers is more important from the point of view of fuel properties. The isoalkanoic structure of PP is maintained in the thermal decomposition products, thus the octane number of the pyrolysis oil is typically high.

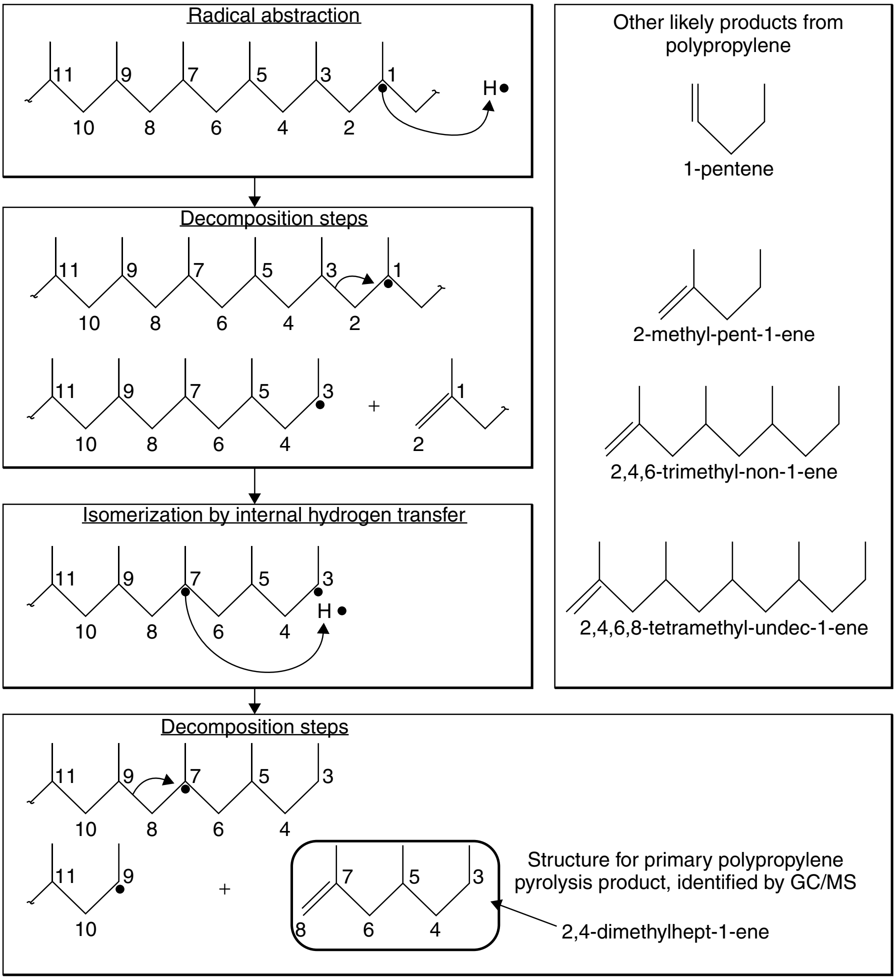


Figure 15.2 Rice–Kossiakoff cracking mechanism for polypropylene showing that the pyrolysis products of PP retain a branched structure

2.3 POLYSTYRENE (PS) PYROLYSIS

Neat polystyrene feedstocks will depolymerize in a pyrolysis process to give predominantly styrene monomer–a liquid fuel with good energy content.

The optimum pyrolysis temperature is 395°C to give a recovery ratio of 0.97 (i.e. 1000 kg polystyrene will yield 970 L liquid monomer) and 5 to 10% char residue. Fuel made from polystyrene feedstock will be high in aromatic character and have an energy content of 50 MJ/kg and a pour point of −67°C. However the flash point is only 26°C and the cetane rating only 12.6. The fuel needs to be blended with polyolefin-derived diesel or regular diesel in order to upgrade the flash point and cetane rating to within specification.

Polystyrene has somewhat lower thermal stability than the polyolefins and its pyrolysis can be undertaken between 380 and 420°C without producing gases or leaving significant amount of residue after total conversion. PS cracks to styrene, ethyl benzene, toluene, trimethylbenzene and some benzene. In spite of the fact that the majority of the carbon atoms are assembled into phenyl side groups in this polymer, a negligible amount of benzene is formed (1–3%) at these temperatures. This is because the aryl–alkyl bond connecting the phenyl group to the polymer chain is stronger than the bond of alkyl carbons along the chain.

The pyrolysis of PS yields dominating components, styrene (bp 145°C) in the gasoline boiling range, styrene dimer in the diesel oil range, and styrene trimer boiling at 400°C. This pyrolysis product distribution suggests that the intermolecular radical transfer is negligible in PS. The pyrolysis of PS produces fuel with a high aromatic content and low storage stability. The high aromatic content of PS-derived oil helps to compensate for the low cetane number of PE oil.

2.4 PET

Pyrolysis of PET under mild conditions predominantly forms terephthalic acid (TPA). Since TPA easily sublimes it is often found in the condensing units of pyrolysis plants. Under high-severity conditions however, little TPA is observed. This is because at higher temperatures TPA is decomposed into benzene, carbon dioxide and benzoic acid (Figure 15.3) [2].

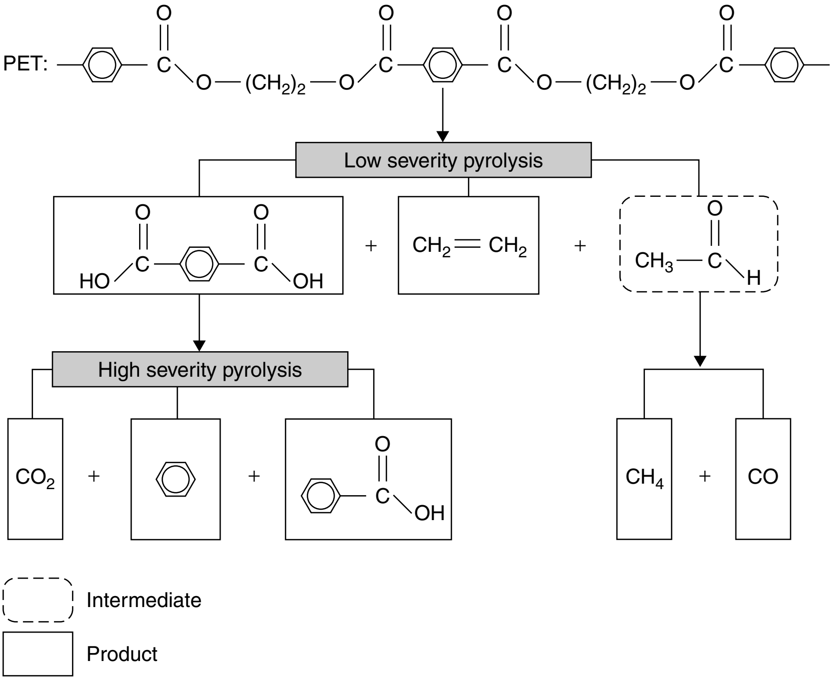


Figure 15.3 Thermal cracking mechanism for polyethylene terephthalate. Note under mild conditions terephthalic acid predominates, but under more severe pyrolysis conditions the terephthalic acid decomposes to benzoic acid and benzene

The pyrolysis of PET by Sakata [3] has been found surprisingly to yield no liquid products. It is widely known that compounds that undergo sublimation, such as terephthalic acid and benzoic acid, are produced by the thermal decomposition of PET and this causes problems in plastic pyrolysis plants. Interestingly Yoshioka *et al.* [4] found that the addition of calcium hydroxide (slaked lime) gives high selectivity for benzene formation without producing sublimation compounds such as terephthalic acid. The yield of benzene is around 35 wt% at 700°C and a 10.0 calcium hydroxide/PET molar ratio.

2.5 PVC

PVC is not recommended as a feedstock material for pyrolysis. The reasons for this being that it contains about 57% chlorine by weight which will affect diesel quality and can produce chlorinated hydrocarbons, and also because it thermally decomposes to hydrochloric acid that is very corrosive and toxic.

The presence of 1–3% PVC in the feedstock stream results in the product fuel oil having a total chlorides level of 5000–10 000 ppm. However at the same PVC levels the total chloride concentration in the diesel can be reduced to less than 10 ppm by the addition of lime hydrate according to the following reaction:

$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$$

PVC in the feedstock stream in limited amounts can thus be tolerated if a HCl removal process based on calcium hydroxide (slaked lime) injection is used. This is essentially a form of *in situ* scrubbing in the pyrolysis reactor itself. This method is used by a number of pyrolysis processes since the fuel oil end products need to be low in chlorine to minimize engine corrosion problems. In the pyrolysis of commingled plastics, lime can be added to the input material and the PVC content reduced down to 2–3% in order to avoid deposits of $CaCl_2$ in pipework. The chlorine content of the final diesel should not exceed 10 ppm.

It has been demonstrated that oil recovered from PVC-containing plastic feedstock can be used as a fuel. Cost is the main obstacle since it requires a large amount of slaked lime to neutralize the HCl gas that is produced by the thermal cracking. Table 15.1 shows the effect that slaked lime has on reducing the chlorine content of fuel oil derived from the pyrolysis of PE (55 wt%), PP (28 wt%) and PS (17 wt%) at a decomposition temperature of 420°C.

Table 15.1 Effect of slaked lime addition on the pyrolysis of plastic containing 1% PVC. (Reproduced by permission of Masataka Tsukada)

Slaked lime added (%)	Total chlorine in fuel (mg/L)	HCl in fuel (mg/L)
0.0	1139.3	490
1.2	72.5	26
2.0	54.2	20

As shown in Table 15.1, adding 1–2% of slaked lime enables the desired level of chlorine in recovered fuel to be achieved, thereby allowing the fuel to be suitable as a diesel fuel. However some chlorine still remains. There is always a small percentage of moisture existing in the waste plastic. It is later separated out and condensed as water. This water reacts with chlorine species in the fuel and produces hydrochloric acid.

2.6 HALOGENATED POLYMERS

Since the pyrolytic recycling of waste plastics containing halogen atoms (e.g. Cl, Br, F) poses special problems, the pyrolysis process can incorporate a special halogen elimination step such as dehydrochlorination. Hydrogen chloride, evolved from PVC during heating, can be fixed by metal oxides (e.g. calcium oxide) to form the corresponding metal chlorides. Electronic scrap contains high levels of halogenated flame retardants as well as various metals and fillers in addition to plastic materials. The pyrolytic recycling of the mixed plastics from electrical and electronic waste solves a number of problems such as dehalogenation of the product (see Chapter 20).

2.7 PLASTIC FEEDSTOCK SPECIFICATION

Plastic feedstock specifications are extremely important in order to obtain satisfactory and consistent fuel quality (see Table 15.2). A rigid ‘incoming feedstock specification’ (IFS) ensures that limits are placed on ‘critical’ contaminants. The critical contamination is based around the so-called ‘hetero-atoms’. These are listed below in order of priority:

- S (e.g. vulcanized rubber and S-containing sources such as food preservatives);
- Cl and Br (e.g. PVC, PVDC and brominated flame retardants);
- N (e.g. nylon, ABS, PU foam)

Periodic feedstock audits also need to be conducted to ensure the IFS are being adhered to.

Table 15.2 Properties of fuel produced by pyrolysis of various plastic feedstocks. (Reproduced by permission of Masataka Tsukada)

Fuel property	PE	PP	PS	Nylon	PP 50%, PE 43%, NYLON 7%
Flash point (°C)	33.6	27.8	26.1	34.8	26.0
Pour point (°C)	2.7	−39	−67	−28	−5.0
Water content (ppm)	0.18	0.13	0.67	2500	310
Ash (wt%)	0.013	0.010	0.006	0.018	0.001
Viscosity (cSt at 50°C)	2.190	1.9	1.4	1.8	1.485
Density (g/cm^3)	0.858	0.792	0.960	0.926	0.799
Cetane rating		56.8	12.6		54.3
Sulphur (wt%)	0.01	0.01	0.01	0.01	0.013
Nitrogen (ppm)	0.2	0.2	0.2	6400	1750
Energy content (kJ/kg)	52 263	53 371	50 365	44 403	46 270

Table 15.3 Typical Input Specifications (from BP's Grangemouth Pyrolysis Plant)

Property	Specification
Polyolefins (LDPE, LLDPE, HDPE, PP)	80 wt.% (min 70%)
Polystyrene (GP-PS, EPS, HIPS)	15 wt.% (max. 30%)
PET	3 wt.% (max. 5%)
PVC	2 wt.% (max. 4%)
Total plastic content	95 wt% (min. 90%)
Ash	2 wt.% (max. 5%)
Moisture	0.5 wt.% (max. 1%)
Metal pieces	Max. 1 wt.%
Size	1–20 mm
Fines (sub 250 μm)	Max. 1 wt%
Bulk density	400 kg/m^3 (min. 300 kg/m^3)

Typical input specifications for BP's Grangemouth pyrolysis plant are shown in Table 15.3.

3 OPERATIONAL CONSIDERATIONS

The development of commercially viable plastic pyrolysis processes has up to now been hindered by the need to engineer around various process problems such as reactor fouling by carbon deposits, poor heat transfer of molten plastics, the requirement for integrated fractionation of products, separation of water and suspended carbon from the liquid fuels and integrated desulphurization.

3.1 PREVENTING COKING

One of the main technical barriers to the pyrolysis of plastic wastes is the formation of carbon (coke) deposits in the reactor. The coking deposits over the heat exchanging surfaces of the reactor and deactivates catalysts (if used). In this regard, PE and PP are preferred feedstocks over PS due to the high coking potential of PS. Batch reactors with mixers can generally be run only semi-continuously, since after a few days of operation they must be stopped for cleaning and coke/char removal. Carbonaceous coke that accumulates on the inside walls of the pyrolysis vessel can lead to poor heat transfer to the plastic. The char is generally removed by scrapers attached to the agitator shaft. The char is a solid carbonaceous residue that is black, brittle and porous and resembles coke with its honeycomb structure and metallic lustre.

Scraped surface heat exchangers (SSHE) have been used as tubular reactors for plastics pyrolysis. SSHE overcome coking and carbon deposits forming on heat exchanging surfaces when the plastic pyrolyzes to hot gases. A tubular reactor with a special internal screw mixer has been developed in Poland [5]. The purpose of the specially shaped internal mixer is to mix the molten plastic and to scrape coke from the internal surface of the tube reactor. The advantage of these systems is the continuous coke removal from the reactor tubes.

The Thermofuel process uses a simple pot (kettle) design with an internal mixer/scraper that extends up the walls of the chamber to continuously remove the coke deposits. Some pyrolysis processes (e.g. Smuda) have a means for withdrawing the thermal cracking residue from the lower portion of the thermal pyrolysis vessel. The powdered coke or solid residue that forms on the bottom of the vessel can be removed on an intermittent basis either by an auger positioned in the floor of the pyrolysis chamber or through a hollow agitator shaft by a vacuum extraction system. It is critical that the char removal process incorporates an 'airlock' that prevents oxygen ingress into the pyrolysis vessel.

3.2 PREVENTING CORROSION

In general, halogen-containing polymers (e.g. those containing Br and Cl) are not acceptable feedstock for pyrolysis because they would necessitate the use of special alloys to prevent corrosion and pinholing of the plant components (e.g. condensor coils).

3.3 TANK/KETTLE REACTORS

Discontinuous (batch process) and continuous (alternating batch or cascade) stirred tanks reactors are generally used in commercial-scale melt-phase pyrolysis plants. These units are relatively simple, basically consisting of a large stainless steel vessel with indirect heating (either flame or hot air), a large stirrer and possibly internals such as baffles to enhance mixing and heat exchanger surfaces. Internals however may gradually become coated with coke and other impurities and are therefore generally avoided [6].

3.4 REFLUX

Reflux describes the process by which the heavy end of the hot pyrolytic gases are selectively condensed and flow back into the pyrolysis chamber for further cracking. Seth and Sarkar [7] compared the effects of degradation with and without a reflux on the MWD of the product. They found that when polypropylene is heated in an inert atmosphere and the volatile products are condensed, the molecular weight distribution (MWD) of the product obtained is very wide. In addition, this product is very waxy, has poor flow properties, and is unusable as a liquid fuel. To improve the product quality, ZSM-5 and other catalysts are usually used in the recycling process. However, these catalysts are costly. On the other hand, if the higher boiling fractions of the volatiles evolved due to degradation are *not* allowed to escape, then the MWD and chain length distribution of the final liquid product can be improved.

3.5 PROBLEMS WITH BATCH PYROLYSIS

Problems with batch pyrolysis plants are often mechanical in nature and are related to residue extraction problems, coking/fouling of heat exchanging surfaces, corrosion by aggressive products, clogging of condensors and ducts by waxes and other solidified or sublimed products (e.g. terephthalic acid) [6].

3.6 CONTINUOUS SYSTEMS

Extruders are often used in continuous pyrolysis plants for supplying a molten stream of plastic to the main pyrolysis vessel. The extruder may also be vented to eliminate HCl (from PVC) and water vapour from the waste plastics. In contrast to conventional extrusion, there is no need to build up high melt pressure or to shear the polymer. These pyrolysis extruders are more like heated augers than polymer processing equipment.

3.7 FLUIDIZED-BED PROCESSES

For large-scale continuously operating pyrolysis plants, a fluidized-bed reactor has numerous advantages such as improved heat transfer to the plastic, continuous dosing of catalyst and continuous coke removal. Fluidized-bed processes are however not efficient when applied on a relatively small scale.

Fluidized-bed processes are either bubbling or internally circulating. The fluidized-bed reactor is very versatile for the pyrolysis of polyolefins. Nevertheless one of the problems with fluidized-bed pyrolysis of post-consumer plastics relates to the stickiness of the sand particles (the fluidization medium) that becomes coated with fused plastic. In order to solve these problems, new reactors have been proposed, such as the conical spouted bed, the conical rotary reactor, a sphere circulation reactor and a reactor with mechanical particle stirring.

3.8 FLUID-BED COKING

Fluid-bed coking is a continuous version that delays coking. Here the cokes are formed on fludized coke particles that are circulated between the coking unit where the endothermic pyrolysis reaction takes place and the regenerator in which the coke particles are reheated by partly burning off.

3.9 FLUID CATALYTIC CRACKING (FCC)

Fluid catalytic cracking (FCC) has been used since the 1950s to turn heavy distillates (vacuum gas oil) into a series of light and dense fractions. The FCC catalysts can also be used as pyrolysis catalysts.

3.10 CATALYTIC CRACKING

It has been found for the catalytic cracking of a plastic mixture consisting of LDPE and ethylene–vinyl acetate (EVA) copolymer (86/14 w/w), that nanometer sized HZSM-5 was more active at cracking this plastic mixture at 420°C than the mesoporous catalyst

Al-MCM-41. This was ascribed to the occurrence of cross-linking reactions, leading to a fast deactivation of the mesoporous Al-MCM-41 catalysts by coke fouling [8].

4 ENGINEERING DESIGN ASPECTS

4.1 PYROLYSIS CHAMBER DESIGN

The pyrolysis and/or catalytic cracking process is generally carried out in a continuous stirred tank reactor (CSTR) also called a chamber or vessel. Pyrolysis vessels generally have a dished or cone bottom for strength. Flat-bottom vessels tend to distort readily, especially at process temperatures of 390–425°C. The floor of the vessel is either conical or torispherical. The torispherical shape of the bottom of industrial vessels allows the agitator/scraper to be placed very close to the bottom, making this impeller/tank configuration very efficient for suspending heavy dispersions and minimizing coking and fouling of the base. A typical stirred tank pyrolysis vessel is shown in Figure 15.4. A torispherical or conical base allows the solid residue or coke to accumulate at a central point for removal.

Pyrolysis vessels can range from 3 to 20 m^3 in volume. Towards the upper end of the size range, heat transfer limitations occur and it is necessary to use heat exchanging pipes internally to assist with heat transfer. The problem with an array of heat exchanging pipes internally however is that they are susceptible to fouling and coking by a carbonaceous residue.

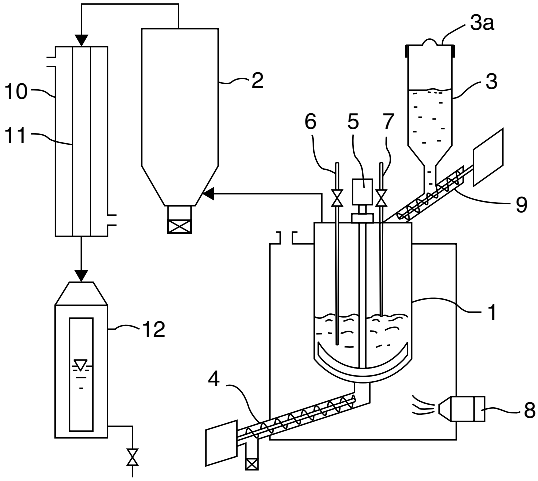


Figure 15.4 A schematic of a typical continuous stirred tank pyrolysis process. Legend: 1 pyrolysis vessel with internal agitator; 2 catalyst chamber; 3 plastic feedstock hopper; 4 char auger to remove solid residue; 5 agitator drive motor; 6 lower temperature sensor; 7 upper temperature sensor; 8 burner for furnace; 9 feed auger for plastic feedstock; 10 condenser cooling jacket; 11 condenser; 12 oil recovery tank (adapted from Saito, K. and Nanba, M., United States Patent 4,584,421 (1986) 'Method for thermal decomposition of plastic scraps and apparatus for disposal of plastic scraps')

4.2 PYROLYSIS VESSEL CONSTRUCTION

Pyrolysis vessels are generally made from SS316 or 9Cr 1Mo steel. Maximum corrosion allowance should be made for the pyrolysis chamber as the metal will potentially be exposed to hydrochloric acid and hydrobromic acid that can cause pinholing of SS304. The pyrolysis chamber needs to have a relief valve or PSV (pressure safety valve) to vent to a safe location in case of a sudden pressure build-up.

4.3 AGITATOR SPEED

In kettle-type pyrolysis systems the melt is agitated to ensure good heat transfer, heat distribution and to keep char particles from caking out. Stirring of the melt in a pyrolysis vessel greatly accelerates the heat transfer process. In the Thermofuel process the agitator currently runs at 6–7 rpm. In the Smuda process in Korea the agitator speed is 30 rpm. Higher agitator speeds are clearly beneficial in ensuring better heat transfer, heat distribution and anti-coking. In the Fuji Process the melt in the pyrolysis chamber is not stirred, but instead recirculated *via* a centrifugal blender to a melting pot and back again.

Curved-blade impellers are generally used in CSTR pyrolysis vessels. Generally the gap between the scraper and the vessel wall is between 6–9 mm to allow for thermal expansion effects.

4.4 BURNER CHARACTERISTICS

The pyrolysis chamber is generally heated with a high velocity gas burner. In order to avoid hot-spots, an impingement plate is used such that there is no flame impingement on the vessel itself. In newer designs however the chamber is heated indirectly with a hot air burner so that hot spots and flame impingement problems are eliminated.

4.5 INERT PURGE GAS

After filling the chamber it is necessary to purge with inert gas (i.e. nitrogen) in order to exclude oxygen or alternatively to apply a vacuum. It is customary to purge the pyrolysis chamber with nitrogen to evacuate any residual air in the vessel before pyrolysis. After pyrolysis N_2 purging is also required to evacuate hydrocarbon gases until the hydrocarbon levels are low enough (in the order of parts per million) to open the vessel and to commence air purging.

Instead of using an inert purge gas to blanket the polymer in the chamber the chamber atmosphere can also be evacuated to remove air/oxygen. Pyrolysis under vacuum reduces the incidence of secondary reactions in the gas phase in contrast to pyrolysis at atmospheric pressure. Under vacuum, the residence time of the pyrolysis products is short and so the secondary reactions are limited.

4.6 DISTILLATION COLUMNS

The pyrolysis gases typically contain a broad boiling point range of materials. Most state-of-the-art pyrolysis processes that convert waste plastics into liquid fuels send the pyrolysis gases into some form of separator such as a distillation column; where the stream is separated into typically at least three fractions – a light, middle, and heavy fraction. The light fraction contains (e.g. 177°C) gasoline range material and gases. The middle fraction is typically a middle distillate range material, such as the diesel fuels range, (e.g. 177–343°C). The heavy fraction is lube oil range material (e.g. 343°C).

Distillation columns can have trays or packing. The advantage of packing is that the column can be smaller in diameter and marginally shorter.

4.7 CENTRIFUGE

In order to remove water and particulate impurities from the liquid fuel products, a liquid centrifuge is normally employed, running at 12 000 rpm (for example Alfa Lavel 2000 which has a capacity of 1200 L/hr). Such a system gives three-phase separation of diesel, water and sludge. It is important that the diesel is cooled (using a pipe-in-pipe heat exchanger for instance) since the centrifuge should not process diesel over its flash point range (i.e. 60–70°C) due to explosion risks.

4.8 SCRUBBER

A wet alkali scrubber is generally employed to scrub acidic impurities from the non-condensable gas stream. The gaseous, water-soluble inorganic compounds are removed by scrubbing the noncondensable pyrolysis gas with an alkaline aqueous stream. In the scrubber, desulphurization and/or denitrogenation and/or dechlorination occurs. Most of the acidic gases such as HCl, SO_2, SO_3, H_2S, etc. resulting from pyrolysis are absorbed in the scrubber.

4.9 DECHLORINATION

The plastic feed may contain chlorine in the form of PVC or PVDC. Preferably, a substantial portion of any chlorine in the feed is removed by the addition of a chlorine scavenger compound to the feed, for example, sodium carbonate or slaked lime (calcium hydroxide) to the feed. It reacts in the pyrolysis zone with the hydrogen chloride to form sodium chloride or calcium chloride which becomes part of the residue at the bottom of the pyrolysis vessel. Preferably, the chlorine content should be removed to less that about 5 ppm.

4.10 HYDROTREATING

Hydrotreating of pyrolysis-derived fuels is particularly desirable as a means of saturating olefinic end groups (i.e. unsaturation) and for the reduction of sulphur levels to meet fuel standards. A hydrotreating step is advantageous to improve thermal and oxidative stability and colour of the liquid fuels. In the Smuda process prior to catalytic isomerization dewaxing, the pyrolysis effluent is hydrotreated to remove compounds such as N-, S- or O-containing compounds, that could deactivate the isomerization dewaxing catalyst or produce an unstable fuel oil composition (e.g., colour instability). Hydrotreating is typically conducted by contacting the pyrolysis effluent heavy fraction with a hydrotreating catalyst at hydrotreating conditions. A conventional catalytic hydrotreating process may be used. The hydrotreating is done under conditions to substantially remove all heteroatoms, while minimizing cracking. Typically, hydrotreating conditions include temperatures ranging around 190–340°C, pressures of from about 400 psig to about 3000 psig.

4.11 CATALYTIC DEWAXING AND ISOMERIZATION DEWAXING

Dewaxing is required to reduce the concentration of highly paraffinic oils which are produced from PE-rich feedstocks. The higher-molecular-weight straight chain normal and slightly branched paraffins present in such fuel cause the fuel to exhibit high cloud points and high pour points. If adequately low pour points are to be obtained, the waxes must be wholly or partially removed. In the past, various solvent removal techniques were employed to remove such waxes, such as propane dewaxing and MEK dewaxing, however, these techniques are both costly and time consuming. Catalytic dewaxing processes are more economical and remove the waxes by selectively cracking the longer-chain *n*-paraffins. Both catalytic dewaxing and selective paraffin isomerization dewaxing technology has been applied to plastic-derived fuels.

Because of the requirement for selectivity, dewaxing catalysts generally comprise an aluminosilicate zeolite, having a pore size which admits the straight chain *n*-paraffins but which excludes more highly branched materials, cycloaliphatics and aromatics. Zeolites such as ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 and ZSM-38 have been used for catalytic dewaxing.

Catalytic isomerization dewaxing on the other hand preferentially isomerizes the paraffins, reducing the diesel pour point and cloud point while keeping the high-cetane components in the diesel product. It also favourably decreases the boiling range of the fuel (T95) and produces a higher mid distillate yield.

Isomerization dewaxing is carried out using a large-pore, high-silica zeolite dewaxing catalyst such as high-silica Y or zeolite-beta which isomerizes the waxy components of the base stock to less waxy branched chain isoparaffins. Catalytic isomerization dewaxing uses such large pore zeolites as ZSM-22 or ZSM-23. In this process the *n*-paraffins become isomerized to iso-paraffins to form liquid range materials which contribute to a low-viscosity and low-pour-point product. Isomerization dewaxing is generally a higher-cost process, but delivers higher yields and better properties at the same level of cloud point reduction.

Dewaxing catalysts are manufactured by both Akzo Nobel and Mobil. Mobil's Isomerization Dewaxing (MIDW) first commercialized in 1990 uses a Pt-based zeolite catalyst to crack and isomerize *n*-paraffins to iso-parrafins, thereby converting fuel oil to low-pour-point distillates.

5 QUALITY OF THE OUTPUT FUELS

Many pyrolysis processes produce a petrol fraction with a favourable octane number, but strong gum-forming tendency due to the presence of mainly branched olefins.

A common method of classification for petroleum is the PONA system (PONA is an acronym for paraffins, olefins, naphthenes, and aromatics). Paraffins are straight-chain or branched hydrocarbons in which there are no double or triple bonds between carbon atoms. Olefins are similar to paraffins, but they contain at least one multiple bond in their chemical structure. Naphthenes are saturated hydrocarbons, just like paraffins, but they incorporate a ring of carbon atoms into their chemical structure. Aromatics contain a benzene ring in their structure.

5.1 UNSATURATION

Similar to petroleum-derived cracking the fractions from plastics pyrolysis can contain a significant concentration of unsaturated hydrocarbons (especially α-olefins) [9]. The mono- and diolefin content makes the diesel fuel prone to instability due to polymerization and the formation of deposits (i.e. gums). Since the plastic-derived diesel fuel has an appreciable olefins content it is important to subject it to a hydrogenation step (e.g. hydrogenation over Pd/Al_2O_3 at 300–320°C and 3 MPa H_2) which lowers the bromine number from typical values of 22–28 g Br_2/100 g to less than 0.5 g Br_2/100 g [9].

5.2 CARBON RESIDUE IN THE FUEL

Carbon residue may be present in the diesel fuel in suspended form. The carbon residue can be removed by ultracentrifuging. In the Smuda process some of the light layered clays can be carried out of the pyrolysis vessel with the hot pyrolytic gases and can be entrained in the condensed fuel.

5.3 LOW-TEMPERATURE PROPERTIES

Polyethylene-derived diesel is susceptible to waxing problems. It is not just the molecular weight (i.e. chain length) that will cause waxing, it is the presence of linear (unbranched) *n*-alkane chains (i.e. paraffins) and these are more likely to be formed from PE feedstocks. Such straight chains can readily fold and pack tightly to form crystals.

The solubility of linear alkanes present in diesel quickly decreases with temperature. The temperature at which the first crystals appear is called the cloud point and is one of the most important specifications for fuels concerning their low temperature behaviour. The utilization of a fuel is restricted to temperatures above their cloud point. Cloud point measures the temperature at which the wax crystals form a haze. Below the cloud point, the presence of crystals in suspension impairs the flow, plugging fuel filters. Immediately below the cloud point the fluid stops flowing, reaching what is known as pour point. The CFPP test measures the highest temperature at which wax separating out of a sample can stop or seriously reduce the flow of fuel through a standard filter under standard test conditions.

The exact temperature at which the cloud point is reached depends on the total n-alkane content of the fuel, the average size of the n-alkane molecules, their size distribution and chain structure (e.g. degree of branching). Conventional diesels contain as much as 20% of long-chain n-alkanes of limited solubility in the fuel. Pyrolysis-diesels from PE feedstocks can contain more than 40% long-chain n-alkanes. Paraffins crystallize at low temperature into very thin rhombic plates which can clog filters, transfer lines, and pumps, and can lead to engine failure at low temperatures.

Two processes are commonly used to produce fuels within a given specification. The use of additives, such as cloud point depressants, and, fuel blending where a fuel with an excessively high cloud point is mixed with a low-cloud-point fluid to produce a fuel that meets the specifications. Most often both approaches are used simultaneously, since cloud point depressants have a limited action.

5.4 FUEL INSTABILITY

Newly manufactured diesel fuel from waste plastics can sometimes begin to deteriorate as soon as it is produced. Within days of the diesel fuel being produced it goes through a repolymerization and oxidation process. This process forms sediment and ‘insoluble gums’ in the fuel caused by the unsaturated fuel molecules (i.e. reactive olefins) lengthening and linking together. These components then drop to the bottom of the fuel storage tanks and form a sludge. The fuel also begins to turn dark in colour and develop a strong smell.

This will result in an increase in asphaltene agglomerations, polymerization and a dramatic loss of combustion efficiency. The chemistry of diesel fuel instability involves the chemical conversion of precursors to species of higher molecular weight with limited solubility. The conversion process often involves oxidation of the precursors. Fuel solvency plays a role, since the development of insolubles is always a function of both the presence of higher molecular weight species and the fuel’s capacity to dissolve them.

‘Dark fuel’ is in general indicative of oxidation and is a sign that the process of fuel degradation is in a far advanced stage. Hazy fuel is indicative of polymerization of the fuel. These components sink to the bottom of the fuel tank and form asphaltene also known as diesel sludge. The fuel begins to turn dark, odorous and in most cases causes engines to smoke. The engines smoke because some of these clusters in the early stages are small enough in size to pass through the engine filtration and into the combustion chamber. As these clusters increase in size, only part of the molecule gets burned. The rest exits the exhaust as unburned fuel and smoke. With increases in cluster size they begin to reduce the flow of fuel by clogging filters.

The diesel needs to be ‘stabilized’ with diesel fuel additives that will inhibit ‘diesel polymerization’ and inhibit oxidation, darkening and agglomeration of certain components of the diesel. One such effective stabilizing additive is Octel FOA-6. Octel FOA-6 and FOA-3 are amine-based antioxidants that are recommended for antioxidant protection of distillate fuels such as diesel. FOA-3 and FOA-6 together with AO-22, generally give their best performance when added ‘hot and early’ to the fuel, usually to a cracked component in the run-down from the cracker.

5.5 DIESEL ADDITIVES

Additives are often required to bring the low-temperature properties of the diesel into specification. The most important parameter for measuring the low-temperature characteristics of diesel fuel is the cloud point (or more simply, CP) which indicates the temperature corresponding to the commencement of segregation of wax crystals representing linear high-boiling paraffins. These crystals, particularly just after starting a diesel engine, block the filters which protect the injection system. This causes the engine to stop, which then requires a very elaborate procedure for its restarting.

Other significant parameters related to the low-temperature characteristics are pour point (PP) and cold filter plugging point (CFPP). These parameters are coded and measured by the ASTM and DIN methods and generally vary in a mutually coherent manner. The pour point can be reduced by using additives, but these have no appreciable effect on the cloud point.

As diesel is cooled, there comes a point at which the waxes begin to separate and appear as a cloud or haze. The temperature at that point is known as the cloud point. As discussed in Section 5.3, the cloud point is basically the temperature at which small wax crystals start to form in the diesel. This is simply performed by placing the diesel into a fridge and cooling to −5°C and then allowing it to come to room temperature. The temperature at which a thermometer can be inserted into the gelled diesel is the ‘pour point’ and then the temperature at which the crystals disappear is the ‘cloud point’. Mixing heating oil with diesel fuel has the effect of reducing the cloud point of the diesel. For example, mixing 23 parts of heating oil to 100 parts diesel (1:4 mixture), reduces the cloud point by 2°C. Kerosene may also be blended with diesel fuel to improve its low temperature flow performance. The addition of 25 parts kerosene to 100 parts diesel will lower the cloud point of the diesel fuel by 8°C. However kerosene may then bring the flash point out of the lower specification range.

Diesel made predominantly from polyethylene has a higher proportion of paraffins and therefore a higher cloud point. The paraffins crystallize as the temperature is lowered, leading to small visible crystals forming in the diesel. It is these wax crystals that can plug filters at low temperatures.

The addition of small amounts of cold flow improvers (also known as pour point depressants) brings the pour point of the diesel into the normal range. This can be achieved for example by addition of 1000 ppm of Callington Haven Roxdiesel Pour Point Depressant.

It has been found that additives such as pour point depressants can lower the pour point, but not the cloud point. It has been found empirically that styrene monomer can lower the cloud point since the paraffinic wax crystals are more soluble in the styrene than in the diesel. Styrene monomer is proposed as a suitable additive to depress the cloud point.

5.6 STORAGE STABILITY OF PLASTIC-DERIVED DIESEL FUEL

As diesel ages a fine sediment and gum forms in the fuel brought about by the reaction of diesel components with oxygen from the air. The fine sediment and gum will block fuel filters, leading to fuel starvation and engine failure. Frequent filter changes are then required to keep the engine operating. The gums and sediments do not burn very efficiently in the engine and can lead to carbon and soot deposits in injectors and other combustion surfaces.

Diesel fuel made from the thermal cracking of plastics is more susceptible to oxidation and polymerization than refinery-made diesel fuels. This is because plastic-derived diesel fuels generally have terminal unsaturation (i.e. double bonds) at the ends of the diesel chains as a result of the β-scission chain cleavage. Over time free radicals that form in the plastic-derived diesel fuels during storage cause the diesel chains with double bonds (α-olefins) to polymerize resulting in a sludgy sediment also known as 'gum'.

Factors which decrease storage life of diesel:

- fuel composition, especially the presence of olefins and styrene monomer in the plastic-derived fuel;
- exposure to high temperatures;

The ageing process can be accelerated by the following conditions:

- contact with zinc, copper or metal alloys containing them. These metals will quickly react with diesel fuel to form unstable compounds;
- exposure to dust and dirt containing trace elements, that can destabilize the fuel (such as copper and zinc).

The expected life of a diesel fuel is indicated by the oxidation stability test (ASTM D-2276). The test measures how much gum and sediment will be deposited after conditioning the fuel at 120°C in the presence of oxygen for 16 h. It roughly corresponds to a years storage at 25°C. A result of less than 20 mg/L of sediment and gum after the test is considered acceptable for normal diesel.

In order to improve the stability of synthetic diesels and biodiesels it is necessary to add free-radical trapping additives known as antioxidants (such as DTBHQ, IONOX 220, Vulkanox ZKF, Vulkanox BKF, and Baynox). Butylated hydroxy toluene (BHT) in particular prevents oxidation and radical polymerization reactions that can lead to diesel fuel ageing.

The nominal antioxidant concentration required to give diesel fuel an extended storage stability and suppress polymerization, is 1000 ppm (i.e. 1000 mg/kg).

HSD Stabilizer (Diesel Stabilizer) additive is a multicomponent, oil soluble formulation, specially designed to maintain the total sediments level in diesel fuel within the specified limits, as per ISO 1460:1995. The additive will ensure that the diesel does not deteriorate on storage and the fuel system is protected from deposit formation and corrosion. The additive consists of three major components, namely:

Antioxidant. Fuel oils are subject to deterioration due to oxidation and this occurs both during storage and in service. Oxidation gives rise to formation of gums and sludge. Olefinic compounds produced by cracking are more susceptible to oxidation. Gum is the product of a series of oxidation and polymerization reactions. Antioxidants function by combining with peroxide free radicals and by decomposing hydroperoxides into stable substances. The antioxidants used in the additive are a combination of sterically hindered phenol-type antioxidants.

Detergent. The detergent and dispersant, keeps oil insoluble combustion products in suspension and also prevents resinous-like oxidation products from agglomerating into solid particles. Thus they prevent formation of deposits on metal surfaces, oil thickening and sludge deposition. The component used is ethoxylated products of alkyl phenols.

Metal deactivator. Metal deactivator prevents precipitation of metal ion oxidation reactions and precipitation of insoluble metal compounds. Metal deactivator in combination with other antioxidants, shows strong synergistic effects. Oxygen and moisture present, diffuse through oil film and cause corrosion. Amine derivative, used in the additive has good water-displacing properties. They impede sludge formulation, disperse sediments and reduce corrosion in various fuel systems.

5.7 CHARACTERISTICS OF THE SOLID RESIDUE

The carbonaceous coke formed during plastics pyrolysis is automatically scraped off and accumulates in the bottom of the pyrolysis chamber where it is reduced by attrition to a free-flowing black powder. The internal agitator/scraper constantly removes the carbonaceous char by-product before it acts as a thermal insulator and lowers the heat transfer to the plastic. The char residue produced is about 2–3% of the output for relatively clean polyolefin feedstocks and up to 8–10% for PET-rich feedstocks.

It is difficult to generalize about the chemical composition of the coke stream, since it is directly dependent on the composition of the feedstock stream, which of course varies from one location to another. It is to be expected however that the char stream from a mixed plastic packaging feedstock will be rich in the following elements: Cr, Cd, Mn, Co, Fe, etc., since compounds containing these metals are used in additives (such as pigments and catalysts) used in commodity plastics. The carbon matrix has a metal ‘fixing’ effect and binds up the metal ions so that limited leaching occurs after disposal. The leachability potential of the coke (known as TCLP) needs to be determined before the coke can be landfilled. TCLP stand for toxicity characteristic leaching procedure. The TCLP provides a means to determine the potential for waste leaching in a landfill environment.

5.8 GASEOUS EMISSIONS

Ammonia (NH_3) and other nitrogen-containing compounds in the fuel gas can lead to the emission of the oxides of nitrogen (NO_x) in the combustion product gases. Ammonia is a potential product in all pyrolysis processes whenever protein materials are being processed. Proteins are collections of amino acids that contain small quantities of the amine group (NH_2) attached to a carbon atom. The nitrogen in amino acids would be the ‘fuel nitrogen’ for protein material if it were used directly as pyrolysis feedstock. A portion of these amine groups will convert to ammonia during the pyrolysis process and thus can be released into the fuel gas. The most common way to treat the fuel gas in order to remove ammonia is to scrub it with water at modest temperature conditions. There can also be sulphur in the feedstock used for pyrolysis. In the normal range of temperatures for pyrolysis processes, only a portion of the sulphur is released into the fuel gas. Most of this sulphur is in the form of hydrogen sulphide (H_2S) that can be removed by an alkaline scrubbing of the fuel gases.

6 CATALYTIC CRACKING

6.1 CATALYST ACTIVITY AND SELECTIVITY

Zeolite catalysts produce liquid products with a boiling point distribution in the range of motor engine fuels. The acidic zeolite catalysts (HZSM-5, H-ultrastable Y-zeolite (H-US-Y)) are more effective in converting polyolefins than the less acidic, amorphous silica–alumina and mesoporous MCM-41. There are considerable differences in product selectivities among the various catalysts. For instance, nanosized HZSM-5 zeolite (with high external surface area and strong acid sites) promotes end-chain scission reactions of the polyolefins, producing mainly light hydrocarbons (C_3-C_6); while heavier products are obtained over mesoporous HMCM-41. Thus indicating that random scission reactions are predominant as a result of the large pores and mild acidity of this material. From a commercial perspective, the cheaper silica–alumina catalyst give very good selectivity, and their lower activity can be compensated for by increasing the catalyst to polymer ratio.

The larger pore zeolites (H-Y) show rapid deactivation in contrast to the more restrictive HZSM-5 and the non-zeolitic catalysts (silica-alumina, MCM-41), since coke deposits can accumulate inside the channel system of large pores. In contrast, coke deposits only on the outer surface of the zeolites having narrow pores. Furthermore the catalysts having weaker acid sites of lower density are better at tolerating coke deposition. For instance, the mild acidity of clays (and their pillared versions, e.g. pillared montmorillonite) show good resistance to deactivation by coking.

Walendziewski [10] has reported that the optimum thermal cracking temperature of waste polyolefins is 410–430°C, whereas in the case of catalytic pyrolysis, lower temperature (e.g. 390°C) can be used. Higher than 90% yield of gas and liquid fractions with bp <360°C was attained.

Manos [11] studied the catalytic degradation of high-density polyethylene to hydrocarbons over different zeolites. The product range was typically between C_3 and C_{15} hydrocarbons. Distinctive patterns of product distribution were found with different zeolitic structures. Extra large-pore ultrastable Y-, and β-zeolites, alkanes were the main products with less alkenes and aromatics and only very small amounts of cycloalkanes and cycloalkenes. Medium-pore mordenite and ZSM-5 gave significantly more olefins. In the medium-pore zeolites, secondary bimolecular reactions were sterically hindered, resulting in higher amounts of alkenes as primary products. The hydrocarbons formed with medium-pore zeolites were lighter than those formed with large-pore zeolites. The following order was found regarding the carbon number distribution: (lighter products) ZSM-5 $<$ mordenite $< \beta <$ Y $<$ US-Y (heavier products). A similar order was found regarding the bond saturation: (more alkenes) ZSM-5 mordenite $< \beta <$ Y $<$ US-Y (more alkanes).

The catalytic cracking of polypropylene waste in a fluidized-bed reactor was reported by Ji [12]. It gave a yield of liquid product of 50%, the research octane number of the gasoline produced from plastic waste was 86, and the cetane index of the diesel fuel produced from the plastic waste was 43.

Modification of ZSM-5 zeolite can result in improved liquid yields and a doubling of the isoparaffin index of the liquid fuels which indicates higher liquid quality compared with the parent ZSM-5 zeolite. The high catalytic activity of modified ZSM-5 was explained by its unique acidic properties with a sharp increase of the number and strength of weak acid sites and a decrease of strong acid sites [13].

A major shortcoming of zeolite-type catalysts is their sensitivity to hydrogen chloride and HCl acid, which causes destruction of a catalyst in concentrations above 200 ppm HCl. Considering the fact, plastic wastes often contains PVC the application of expensive zeolite-type catalysts is disadvantageous.

6.2 LAYERED CLAY CATALYSTS

A layered silicate clay framework with ordered nickel (or iron) atoms inside can be used as an effective cracking catalyst. Manos [14] showed that two natural clays and their pillared analogues were able to completely decompose polyethylene although these clays were found to be less active than US-Y zeolite their yields to liquid products were around 70%, compared with less than 50% over US-Y zeolite. Moreover, the liquid products obtained over the clay catalysts were heavier. Both of these facts are attributed to the milder acidity of clays, as the very strong acidity characterizing zeolites leads to ‘overcracking’. Furthermore, this milder acidity leads to significantly lower occurrence of hydrogen transfer secondary reactions compared with US-Y zeolite, and as a consequence, alkenes were the predominant products over the clay catalysts. An additional advantage of these catalysts is the considerably lower amount of coke formed.

Another important group of catalytic compounds contain the layered double hydroxides (sometimes called ‘anionic clays’ or ‘hydrotalcites’). Presently, many researchers study these materials because of their adsorptive and catalytic properties.

Unlike thermal cracking, the use of catalysts requires less energy and forms valuable hydrocarbons in the gasoline and diesel ranges, thus eliminating the requirement for further processing.

Tu *et al.* [15] report on the catalytic cracking of low-density polyethylene (LDPE) over three types of base catalysts based on layered double hydroxides (LDH) [15]. LDH constitutes a class of layered compounds, resembling the naturally occurring hydrotalcite, and are generally considered complementary to the clays in that they contain positively charged layers and anions in the interlamellar space. Due to the relative ease of their synthesis, LDHs represent an inexpensive and versatile source of a variety of solid catalysts [16]. The catalytic cracking of low-density polyethylene (LDPE) over the three LDHs (MgAl, NiAl, and ZnAl) was examined at 350 and 400°C. The catalytic activities and product distributions obtained with these materials were compared with those corresponding to thermal cracking and cracking over acid solid HY-Zeolite catalyst. All cracking reactions were performed by a semi-batch operation with polymer to catalyst ratio of 100:1. Volatile hydrocarbons were collected from a stream of inert helium gas. Both liquid and gaseous products were analysed by gas chromatogram [15].

At 350°C, the thermal cracking of low-density polyethylene was almost negligible ($<1\%$ conversion). The final product after the reaction was that of the melted LDPE, showing that the thermal degradation of LDPE at 350°C was very slow. In all experiments at 400°C, the initial LDPE was totally converted to liquid product, gaseous product, wax and coke. At 400°C, catalytic cracking of LDPE over LDH catalysts showed higher cracking activity than thermal cracking. The liquid yields are: 40 wt% wt. for NiAl, 38 wt% for ZnAl-, 27 wt% for MgAl and 20 wt% for purely thermal cracking. NiAl and ZnAl-LDHs proved to have better potential catalytic properties for LDPE cracking rather than MgAl-LDH. Solid HY acid catalyst was also tested to compare the performance of the LDHs. HY showed similar activity with NiAl and ZnAl-LDH. However, being more basic in nature, LDHs produced heavier hydrocarbon liquid than the HY. The order was as follows: (lightest products) HY-Zeolite < NiAl < ZnAl < MgAl < thermal only (i.e. no catalyst) (heaviest products). In addition, LHDs showed less coking than their HY counterpart, this is due to the negligible or nonoccurrence of hydrogen transfer secondary reactions. HY showed a high level of isobutane production, which is indicative of high level of secondary reactions. The production of isobutane however decreased considerably as the cracking process progressed, hence HY showed rapid deactivation [15]. Furthermore, all reactions produced considerably lower gaseous products (less than 5 wt%). This is of great benefit as gaseous products are considered less superior to the more valuable liquid product. It was concluded that NiAl and ZnAl LDHs proved to be promising candidates for the catalytic cracking of polyethylene. Catalytic cracking of LDPE over these two catalysts produced a high level of valuable hydrocarbons liquid, with very little gaseous product and coke [15].

6.3 EXTERNAL CATALYSTS

A major problem with using catalysts in the pyrolysis of mixed plastics is that of coke formation, which gradually deactivates the catalyst. For this reason the catalyst is often positioned outside the main pyrolysis reactor such as in a second reactor where the pyrolysis oil is upgraded over a suitable catalyst (e.g. zeolite HZSM-5 or Ni-supporting rare earth metal exchanged Y-type zeolite (REY)) in order to obtain a high quality gasoline. For instance a two-stage catalytic degradation of polyethylene using amorphous silica–alumina and HZSM-5 zeolite catalysts in series has been developed for converting the polymer into high-quality gasoline-range fuels. Firstly the silica–alumina catalyzes the degradation of polyethylene into a low quality pyrolysis oil, which is then transformed into high-quality gasoline on the strongly acidic sites of the zeolite.

6.4 PS CATALYTIC CRACKING

Thermal cracking and catalytic degradation of polystyrene (PS) at 375°C over HZSM-5 catalyst yields mainly styrene (over 50 wt% yield). On the contrary, the main products resulting from the catalytic cracking over HMCM-41 and SiO_2-Al_2O_3 are benzene, ethylbenzene and cumene, but in proportions lower than 20 wt% [17]. The results obtained over HZSM-5 zeolite are attributed to both its microporous structure and acid features. The external acid sites of the HZSM-5 zeolite are practically the only ones active for PS degradation, since this polymer is too bulky to enter the zeolite micropores. In addition, competitive cross-linking reactions also take place, which are highly promoted by the strength and Brönsted nature of the zeolite acid sites. Finally, the superior activity obtained over HMCM-41 is explained in terms of its uniform mesoporous structure and its medium acid strength [17].

Similarly the fluidized-bed pyrolysis of polystyrene in the presence of fluid catalytic cracking (FCC) catalysts was investigated at temperatures between 370 and 515°C [18]. In the catalytic pyrolysis of polystyrene, the product distribution is changed from the usual main product styrene (61 wt%) (in noncatalytic experiments with simple quartz sand) to feedstock chemicals (18–26% ethylbenzene, 9–22 wt% benzene: 1–7 wt% styrene, 3–5% toluene) and coke (15–23 wt%).

6.5 CATALYTIC DECHLORINATION

Waste-plastic-derived oil that was prepared by thermal degradation of municipal waste plastics at 410°C was dehydrochlorinated to remove chloroorganic compounds using various catalysts such as iron oxide, iron oxide–carbon composite, ZnO, MgO and red mud. The iron oxide catalysts were effective in removing the chloroorganic compounds. MgO and ZnO catalysts were deactivated during the reaction by HCl, which is produced by the dehydrochlorination of chloroorganic compounds. Iron oxide and its carbon composite were found to be stable in the dehydrochlorination of municipal waste plastic derived oil [19].

A red mud catalyst (waste from alumina production) was evaluated as both a cracking and dechlorination catalyst for the catalytic degradation of PVC-containing mixtures (such as PVC/PE, PVC/PP and PVC/PS) by [20]. Using stepwise pyrolysis, over 90% chlorine in the feed plastic was recovered as HCl gas. A silica–alumina catalyst accelerated the rate of polymer degradation and lowered the boiling point of liquid products, but the chlorine content of oil over silica-alumina was also the highest. Red mud and iron oxides sorbents showed good effect on the fixation of evolved HCl however, they had no effect on the cracking of polymers.

7 COMMERCIAL PLASTIC PYROLYSIS PROCESSES

7.1 THERMOFUEL™ PROCESS

In the Thermofuel process, plastic waste is first converted to the molten state and then ‘cracked’ in a stainless steel chamber (Figure 15.5) at temperatures in the range 350–425°C under inert gas (i.e. nitrogen). The hot pyrolytic gases are condensed in a specially designed two-stage condenser system to yield a hydrocarbon distillate comprising straight- and branched-chain aliphatics, cyclic aliphatics and aromatic hydrocarbons. The resulting mixture is essentially equivalent to regular diesel. A process flow diagram of the Thermofuel process is shown in Figure 15.6.

The essential steps in the Thermofuel™ pyrolysis of plastics involve:

- uniformly heating the plastic within a narrow temperature range without excessive temperature variations;
- ensuring the plastic is homogeneous and stirred to prevent hot-spots;
- excluding oxygen from pyrolysis chamber, yet at the same time allowing rapid egress of the hot pyrolytic vapours;
- constantly removing the carbonaceous char by-product before it builds up on the pyrolysis chamber walls and acts as a thermal insulator, thereby lowering the heat transfer to the plastic;

Figure 15.5 Close-up of pyrolysis chamber of commercial plastics pyrolysis plant which can convert 10 tonne of unwashed, mixed plastics into 10 000 L of diesel fuel per day. (Reproduced by permission of Ozmotech Pty Ltd)

- reactive distillation, which means the hot pyrolytic vapours can condense and be returned to the main pyrolysis chamber until the correct carbon chain length is achieved;
- careful condensation and fractionation of the pyrolysis vapours to produce diesel of good quality and consistency.

The core technology of the Thermofuel process is the catalytic reaction tower (or catalytic converter, Figure 15.7). The catalytic reaction tower contains a system of plates made from a special catalytic metal alloy. The metal plates are positioned so that the hot pyrolytic gases must travel a tortuous path, in order to maximize contact area and time. The catalyst chamber is heated to 220°C using the exhaust gases (not pyrolysis gases) from the furnace of the pyrolysis chamber.

The metal catalyst 'cracks' paraffinic chains longer than C_{25} and 'reforms' chains shorter than C_6. This is especially important to convert the α-olefin chains (1-alkenes) to saturated alkanes. The catalyst ensures that the final fuel has a carbon chain distribution in the range C_8–C_{25} peaking at C_{16} (cetane) (Figure 15.8). The catalytic tower uses technology borrowed from the petrochemical industry for the hydrogenated of C=C double bonds, e.g. Raney Nickel or so-called Adams catalyst.

The catalyst is not consumed or poisoned, unlike zeolite type catalysts. The metal plates do however get fouled with a tar-like residue and terephthalic acid and therefore the reaction tower needs to be stripped down periodically and the plates polished back to their pristine form.

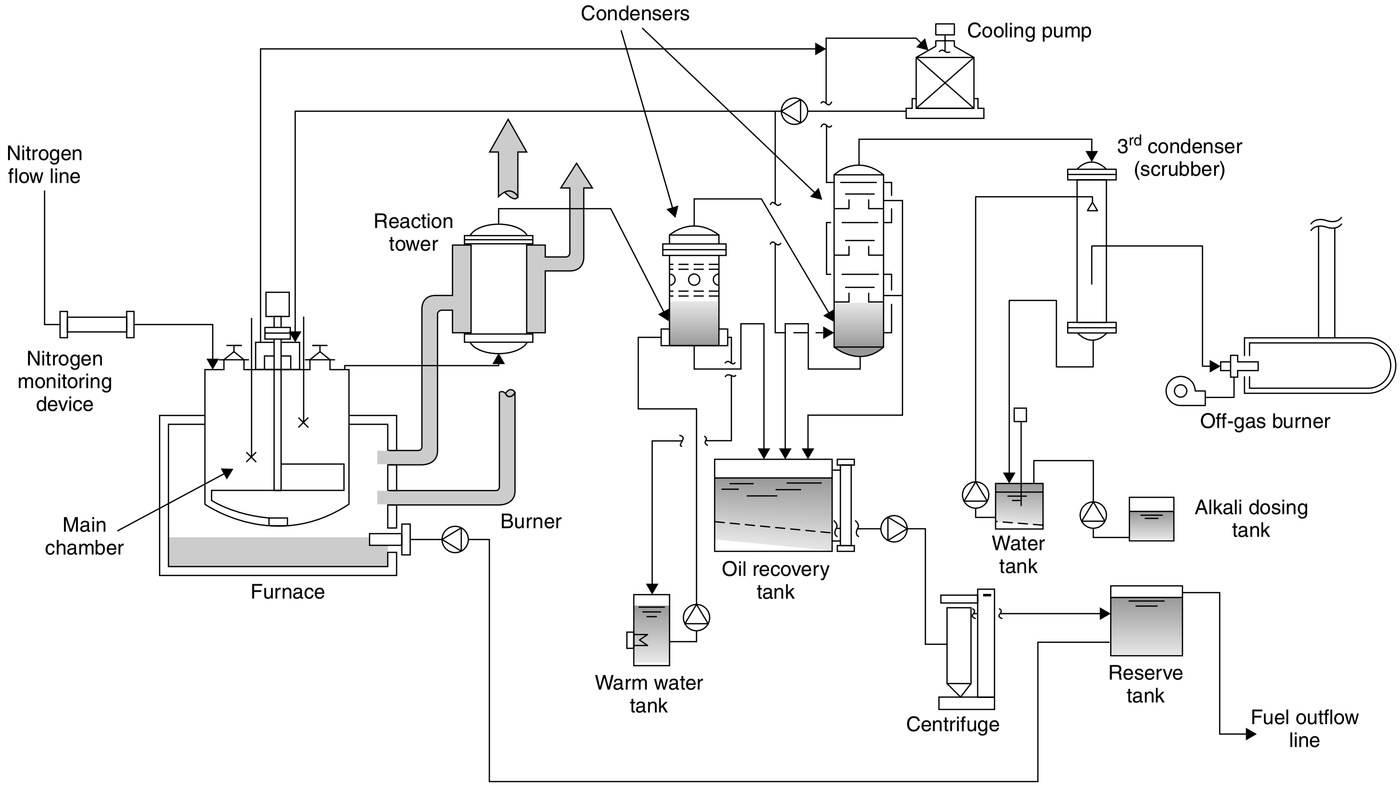


Figure 15.6 Process flow for commercial pyrolysis plant (Thermofuel™) for converting waste plastics into diesel fuel. The plastic is heated to 375–425°C and the pyrolysis vapours are catalytically cracked and then selectively condensed. Note that the pyrolysis vessel is purged with nitrogen gas and that the hot pyrolytic vapours pass from the pyrolysis vessel to the catalytic reaction tower where they are cracked and reformed to give a high-purity diesel stream. (Reproduced by permission of Ozmotech Pty Ltd)

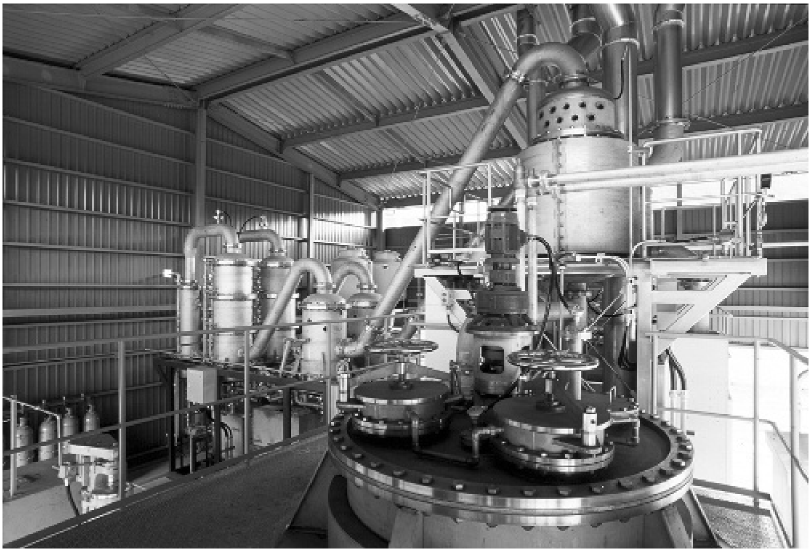
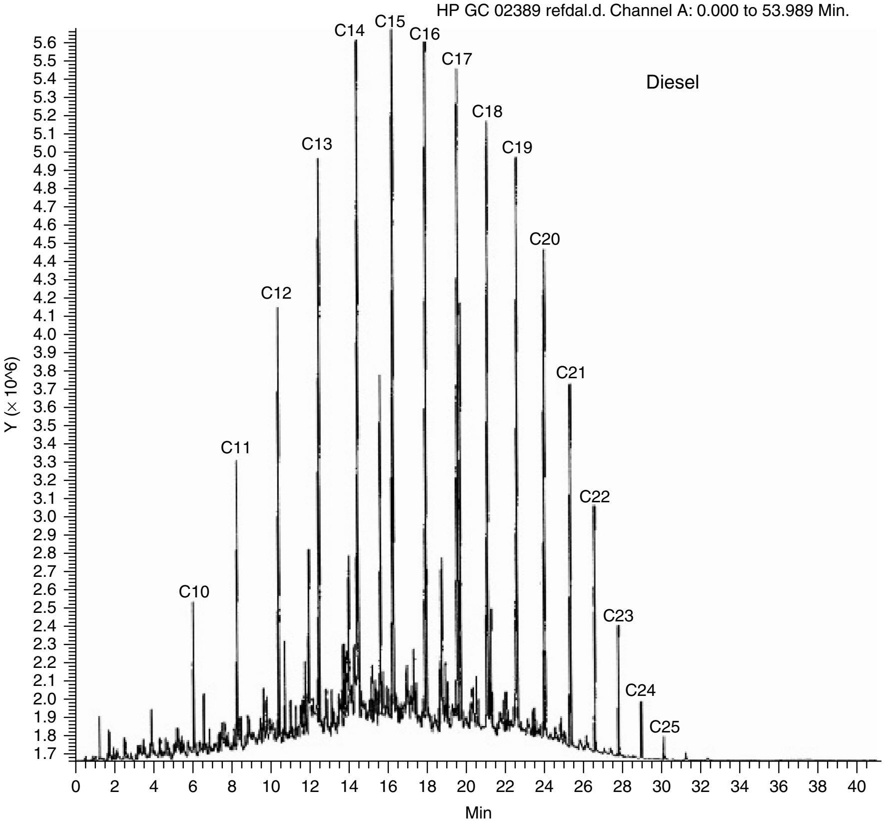


Figure 15.7 Close-up of catalytic reaction tower and condensers of the Thermofuel process. (Reproduced by permission of Ozmotech Pty Ltd)



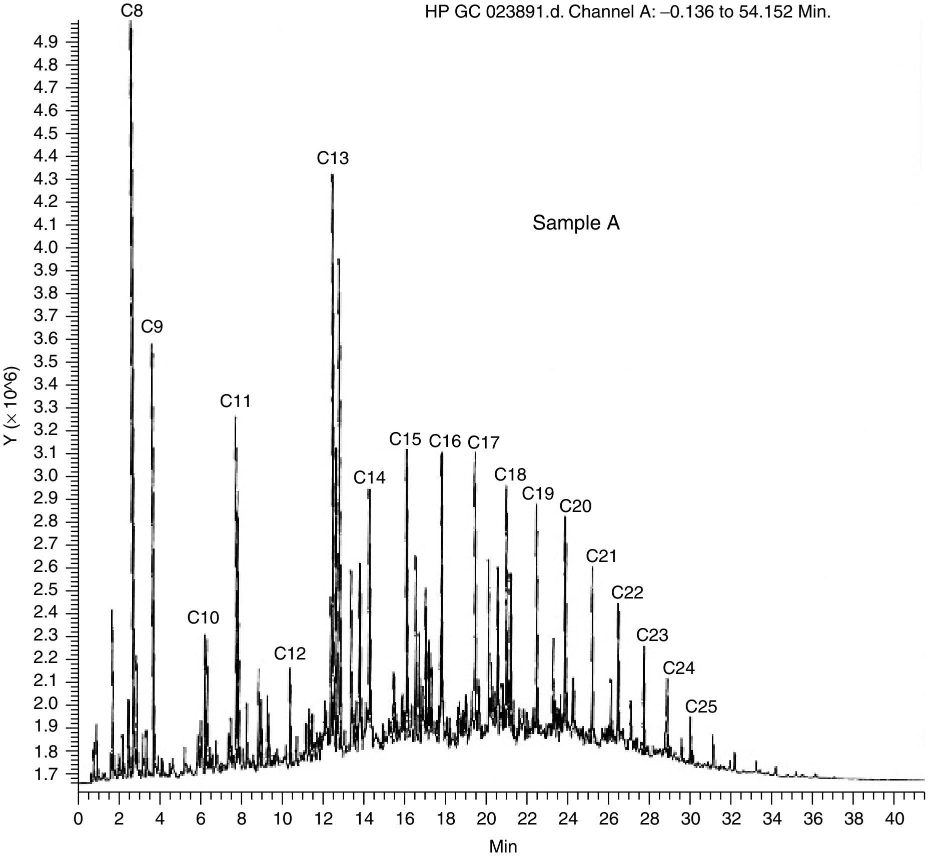


Figure 15.8 Gas chromatogram (GC) of regular diesel (upper) and plastic-derived diesel (lower). The regular diesel exhibits a series of regular hydrocarbon with a normal distribution peaking close to C_{16} (cetane). The plastic-derived diesel was produced by the Thermofuel process (before fractionation) from a mixture of polyethylene, polypropylene and Nylon film as feedstock. This fuel sample also exhibits regularly spaced, hydrocarbon peaks approximating a normal distribution and peaking at C_{16} and concluding at approximately C_{30}. Also apparent are large peaks at C_8 (octane), C_9 and C_{11}. Collectively these additional peaks are 'light' hydrocarbons. 'Lights' are defined as paraffins or carbon chains with a length less than C_{11}, that is, less than 11 carbon atoms long. (Reproduced by permission of Ozmotech Pty Ltd)

The catalyst chamber is the heart of the Thermofuel process and is directly responsible for the high quality of the output fuel from this process. The technology in and around this unit is highly proprietary since competitive processes do not have this type of long-life catalytic converter. Many other pyrolysis processes add zeolite catalysts directly to the pyrolysis chamber, however, these are expensive and quickly become fouled and deactivated.

A single-chamber demonstration plant in Fujioka City, used for running trials and process development, has been operational since 1996. Inspection of the inside of the main pyrolysis chamber during a shut-down showed it to be in excellent condition with minimal scoring or corrosion.

A twin-chamber Thermofuel plant at the Totai Company in Yamanashi Province has been in operation since 2002. The plant at this site processes post-industrial plastic packaging film based mainly on polyethylene, polypropylene and nylon. The plant operation is highly automated.

A twin-chamber Thermofuel plant at an agricultural cooperative on the island of Okinawa has been in operation since 2003 (Figure 15.9). This plant processes agricultural

Table 15.4 Thermofuel plants in Japan

Location	Description	Started
Totai	Dual chambers, mixed plastics	2002
Okinawa	Dual chambers, agricultural film	2003
Nakamoto	One chamber, similar to Totai (mix plastics)	2004
Watanuki	Dual chambers, commercial and industrial waste(recycling)	1993
Tih-Tay	Dual chambers, polyethylene from cables (cross-linked EVA)	1998
Nabari	One chamber, industrial waste (packaging)	2004
Fujioka	Original pilot plant	Now disassembled

Figure 15.9 A commercial Thermofuel™ plant in Okinawa in Japan which processes agricultural plastics such as mulch and greehhouse films into diesel fuel to run greenhouse boilers for heating, tractors and other agricultural machinery. (Reproduced by permission of Ozmotech Pty Ltd)

plastics such as mulch and greenhouse film based mainly on polyethylene. The diesel fuel is used to run greenhouse boilers, tractors and other farm equipment.

Thermofuel-based fuel produces much lower sulphur oxides (SO_x) than conventional diesel since sulphur levels in the fuel are typically less than 0.01% (100 ppm) as compared with conventional diesel which has sulphur around 400–500 ppm. SO_x emissions for Thermofuel diesel are thus correspondingly 4–5 times lower than that of conventional diesel. Furthermore the Thermofuel incorporates an integrated desulphurization plant to ensure the sulphur content of the diesel produced is always within specification.

Nitrogen oxides (NO_x) emissions from diesel engines run on Thermalysis fuels evaluated at 3000 rpm was found to vary with the load on the engine [21] (Table 15.5)

Generally, the Thermofuel fuel gives lower NO_x than conventional diesel, especially at lower engine load. Particulate emissions from diesel engines run on Thermofuel diesel, also at 3000 rpm, varies with the load on the engine [21] as shown in Table 15.6.

It is apparent from the above data that Thermofuel diesel produces significantly less particulates (smoke) at all engine loadings than conventional diesel. This is environmentally significant, as the particulates formed from diesel combustion contain polycyclic aromatic hydrocarbons (PAH) which have carcinogenic potential. The hotter burning characteristic of the Thermofuel relative to conventional diesel is likely to be responsible for the better burn-out of particulates [21].

In the Thermofuel process the first reaction occurs in the pyrolysis chamber where the plastic is thermally pyrolyzed, causing random scission of carbon chain lengths. While secondary reactions occur in the catalytic converter (i.e. catalyst tower) where shorter carbon chains are reformed and further cracking of longer carbon chains occurs such

Table 15.5 Nitrogen oxides (NO_x) emissions from Thermofuel diesel as compared with conventional diesel

Engine load	NO_x (ppm) (Thermofuel fuel)	NO_x (ppm) (conventional diesel)
1/5	90	150
2/5	180	215
3/5	300	330
4/5	420	400
5/5	500	450

Table 15.6 Particulate engine emissions from Thermofuel diesel as compared with conventional diesel

Engine Load	Particulates % (Thermofuel™ fuel)	Particulates % (conventional diesel)
1/5	0	0
2/5	0	2
3/5	5	17
4/5	22	40
5/5	43	70

that the carbon chain length distribution in the range from C_8 to C_{25} and peaking at C_{16} (cetane) is achieved.

In the Thermofuel process, carbon and coke deposits formed during the pyrolysis are continuously scraped from the pyrolysis chamber walls and reduced to a free-flowing black powder. Inorganic additives such as cadmium pigments from the plastics also end up in the char stream. The carbon matrix has a metal ‘fixing’ effect and binds up the metal ions so that no leaching occurs after disposal.

The noncondensable gas from the pyrolysis reactor is scrubbed of acidic gases in a water scrubber and then burnt in a noncondensable gas burner. The typical emissions from this burner are as follows:

Emission type	*Value*
SO_x	<5 ppm
NO_x	198 ppm
Dust density	0.06 g/cm^3
Temperature	438°C
Water vapour	13%

The above emissions data is for the Totai plant in Japan running a mix of PE (43%), PP (40%) and nylon (17%).

7.2 SMUDA PROCESS

The Smuda pyrolysis process developed by Dr Heinrich W. Smuda (Figure 15.10a) is a continuous process where the mixed plastic feedstock is fed from an extruder into a stirred and heated pyrolysis chamber [22, 23]. The extruder acts as an airlock to exclude oxygen and also to preheat and melt the polymer, so less energy input is required in the main chamber. The pyrolysis vessel operates at a constant level of 60% and the headspace is purged with nitrogen gas. A layered silicate catalyst (5–10% by vol) is added to the plastic melt to give a catalytic cracking reaction [24]. The fuel from the Smuda process is both transportation-grade diesel (85%) and gasoline (15%). The gasoline produced by the process is used in a cogenerator to produce electricity for the process. The diesel has an average olefin content of 10%, a flash point of 70°C and a pour point of −40°C. Since the diesel produced catalytic cracking contains approximately 10% olefin and inhibitor such as 0.01% BHT is required to suppress polymerization and gum formation [24].

The original Smuda Process is covered by a United States Patent entitled ‘Method of obtaining liquid fuels from polyolefine wastes’ [22]. The process charges a non-zeolite metal silicate catalyst directly into the main reactor which reduces the energy level required to scission the carbon chains of plastics and produces superior and stable-quality hydrocarbon products. In contrast to fluidized-bed pyrolysis processes, the Smuda process requires less capital investment and less operating cost. Pyrolytic vapours of the molten plastic are condensed in a cooler and then separated on a distillation column to give transportation-grade diesel. The diesel product (the fraction with boiling point in the range 170–300°C) shows very good low-temperature properties such as a cloud point and cold filter blocking temperature (CFPP) of −45°C and also very high cetane number of 65 [22].

Figure 15.10 (a) Photograph of the inventor of the Smuda Process, Professor Heinrich Smuda (right) and the editor Dr John Scheirs (left). (Copyright © J. Scheirs). (b) Photograph of Smuda stirred-tank reactor (left) and bottom of distillation column (right). (Copyright © J. Scheirs)

Nickel silicate and ferrous silicate are the preferred catalysts in the Smuda process. The Smuda catalyst is a layered silicate clay framework with ordered nickel (or iron) atoms inside. The catalyst is charged at 10 wt% ratio of the plastic feedstock. The catalysts are based on layered silicates with Lewis acid activity [24]. Catalytic cracking results in very little noncondensable gas ($<1\%$) and minimal carbonaceous char. The life of the Smuda catalyst is approximately 1 month [24].

Natural minerals and ores containing transition metal ions, steelmaking slags or metal plant wastes can be used as catalysts or sensitizers in the plastic material cracking. These materials include Ni_2O_3, NiO, Fe_2O_4 and Co_2O_3.

A number of low-grade transition metal ores (for example, minerals containing nickel oxides) can be used as catalysts. Smuda has demonstrated that microwave or radiofrequency irradiation of a mixture of such ores with a carbon source initiates reduction of the oxide to metal. With this approach, poisoning the active sites of the catalyst will not be critical for the process since there will be a constant supply and generation of active catalyst with the feed material. In addition to well-known catalytic properties of nickel in organic reactions, it was also shown that Ni on carbon and other supports, catalyzes hydrodechlorination and dehydrochlorination of chlorinated organic waste streams [22–24].

The Smuda process also uses new cracking catalysts based on cobalt resinates which are cobalt salts of resin acids (mainly abietic acid) such as cobalt abietate and cobalt linoleate (these are commonly referred to as driers in the coatings industry) and preferably with admixtures of heavy metal silicates. Smuda has also explored the use of manganese resinate deposited on an aluminium oxide support to maximize active surface area [23].

In the Smuda process the pyrolysis reactor temperature is 350°C and the operating pressure is 4–5 psi. The pyrolysis gases from the pyrolysis vessel are sent directly to a distillation column. The distillation column has a typical temperature profile as follows: top 140°C, Sulzer 250Y; middle 322°C, Sulzer 350Y and bottom 331°C.

The melt is stirred with an agitator running at 30 rpm to keep the catalyst in suspension. The torque on the agitator is monitored to determine the level of inorganic impurities and carbon residues that have accumulated. At a preset torque level the polymer melt is completely pyrolyzed and the carbon residues and impurities are then evacuated from the chamber using an auger positioned in the base of the vessel. Char removal is only activated when the vessel is cooled.

The Smuda catalysts, due to their acidic nature, have a low tolerance to alkaline compounds. Accordingly Nylons (which form ammonia) and ABS (which form amines) are not suitable since these polymers form by-products which are alkaline in nature. PVC does not pose a problem since the acidic by-products do not deactivate the catalyst [24].

Due to the sensitivity of the catalyst, the Smuda process requires that the plastic feedstock be pre-processed and cleaned by mechanical processing (i.e. other than washing). In this way dirt, food impurities, etc. can be removed before they deactivate the catalyst [24].

An additional problem with the powdered silicate catalyst in the polymer melt is that carryover (i.e. entrainment) of fine catalyst particles into the diesel stream can occur.

Advantageously, the Smuda Process can tolerate high levels of PET. In catalytic pyrolysis the terephthalic acid is decarboxylated to give benzoic acid and benzoates [24] (see also Figure 15.3). PET gives fuel with appreciable aromatic content (e.g. level of 10% or higher). In other competitive processes PET proves problematic due to the formation of troublesome terephthalic acid (TPA) deposits in the downstream pipework and condensors.

The Smuda process uses a reflux return where longer paraffin chains that condense shortly after exiting the main chamber are allowed to flow back to the main chamber (the 'reflux effect'). Also the heavies from the bottom of the distillation column flow back to the pyrolysis chamber for re-cracking (Figure 15.10b).

In 1997, the world's largest catalytic cracking plastics recycling plant began operation by AgRob EKO, S.A. in Zabrze, Poland. The plant has six cracking reactors each with a volume of 20 m^3 and equipped with agitators and internal heat exchangers. The reactors are run in a semi-continuous mode and after cracking approximately 60 tonnes of waste plastic and spent lubrication oil, they are stopped for cleaning and coke removal by scraping the internal heat-exchanging surfaces of the reactor. Since the plant runs a catalytic cracking process with silica alumina catalysts, coke formation is minimized (as compared with thermal cracking). In 2000, Dr Smuda began an association with a South Korean company to develop the Smuda Process, - an integrated process for catalytically converting post-consumer plastics into gasoline and low-sulphur diesel fuel.

7.2.1 Specific Advantages of the Smuda Process

- The process is continuous.
- Vessel is filled with 60% plastic melt and the level is maintained there using a level sensor.
- Excellent temperature uniformity and control of pyrolysis vessel (chamber is heavily insulated).
- Solid residue (coke) removal is automatic (by auger).
- Fractionation column ensures the boiling point range of liquid outputs.
- Liquid yield is high (95%) due to low temperatures used (350–370°C).
- Heavies from fractionation column are re-fed to reactor.
- Process also incorporates a diesel side-stripper, gasoline stabilizer and fuel dechlorinator.
- The process uses a 'catalytic isomerization dewaxing' step to preferentially isomerizes the paraffins, thus reducing the diesel pour point and cloud point while keeping the high-cetane components in the diesel product.
- Rapid stirring of the melt (30 rpm) ensures proper catalyst distribution and dispersion as well as satisfactory heat distribution

7.2.2 Specific Shortcomings of the Smuda Process

- Catalyst is consumable and hence has an associated operating cost (~ US$20/kg).
- Impurities and dirt in feedstock dramatically shorten catalyst life.
- Process requires feedstock pre-processing in order to remove impurities.
- Catalyst is charged into reactor monthly with catalyst activity decreasing over time.
- Catalyst is acidic and is especially deactivated by Nylons and other polymers that produce alkaline (i.e. basic) by-products.
- Catalyst type (there are some 20 to choose from) is determined by the composition of the feedstock.
- The only indication of catalyst deactivation is a gradual deterioration in diesel quality.

- The above situation necessitates frequent quality control checks on the diesel.
- There is no centrifuge in the process to remove water and carbon residues from the diesel.
- Close proximity of multiple heating pipes in larger reactors renders them prone to coking and fouling.
- The diesel fuel has 10% α-olefin content (i.e. terminal unsaturation or double bonds) which make the fuel unstable and prone to polymerization (i.e. sludge formation).
- There is no proven track record for producing transportation-grade diesel from the Smuda Process (Poland plant produces crude oil from plastics which is subsequently sent to a refinery).

7.2.3 Similarities of the Smuda Process and the Thermofuel Process

- Both use a stirred tank reactor.
- Both use a paddle agitator that also serves to prevent coking.
- Both are fed with molten plastic from an extruder.
- Both use nitrogen purging before the pyrolysis begins.
- Both use low temperature pyrolysis (350–425°C).
- Both employ a reflux philosophy where 'heavies' are sent back to the reactor for further cracking.
- Both produce predominantly diesel, along with gasoline, some LPG and a coke residue.

7.3 POLYMER-ENGINEERING PROCESS (CATALYTIC DEPOLYMERIZATION)

A catalytic diesel process (Figure 15.11) is being offered by a German company called Polymer-Engineering (Bielefeld, Germany). The process was developed by Alphakat GmbH (Buttenheim, Germany) and Siemens and is described in German Patent DE 100 49 377 C2 by the inventor Dr Christian Koch. The process which has been trademarked as NanoFuel® Diesel produces high-grade stabilized diesel fuel from waste plastics. Further information can be found at <http://www.globalfinest.com/tech/>. The process converts waste plastics by catalytic depolymerization at 270–370°C in the presence of an ion-exchanging catalyst (disclosed as a crystalline, highly active Y sodium aluminosilicate zeolite catalyst). The composition of the end products of the catalytic depolymerization is:

• liquid fuel (diesel)	93–95%
• noncondensable gas	4–5%
• residue	<1%

The process uses hot oil (high boiling bunker oil) as the pyrolysis medium to ensure good thermal conductivity and eliminates the need for an expensive hot melt extruder, as the plastic flakes melt instantly on contact with the hot oil. The heat required for melting the mixed thermoplastics is quoted at 0.28 kW h/kg [25].

The catalytic pyrolysis process is characterized by the very high liquid fuel yield and the low noncondensable gas and solid residue yields in contrast to thermal pyrolysis. The diesel product from the NanoFuel® Diesel process has a cetane number of >56, is completely desulphurized and the chain-end double bonds are saturated in the process,

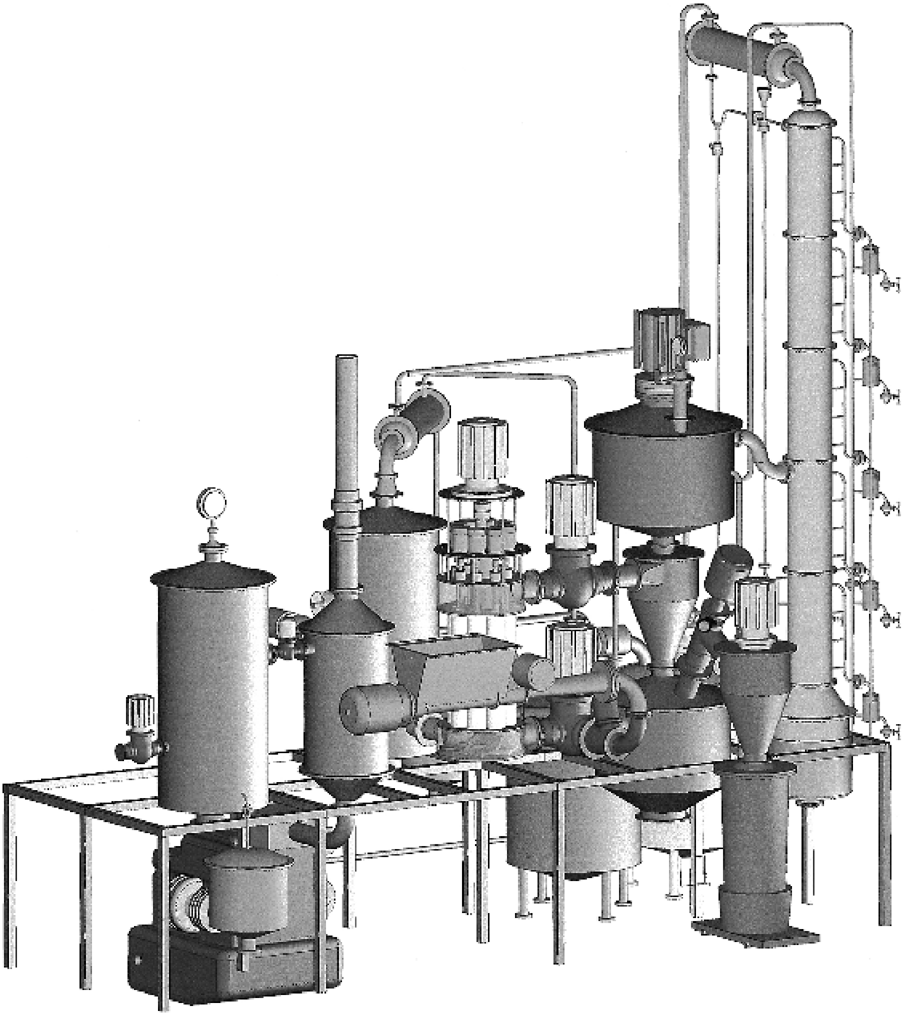


Figure 15.11 Overview of the NanoFuel® catalytic diesel process process developed process developed by Dr Christian Koch. The process converts waste plastics by catalytic depolymerization at 270–370°C in the presence of an ion-exchanging catalyst based on a highly active Y sodium aluminosilicate zeolite catalyst. (Courtesy of Polymer-Engineering, Bielefeld, Germany)

thus stabilizing the diesel fuel. The diesel fuel is intended for use as substitute diesel for transportation. The desired boiling range for the diesel fuel is achieved by the use of a distillation column above the pyrolysis reactor. The process can convert an input stream of 1000 kg of mixed polyolefins (LDPE/PP/HDPE) into >900 L of low-sulphur diesel fuel [25].

The plastic flake and catalyst are fed into the stirred reactor *via* a feeding chute. The diesel vapours are produced in the evaporator and sent to the distillation column for diesel fractionation (Figure 15.12). In the lower part of the reactor the chlorine-bound salts and

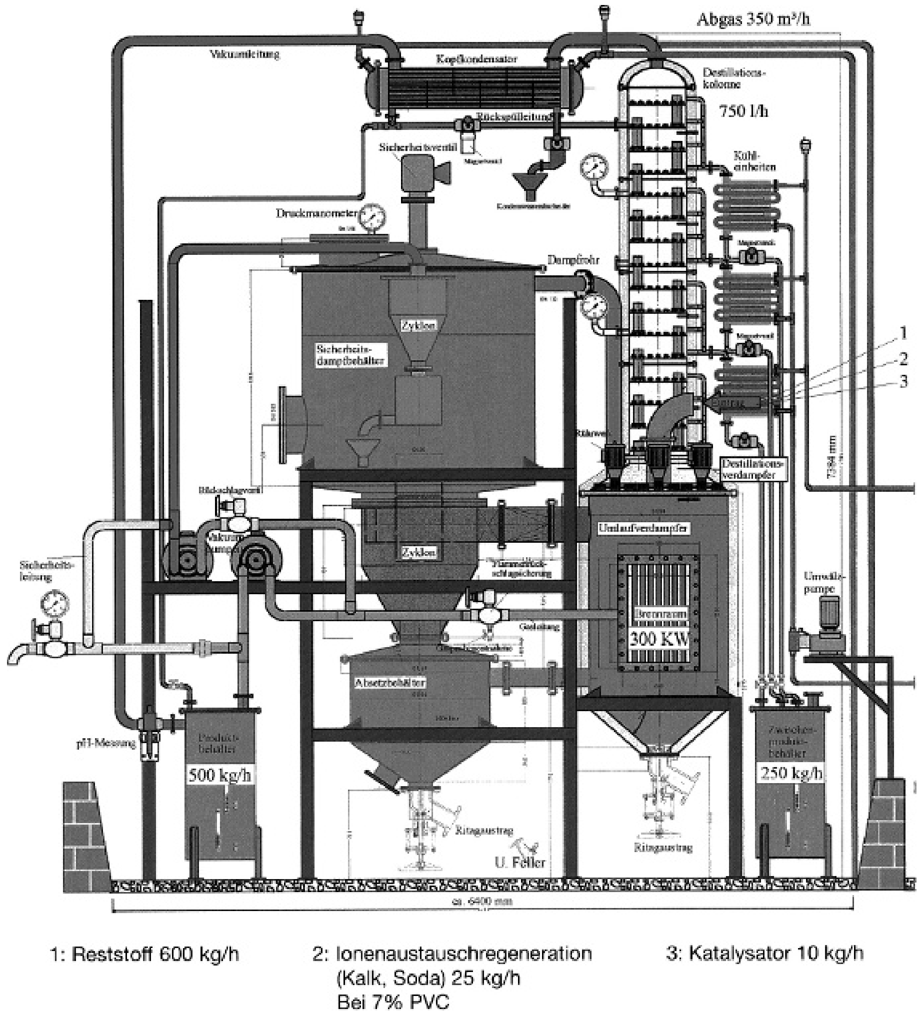


Figure 15.12 Schematic of the NanoFuel® catalytic diesel process process developed by Dr Christian Koch. (Courtesy of Polymer-Engineering, Bielefeld, Germany)

spent catalyst are removed from the reactor by an auger positioned at the outlet [25]. An annotated schematic of the NanoFuel® Diesel process is shown in Figure 15.13.

The depolymerization catalyst possesses cations that make it act as an ion exchanger. Before the hydrocarbon plastics begin to thermally crack, they are dechlorinated and dehalogenated by neutralization by the ion exchanger.

The ion-exchange catalyst dechlorinates the plastics (e.g. PVC) and therefore avoids issues with HCl generation and chlorine contamination of the diesel. The company claims to have processed cable waste consisting of almost 100% PVC and the catalytic depolymerization process produced diesel fuel with a chlorine content below the detection limit. The catalyst needs to be activated before use via ion exchange using soda (sodium carbonate) and lime (calcium hydroxide) in order to insert the sodium and calcium ions

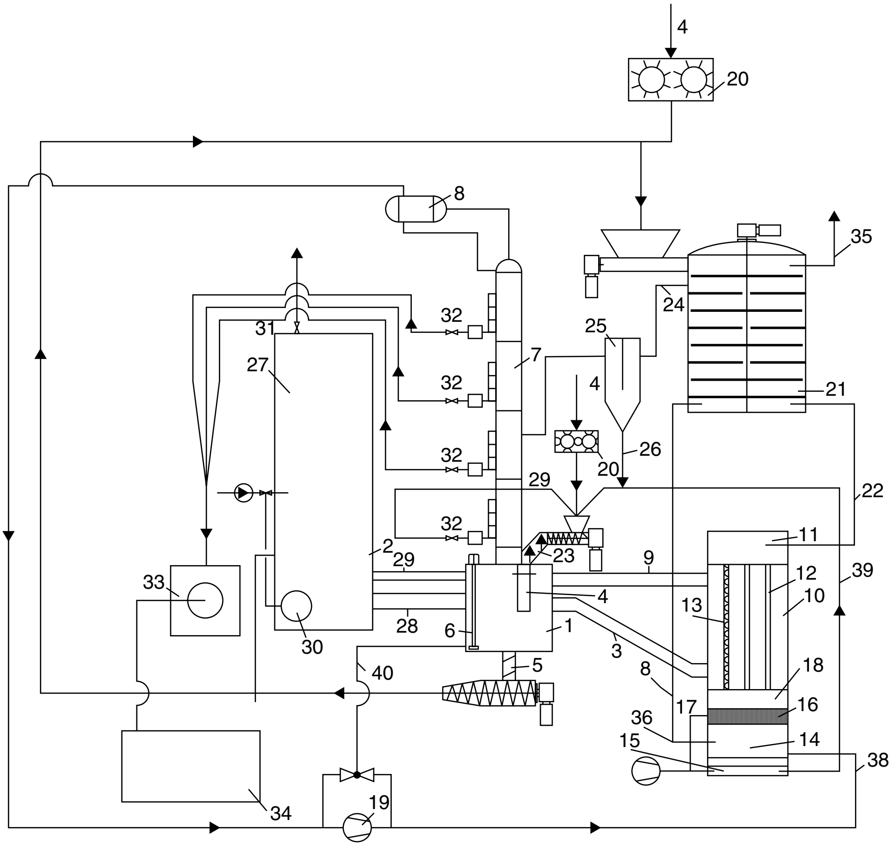


Figure 15.13 Schematic of the NanoFuel® catalytic diesel process plastic-to-diesel plant from German Patent DE 100-49-377-C2

Legend:
1 reactor; 2 pressure-free tank; 3 oil; 4 inlet; 5 waste catalyst gate; 6 mixer; 7 distillation line; 8 condensor; 9 connecting pipes; 10 cycle vaporizer; 11 tank; 12 exhaust pipes; 13 swirl spiral; 14 combustion; 15 burner; 16 honeycomb catalyst layer; 17 temperature control; 18 honeycomb layer; 19 vacuum pump; 20 shredder; 21 regenerator; 22 connecting pipe; 23 inlet gate; 24 smoulder exhaust; 25 seperator; 26 water treatment; 27 release tank; 28 pipes to release tank; 29 pipes from release tank; 30 fluid level indicator; 31 pressure release valve; 32 cooler with outlet (withdrawal); 33 liquid separator; 34 tanks; 35 smoke gas exhaust; 36 connecting pipe between catalyst dryer and combustion chamber; 37 ash exhaust pipe; 38 gas pipe from vacuum pump to combustion chamber; 39 oil pipe from lowest level to entry; 40 return pipe from lower line to reactor. (Courtesy of Polymer-Engineering, Bielefeld, Germany).

into the zeolite catalyst. The usage rate of catalyst is stated to be 1.5% of the output of diesel (which is 12 000 L/day) and this equates to 180 kg of catalyst usage per day. It is the ion exchange capability of the catalyst that enables the considerably lower cracking temperatures compared with conventional catalysts [25].

The acid cracking catalysts produce carbonium ions by the addition of protons to polyolefin chains or by abstraction of hydride ions from hydrocarbon molecules. This is followed by chain scission, which yields $C_{30}-C_{50}$ oligomeric hydrocarbons. Secondary cracking by β-scission of the $C_{30}-C_{50}$ hydrocarbons yields liquid ($C_{10}-C_{25}$) hydrocarbon fuel.

Specific advantages of the Polymer-Engineering Process include:

- Molecular depolymerization at low temperatures (270–370°C) and under virtually pressure-free (<0.1bar) conditions.
- The ion exchanger catalyst binds the chlorine in the waste plastic to form neutral salts. The catalyst splits the long-chain hydrocarbons into shorter chains at a maximum temperature of 390°C.
- Virtually no carbon is formed during catalytic depolymerization and therefore no carbon residue accumulates on heat exchanging surfaces.

Catalytic depolymerization plants (KDV 500) with a capacity of 500 L/h have been constructed for Germany, Mexico, Japan and Korea while a KDV 150 B plant with a capacity of 1 500 000 tonne/yr is under construction for Bayern Oil in Germany to treat vacuum residue [25].

The Polymer-Engineering process is very similar to the Thermofuel system design, except that the main chamber contains a heavy thermal oil with a high boiling point. The waste plastic is continuously added as flake and it quickly melts in the thermal oil and pyrolyzes. The heavy oil is held at 390°C and the plastics quickly pyrolyze since it is an excellent heat transfer medium.

In a related process Arandes *et al.* [26] dissolved polyethylene and polypropylene in light cycle oil (LCO) and then catalytically cracked the polymers using a mesoporous silica (pore size between 3 and 30 nm) in a commercial fluid catalytic cracking (FCC) unit at 450°C. This strategy for upgrading plastics and oils together avoids heat transfer limitations and other problems inherent to the cracking of molten plastics. The polyolefins gave fuel with increased content of paraffins and iso-paraffins.

7.4 ROYCO PROCESS

The Beijing Roy Environment Technology Co., Ltd (also known as Royco) has developed a commercial pyrolysis process for turning waste plastics into oil known as the EZ-Oil Generator™ process.

The EZ-Oil waste plastics cracking unit converts waste plastics (e.g. waste plastics including PP, PE, PS mixed plastics) into oil by low-temperature thermal cracking in the absence of air and utilizes the output to produce electricity. The system includes a feeding unit, reaction vessel, distillation tower, solid residue extractor/drying unit, circulation water unit, oil storage unit, wastewater treatment unit, a scrubbing unit, and power-generating unit. The company's Web site is at www.roycobeijing.com.

A 20 t/day plant (6000 t/yr) is equipped with two pyrolysis vessels (with dimensions of 2800 mm ID and 2000 m height). The vessels are fed with molten plastics by four extruders each with a capacity of 250 kg/h. The plant runs continuously and can feed waste plastics and discharge the solid residue while the plant is running. The liquid fuels are fractionated in a fractionation tower. The plant produces a liquid fuel yield of up to 80% (by weight), depending on the nature of the feedstock.

The majority of waste plastic to oil processors utilize flue gases and other means to heat their systems indirectly thereby having loss of heat energy. By so doing, these other systems face problems with costs of operation, coking and inefficient processing of the waste plastics. The Royco system utilizes a novel heating system based on far infrared inner heating which dramatically reduces costs, virtually eliminates coking and is most efficient compared with traditional heating methods. The major advantage of the far infrared system is that it heats the waste plastics much more quickly and more thoroughly, thereby shortening the time needed to melt the plastics to the stage where the hydrocarbon vapours are released. Another significant advantage is that with the inner heating system, the amount of heat loss is greatly reduced so that the unit runs more economically and efficiently than other units who use indirect heating sources.

Notable features of the process are:

- The sediments like sand, mud, sludge, etc. are discharged out of the bottom of the reactor while the plant is running.
- The molten plastic flows into the noncatalytic cracking unit where the liquid is cracked into gas and fuel oil vapour and then leaves out of the top of the unit to go to the condenser and fractionating tower.
- A ‘reflux’ is used where ‘lighter’ liquid is injected at the top of the distillation column and this “strips” by counter-current absorption the heavy components from the rich vapour rising up the packing inside the column.
- The noncondensable gas from the top of the tower is compressed into liquid gas (LPG) and dry gas. The liquid gas is high quality.
- The fuel oil mixture from the cracking process is sent through the extraction and fractionation process where high-grade fuel oils are obtained.

The technology is covered by the following patents:

- WIPO PCT/IB2004/000306 (Pending) ‘Enhanced Oil Recovery From Waste Plastics Reactor’ (February 2004)
- US 60481826 (Pending) ‘A Reactor and Process for Converting Waste Plastics into Oil with the FIR Heater’ (December 2003)
- Japan 2002-145569 (Pending) ‘Movable Apparatus and Method for Extracting Fuel from Waste Plastics and Waste Oil’ (May 2002)

7.5 REENTECH PROCESS

Reentech Limited (Korea) has developed a patented catalytic cracking process (Figure 15.14) which converts mixed plastics (e.g. PE, PP, PS) into gasoline, kerosene and diesel fuel [27–31].

The Reentech moving-bed catalytic cracking process enables the continuous preparation of gasoline, kerosene, and diesel oil from waste plastics. The method comprises the steps of subjecting a melt of the waste plastics to a first catalytic reaction in which the waste plastic melt is in contact with a nickel or nickel alloy catalyst to be dehydrogenated while being thermally decomposed, then subjecting the dehydrogenated and decomposed waste plastic melt to a fluid catalytic cracking (moving-bed catalytic cracking), fractionating the cracked material into a gasoline-based fraction, a kerosene fraction, and a diesel oil fraction; and reforming the gasoline-based fraction to produce a high octane number gasoline [27–31].

Figure 15.14 Photograph of the Reentech catalytic cracking process in Korea. The Reentech process converts mixed plastics (e.g. PE, PP, PS) into gasoline, kerosene and diesel fuel. (Courtesy of Reentech, Korea)

The incoming waste plastic melt is brought into contact with a catalyst impeller (preferably made of nickel or nickel alloy) at a temperature of 350°C. to 370°C., thereby being dehydrogenated and decomposed. The downstream process consists of a moving-bed catalytic cracker, in which a melt of the waste plastics and an alumina silicate solid acid catalyst particles are introduced downward from the upper portion thereof, and cracked and isomerized, and into which steam is injected through its lower portion to vaporize nonvaporized gaseous oil present on the catalyst surface. The cracked gases are sent to a fractionating column to give various hydrocarbon fractions. The fractionating column is an Aspen fractionating column having a bubble cap tray type [29].

A cyclone outside the moving-bed catalytic column serves to sort only catalyst particles of a desired size among the catalyst particles dropped to the lower portion. A nickel–molybdenum catalyst regenerator with an air injector serves to regenerate the catalyst transferred from the cyclone and the regenerated catalyst is then returned to the moving-bed catalytic cracker [29].

The process yields the following products:

- 75% fuel oil (comprising 55% gasoline, 25% kerosene and 20% diesel);
- 15% noncondensable gas (used as energy in the plant);
- 10% carbon (coke).

The annual capacity of the Reentech plants is 6000 tonne/yr of plastic input yielding some 4.2 million litres of fuel oil [27].

The gasoline fraction has the following property profile:

iso-C4, C5	25%
Aromatics	13%
olefins	8.6–10%
benzene	1.4%
octane number (RON)	91–94
Reid vapour pressure (RVP)	144 kPa

The Reentech process incorporates the following key process steps:

- melting;
- dehydration and polymer decomposition (first catalytic reaction);
- contact catalytic cracking (second catalytic reaction);
- fractional distillation;
- refining of gasoline fraction;
- addition of additives.

A process flowchart for the Reentech process is shown in Figure 15.15.

The Reentech process uses a moving-bed catalytic cracking step, which is fundamentally the same concept as a refinery fluid catalytic cracking unit (FCCU). The FCCC converts high-boiling hydrocarbon pyrolysis gases to high-value high octane gasoline and kerosene/diesel mixture. The FCC unit utilizes a microspherodial catalyst that fluidizes when properly aerated by vaporized feed in the reactor riser. The term 'fluid' catalytic cracking unit is derived from this characteristic property. The gas–oil feedstock is vaporized by hot catalyst and thermally and catalytically decomposes in the reactor riser to produce various products. These products undergo additional processing and separation in the FCCU main fractionator and other vessels downstream of the FCCU reactor. As a result of the cracking process, carbon (or coke) is deposited on the catalyst. The spent catalyst is sent to the regenerator, where it is regenerated by burning off the carbon, utilizing atmospheric air. The regenerated catalyst is then circulated back to the reactor, where the process is repeated [27–31].

Reentech has adapted fluid catalytic cracking (FCC) for the small-scale refining of PE, PP, and PS scrap. In FCC, a catalyst is used to accelerate the thermal cracking process. In this form of cracking, the fractions are heated and then passed over zeolites, certain types of clay, or other catalysts. FCC is more widely used than thermal cracking because it requires less pressure and produces higher-octane gasoline. Also FCC can convert the heavy fractions of the distillation process more efficiently than thermal cracking. In theory, FCC is particularly suited for the recovery of the fuel value contained in plastic scrap as gasoline, kerosene and diesel oil. The key to Reentech's technology is a *continuous* catalytic cracking process that Reentech calls *contact catalytic cracking* that continuously regenerates the catalyst stream and thus delivers freshly activated catalyst to the catalyst cracker (Figure 15.16). In contrast, the spent catalyst in a full-scale refinery must be removed and replaced when the catalyst degenerates. The continuous regeneration of the catalyst increases the efficiency of the processes, allowing the process to be run economically on a relatively small scale [27–31]. Figure 15.16 illustrates the principle of continuous regeneration combined with catalytic cracking.

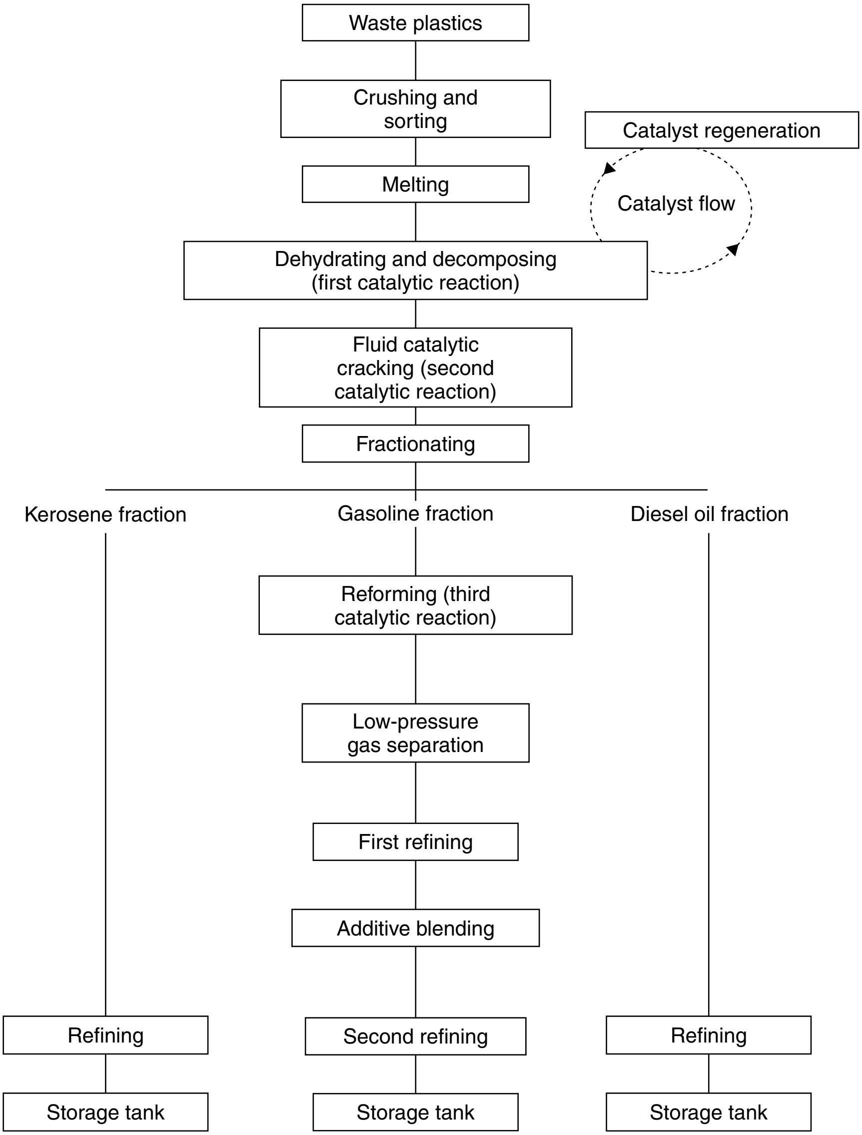


Figure 15.15 Flowchart of Reentech catalytic cracking process. (Courtesy of Reentech, Korea)

The catalyst flow process is as follows:

- regeneration at 700°C;
- transport to cracking reactor;
- vaporization of cracking gasoil;
- lifting up to regeneration tank.

The carbon residues of catalytic cracking are separated by a cyclone.

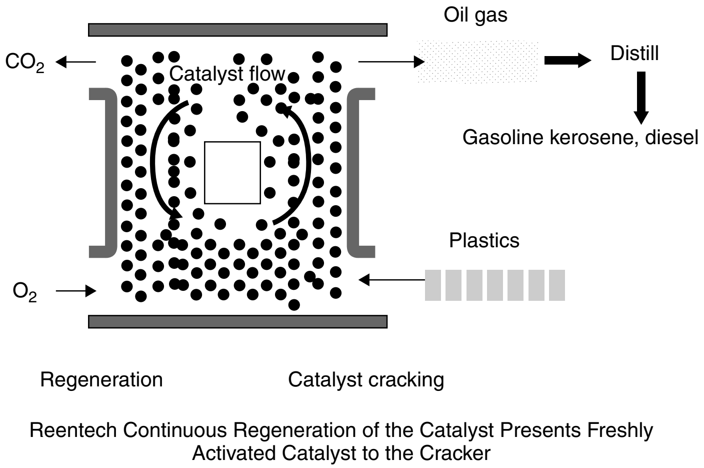


Figure 15.16 Schematic of Reentech continuous regeneration of the catalyst which supplies freshly activated catalyst to the cracker. (Courtesy of Reentech, Korea)

The noncondensable gas separated in the distillation tower is passed through a water scrubber to remove HCl if PVC is present. Then the NCG is contacted with refrigerated gasoline to condense some light fractions and finally the gas is passed through a flame arrestor to a burner in the flame stack.

7.6 HITACHI PROCESS

Hitachi Zosen have developed a stirred tank/kettle pyrolysis process for waste plastic (Figure 15.17) that is characterized by the following features [32, 33]:

- the ability to handle mixed plastic waste;
- a relatively low pyrolysis temperature;
- the automatic removal of char and extraneous matter;
- double (or triple) condensers;
- production of kerosene and gasoline fractions.

Hitachi Zosen have filed two US patents on their plastic-to-oil technology. The relevant US patent numbers are US 5,584,969 and US 5,597,451 [32, 33]. The first patent (5,584,969) ‘Apparatus for thermally decomposing plastics and process for converting plastics into oil by thermal decomposition’ embodies a two-condenser system with an option for a third.

In the Hitachi Process the low-boiling component of the gas flowing out from the top of the column of the pyrolysis chamber is cooled and condensed initially in the primary condenser, whereby kerosene is recovered. The low-boiling component of the gas passing through the first condenser without condensation is transferred to the second condenser where it is cooled for condensation, whereby gasoline is recovered. The decomposition gas portion remaining uncondensed from the second condenser is then sent to the gas combustion furnace by way of the water seal device and burned in the furnace [32, 33]. A mass

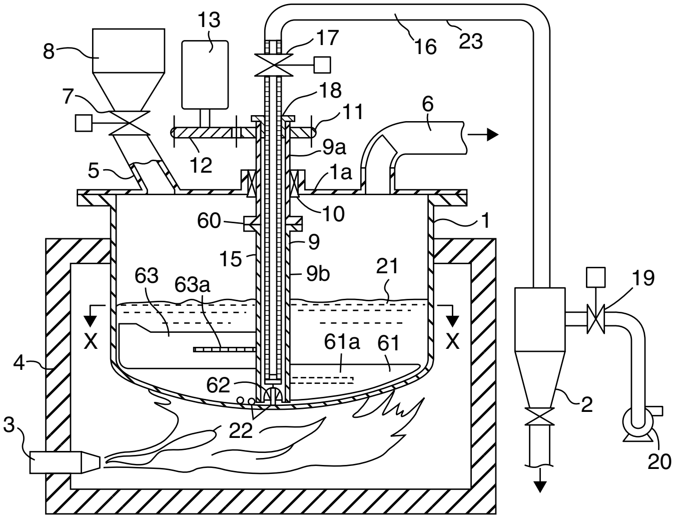


Figure 15.17 Schematic of the pyrolysis vessel of the Hitachi Process. A notable feature of the Hitachi Process is that the solid residue (char) is evacuated from the bottom of the pyrolysis vessel via a suction pipe running down the centre of the hollow agitator shaft. Legend: 1 pyrolysis vessel; 2 cyclone for solid residue; 3 burner; 4 furnace; 5 feed inlet to pyrolysis chamber; 6 outlet for pyrolysis gases; 7 slide gate valve; 8 hopper for plastic flake; 9 agitator shaft; 10 packed seal; 12 agitator drive chain; 13 drive motor for agitator; 15 suction pipe for solid residue; 16 vacuum pipe; 17 vacuum cut-off valve; 18 sealing flange; 19 valve; 20 suction fan; 21 molten plastic; 22 burner flame; 61 char scraper; 63 agitator paddle [32]. (Courtesy of Hitachi, Japan)

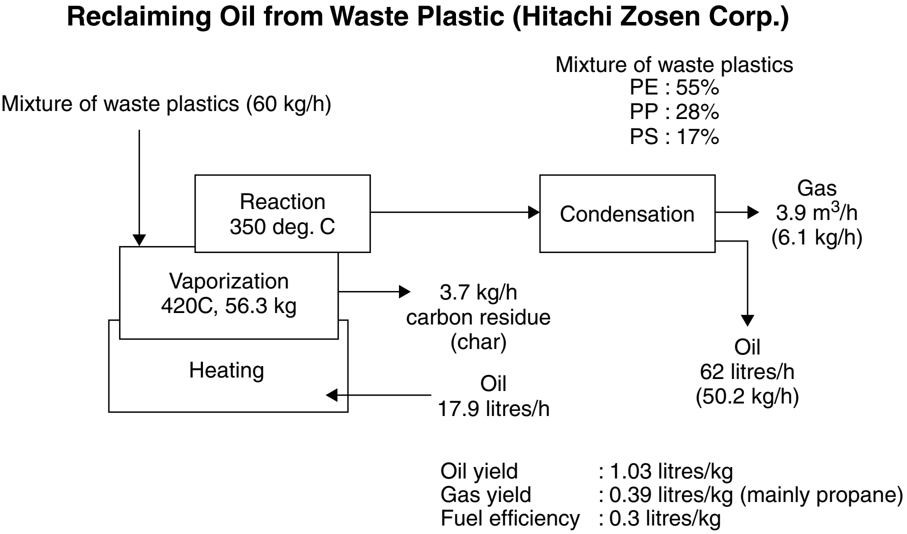


Figure 15.18 Mass balance for Hitachi plastic-to oil pyrolysis process. (Courtesy of Hitachi, Japan)

Table 15.7 Characteristics of the fuel produced by the Hitachi Zosen pyrolysis process

Property	Typical value
Specific gravity	0.8
Cetane number	48
Flash point	37°C
Aromatic content	23%
Sulphur content	110 ppm
Viscosity	1.50
Calorific value	10 800 kcal/kg

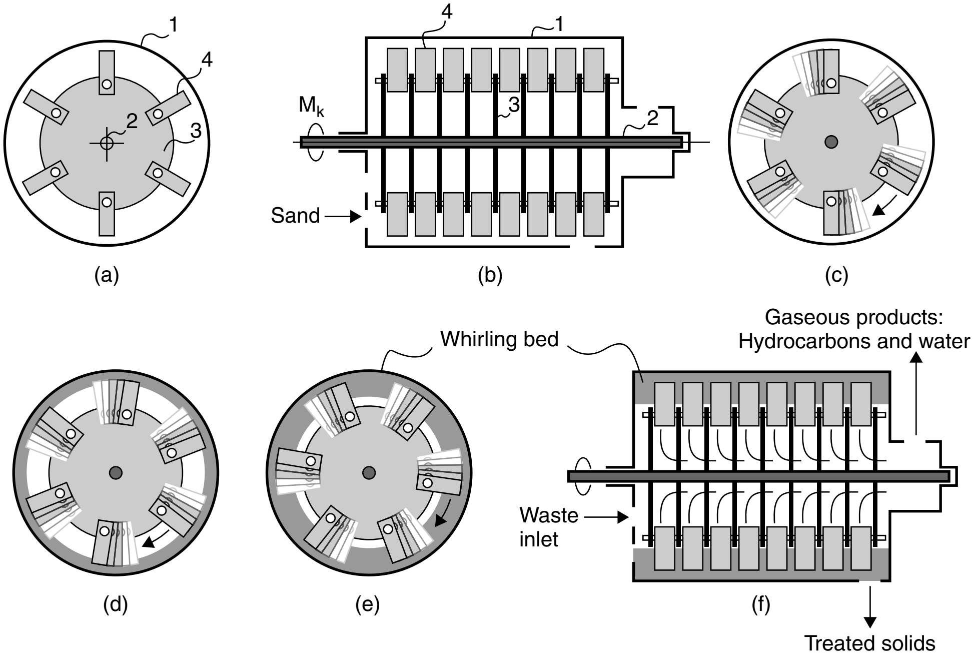
balance for the process is shown in Figure 15.18. The characteristics of the fuel produced by the Hitachi Zosen pyrolysis process from mixed waste plastics are shown in Table 15.7.

7.7 CHIYODA PROCESS

Chiyoda Corp., Japan, has developed a next-generation technology for liquefaction of plastic wastes. The new process facilitates reuse of plastic wastes from household refuse into liquid fuel. In the new method, crushed plastic waste is fed to a dechlorination unit where PVC and PET are thermally degraded into hydrogen chloride, terephthalic acid, etc. These gaseous components are separated from the melted liquid plastic and sent to an incinerator for safe disposal. The melted plastic waste is transferred to a thermal cracking reactor where it is further heated and converted to vapour-phase hydrocarbons and residue. The vapour-phase hydrocarbons are charged to a distillation column and separated as cracked gas, light oil, a middle distillate and heavy oil. A portion of the middle distillate is recycled to the thermal cracking reactor as vapour phase through the heating furnace. The heavy oil is mixed with residue from the bottom of the thermal cracking reactor and the mixture is used as a fuel. The separated light oil can be used as a feedstock for petrochemical plants or as fuel oil. Cracked gas obtained at the top of the distillation column is cooled and separated from the light oil and transferred to the incinerator [34].

7.8 BLOWDEC PROCESS

The Blowdec depolymerization process from Slovakia converts waste plastics into low-sulphur diesel fuel [35]. The main principle is the processing of waste plastics in a hot whirling bed of hot sand in the BLOWDEC reactor (Figure 15.19). The plastic is heated to 430°C. The process allows for simultaneous cracking of hydrocarbons and inhibition of coke formation. The fluidized sand bed products three types of cracking reactions: mechano-activation; thermal; and catalytic (SiO_2/aluminosilicates). The process is covered under the US Patent 6,165,349. The process enables the economical conversion of mixed waste plastics into liquid hydrocarbons, mainly low-sulphur (25 ppm) diesel



Principle of the process.

a, b – Basic scheme of the reactor's construction
c – Start up (movement of the reactor rotor)
d – Creation of the whiling bed (sand filling)
e – Heating of the reactor
f – Process run

Description: 1-process chamber, 2-shaft, 3-arm of the blade, 4-blade, M_k-torque

Figure 15.19 Schematic of the reactor of the Blowdec depolymerization process from Slovakia which converts waste plastics into low-sulphur diesel fuel in a hot whirling bed of hot sand. The plastic is heated to 430°C by the hot sand which also exerts a catalytic effect that enables simultaneous cracking of hydrocarbons and inhibition of coke formation [35] (Reproduced by permission of Slovnaft Virup)

with Pensky–Martens flash point of 62°C and pour point of −15°C, and has the added advantage of the lack of formation of coke residues on heat transferring surfaces [35].

7.9 CONRAD PROCESS

Conrad Industries (Chehalis, Washington) have demonstrated the pyrolysis of post-use plastics into petrochemical feedstocks. The plastic most studied was a mixture of 60% high-density polyethylene, 20% polypropylene, and 20% polystyrene. Yields of liquid products were in the range 65–75% at 482–510°C. Other studies examined the effects of PET and PVC on the liquid yields. The liquid products were determined to be suitable feedstocks for further refining, but the economics were not competitive with conventional petroleum refining in 1994 [36].

7.10 OTHER PROCESSES WITH SEPARATE CATALYST BEDS

The Likun Process (China) uses a two-stage cracking process under normal pressures where the waste plastics are first pyrolyzed at 350–400°C in the pyrolysis reactor and then the hot pyrolytic gases flow to a catalyst tower where they undergo catalytic reforming over zeolite at 300–380°C. By having the catalyst in the second stage this overcomes the problems of rapid catalyst deactivation from coke deposits on the surface of the catalyst.

The Fuji Process also uses a two-stage cracking process comprising a main cracking reactor and a reforming reactor. In the reforming reactor the pyrolysis oil is upgraded to gasoline, kerosene and diesel.

Such two-step processes are also referred to as cracking–catalytic reforming (CCR) processes. The catalytic reforming stage of the primary oil product ensures high-quality diesel or gasoline products are obtained. The catalytic reforming step improves the RON and the contents of isomer, cycloparaffins and aromatics.

8 CONCLUSIONS

A major advantage of plastics pyrolysis is its ability to handle unsorted, unwashed used plastic. This means that heavily contaminated plastics such as mulch film (which sometimes contains as much as 20% adherent dirt/ soil) can be processed without difficulty. Other normally hard to recycle plastics such as laminates of incompatible polymers, multilayer films or polymer mixtures can also be processed with ease, unlike conventional plastic recycling techniques. In fact, most plastics can be processed directly, even if contaminated with dirt, aluminium laminates, printing inks, oil residues, etc. The viability of pyrolysis is assured by the lack of other recovery options for such waste plastics besides landfilling and incineration. The increasing pressure on companies to adopt sustainable outlets for their end-of-life plastics, the introduction of extended producer responsibility and product stewardship directives, together with the implementation of legislative measures to deal with waste plastics are significant drivers which will further increase the interest and adoption of the pyrolysis route for waste plastics.

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16

Fluidized Bed Pyrolysis of Plastic Wastes

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1 INTRODUCTION

1.1 FLUIDIZED-BED TECHNOLOGY FOR WASTE THERMAL TREATMENTS: THE KEY ROLE OF HYDRODYNAMICS

Gas–solid fluidization is the operation by which a bed of solid particles is led into a fluid-like state through suspension in a gas. Compared with other methods of gas–solid contacting (such as fixed beds, rotary cylinders, flat hearths, etc.), fluidized beds have some rather unusual and useful properties that can lead to desirable characteristics for waste thermal treatments in general, and for plastic waste pyrolysis in particular. The reader can refer to some fundamental and exhaustive books for a deepen account of fluidized-bed reactor engineering [1–4]. Here, it is important to highlight the crucial role that hydrodynamics plays in the design and operations of a fluidized-bed reactor. All the physical and chemical processes carried out in fluidized beds are strongly affected by the quality of fluidization: the heat and mass transfer, the gas and solids mixing, the radial and axial temperature profiles, the effective gas and solids residence times as well as the quality of the contact of reactants, all are related to the peculiar features of the fluid bed hydrodynamics. This implies that some variables, such as the size and density of the bed particles, the gas fluidization velocity, the height-to-diameter ratio of the bed, the gas inlet arrangement, the vessel geometry, acquire a key role in determining the overall performance of the reactor [1, 5]; as a consequence, their values must be accurately fixed by fluidization engineering, on the basis of reliable relationships and of results from specific pilot-scale investigations.

Different types of fluidized-bed reactors are commercially available for plastic waste pyrolysis. The term fluidization has been used in literature to refer to dense-phase and

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lean-phase systems, as well as circulation systems involving pneumatic transport. The fluidization engineering deals with all these methods of contacting, but the main focus is on dense-phase systems. *Bubbling fluidized beds* (BFB) belong to the dense-phase fluidized beds as long as there is a fairly clearly defined upper surface of the bed: gas bubbles coalesce and grow as they rise up to the top of the bed and there is a limited entrainment of fine particles from the unit (*captive regime*). When gas fluidization velocity increases, significantly more than the terminal velocity of the solids, there is no more distinct upper bed surface while large amounts of particles are carried out of the bed with the gas (*transport regime*), precluding steady state operations. This state belongs to the lean-phase fluidized beds: steady state operation is possible only if entrained particles are collected by a cyclone and then returned to the bed by means of a downcomer and a non-mechanical valve. These reactors are called *circulating fluidized beds* (CFB), where the term ‘circulating’ signifies that the particle separation and return systems are integral and essential components of the reactor configuration. The convincing advantage of overall economy of fluidized-bed contacting is the explanation of its successful use in industrial operations, even though such success strongly depends on understanding and overcoming its disadvantages. The following main advantages can be listed for fluidized-bed reactors utilized for thermal treatments of waste [1]:

- The rapid and good mixing of solids, which leads to almost uniform isothermal conditions throughout the fluidized bed. This allows an easy and reliable process control.
- The whole reactor of well-mixed solids represents a large thermal flywheel that resists to rapid temperature changes and avoids formation of cold or hot spots.
- The range of operating temperatures is generally lower than that of other gas–solid reactors.
- Heat and mass transfer between gas and particles are high when comparing with those of other gas–solid reactors and there is a very good quality of contact between reactants of a gas–solid reaction.
- The liquid-like flow of particles allows continuous controlled operations with easy handling. In particular, the circulation of solids between two fluidized beds makes it possible to remove or add the high quantities of heat produced or needed in large reactors as well as to substitute part of the (sticky or agglomerated) bed material with fresh solids.
- The high process flexibility makes possible to utilize different fluidizing agents, operating temperatures and gas residence times and to operate with or without a specific catalyst.
- The lower maintenance times and costs, as immediate consequence of the absence of moving parts in the hot regions and of the lower operating temperatures. This allows a wider range of investment alternatives, making fluidized beds suitable for large as well as for small-scale operations.

Several of these advantages are increased in a CFB reactor: improved gas–solid contact given the lack of bubbles; reduced cross-sectional area given the higher superficial velocities; more control over suspension-to-wall heat transfer because of the ability to use the solids circulation flux as an additional variable; less tendency to show particle segregation and agglomeration; superior radial mixing that allows fewer solids feed-points; higher solids flux trough the reactor [3].

The main disadvantages that must be taken into account are [1]:

- Friable solids (bed materials, solid reactants as well as catalysts) are pulverized and entrained by the gas.
- For noncatalytic thermal treatments of waste, the agglomeration and sintering of fine or sticky particles can require a lowering/rise in operating temperature (that implies a variation in process performance) or a continuous withdrawal of bed material that must be substituted with a make-up of fresh material.
- The intensive rapid solid mixing in the reactor leads to a wide range of residence times of individual particles in the reactor: for continuous operations this gives poorer performance since the removal of fully reacted particles will inevitably be associated with removal of unreacted carbon; for catalytic reactions, the movement of porous catalyst contributes to the backmixing of gaseous reactant.
- Erosion of pipes and vessels by abrasion of bed particles can be serious.
- Scale-up is not always easy to realize: pilot plant is often necessary to verify the validity of laboratory-scale tests.

For CFB reactors further aspects have to be taken into account: restricted range of admittable particle properties; increased particle attrition; decreased suspension-to-wall heat transfer coefficients; more complexity in designing and operating the circulating loop; higher capital costs.

1.2 FROM PLASTIC WASTE TO FEEDSTOCKS AND ENERGY BY MEANS OF FLUIDIZED-BED PYROLYSIS

Menzel, Perkow and Sinn presented the first fluidized bed process for pyrolysis of plastics in 1973 [6]. A series of tests on a laboratory-scale bubbling fluidized bed was performed in order to evaluate the reliability of fluidization as a more flexible and controllable technology for plastic pyrolysis. The first batchwise experiments with polyethylene and other wastes demonstrated that ‘plastic scrap or waste, even when contaminated with paper or wood, can be processed in a cracking plant in the same ways as crude oil’ [6]. Since 1980, other authors have presented a considerable amount of experimental data on pyrolysis of plastics in different fluidized beds. In particular, there is the well-known research carried out by Kaminsky and his colleagues at the University of Hamburg, Germany [7–14]. Their pyrolysis plant, expanded and upgraded many times from 1980 until now, has been used in several series of experiments with plastics, rubber, tires and other wastes with the aim of defining the mechanisms of the process and determining the best operating conditions (in particular, the reactor temperature and the type of fluidizing gas) allowing the production of yields with high-heating-value gas and BTX-rich oil or aliphatic oil. Other studies have been published [15–19], referring to experiments carried out under different operating conditions (batch or continuous feeding, different fluidizing gas, different plastic waste, bed material with catalytic properties, etc.) and by means of different reactor apparatus.

Table 16.1 reports a summary of pyrolysis processes for plastic wastes, auto shredder residues, tires and other wastes carried out with different gas–solid reactors. It can be deduced that now fluidized-bed technology appears mature and particularly attractive for

Table 16.1 Pyrolysis processes for plastic wastes, auto shredded residues and tires along with other wastes

Process	Actors involved	Technology	Process description	Input/output	Technical status
Akzo	*Akzo Nobel (NL)*	*Two circulating fluidized beds*	***Fast pyrolysis** in a CFB reactor (700–900°C), where waste is converted with steam into fuel gas, HCl and residual tar, and **combustion** in the second CFB. The process is based on the Battelle process for biomass gasification*	*I: shredded MPW with high percentage of PVC, PVC cable, pipe scrap* *O: HCl, CO, H_2, CH_4, other hydrocarbons, fly ash*	*Pilot (30 kg/h) since 1994. Some tests on a large scale (200–400 kg/h)*
Amoco	Amoco Chem. Corp.		**Catalytic cracking** at 490–580°C	I: PE, PP, PS, plastic wastes mixed with vacuum gas oil O: naphtha, light mineral oil gases	Pilot since 1991
AMRA	*Center of Competence on Env. Risks (I), Univ. of Naples II (I)*	*Bubbling fluidized bed*	***Gasification** in a BFB of sand, fluidized by air, steam and nitrogen at a temperature between 750 and 900°C*	*I: polyolefins and RDF shredded at a size <2.5 cm* *O: syngas, energy*	*Pilot (20–50 kg/h) in Caserta (I)*
Battelle	*Battelle Memorial Inst. (USA)*	*Two circulating fluidized beds*	***Gasification** in a CFB of sand, fluidized by steam and nitrogen at a temperature between 800 and 1000°C*	*I: PE, PS, PVC and MPW shredded at a size <2.5 cm* *O: ethylene, H_2, CH_4*	*Pilot (9 kg/h) in Vermont (USA) since 1992*
BP polymer cracking	*BP Chemicals, Elf Atochem, DSM, Enichem, Fina*	*Bubbling fluidized bed*	***Low-temperature pyrolysis**(500°C) in a BFB of sand. The product is cleaned from HCl and fine particles and then fractionated*	*I: clean plastic wastes (<2% PVC)* *O: mainly waxy hydrocarbon products to be used in existing petrochemical plants and refineries*	*Pilot (50 kg/h) in Grangemouth (UK)*

BASF cracking	BASF AG	Melting vessel, indirectly heated	**Liquid phase pyrolysis** in a 3-stage process: liquefaction at 300°C in a stirred kettle; cracking in a gas fired tubular furnace at 350–480°C; separation of products, oils (60–70%) and gases (20–30%), in a distillation column	I: plastic wastes (max. 8% PVC) O: petrochemical gaseous and liquid feedstocks (naphta, aromatic compounds, high-boiling oils)	Demonstration (15,000 t/y) in Ludwigshafen (D) started in 1994 and shut-down in 1996
Compact Power	Compact Power Ltd (UK)	Tubular reactor + fixed bed	**High-temperature pyrolysis** (800°C) of the shredded waste conveyed by a screw feeder. Fixed-bed **gasification** of the char residue. **Combustion** of gas from pyrolysis and gasification units at 1250°C in a high temperature furnace	I: MSW, sewage sludges, scrap tire crumb O: energy	Pilot (360 kg/h). Demonstration (8000 t/y) in Avonmouth (UK) Operational: 60,000 t/y in Dargavel (UK)
DBA	Deutsche Babcock-Anlagen	Rotary kiln, indirectly heated	**Low-temperature pyrolysis** (450–500°C) in an indirectly heated rotary kiln	I: plastic wastes O: energy	Operational: 6 t/h, Burgau (D)
Eddith	Thide Environment S.A. (F) and Institut Français du Pétrol (F)	Rotary kiln, externally heated	**Drying** to reduce moisture until 10%. **Low-temperature pyrolysis** (450–550°C) in an externally heated rotating tubular reactor. **Combustion** at 1000°C of produced gas with air coming from the dryer	I: MSW, sewage sludges O: energy, CARBOR® (coke-like product)	Pilot (500 kg/h) in Vernouillet (F). Demonstration (1250 kg/h) in Nakaminato (J). Operational: 20,000 t/y, Hoigawa (J) 50,000 t/y, Arras (F)

(*continued overleaf*)

Table 16.1 (*continued*)

Process	Actors involved	Technology	Process description	Input/output	Technical status
Ebara	*Tsukishima (J)*	*Two internally revolving fluidized beds*	***Pyrolysis** in a fluidized bed and **combustion** of the products (mostly oil) in the second fluidized bed reactor*	*I: plastic wastes* *O: energy*	*Operational: 4 t/h, Yokohama (J)* 3 × 6.25 *t/h, Funabashi (J)*
Ebara TwinRec	*Ebara Corp. (J), Alstom Power until 2002*	*Internally revolving fluidized bed + ash-melting system*	***Gasification** of the shredded waste material in a revolving fluidized bed, operated at 500–600°C, which separates combustible part from inert and metallic ones. **Combustion** of syngas and char in a cyclone combustor (1350–1450°C) at a low excess air ratio*	*I: ASR, plastic and electronic wastes, sewage sludge, MSW* *O: energy, ferrous and non-ferrous metals, glass granulate*	*Pilots (0.3 t/h) in Sodeguara (J) and (1 t/h) in Fujisawa (J) since 1997.* *Operational: 19 t/h in Aomori (J), 18 t/h in Kawaguchi (J), etc. and 60 t/h in Selangor (Malaysia, under construction)*
Fuji	Fuji Recycle Ind., Mobil Oil, Nippon Steel Corp., Shinagawa Fuel Corp.	Extruder + fixed bed	**Extrusion** at 300°C; mixing with liquid product recycled from the pyrolysis reactor; **thermal decomposition** in the reactor; **catalytic cracking** in a fixed bed reactor using a zeolite-based ZSM-5 catalyst at 400°C	I: polyolefines industrial wastes O: gasoline, kerosene, diesel	Pilot (400 t/y) in Okegawa City (J) for general plastic waste Demonstration (5000 t/y) in Aioi City (J) for industrial plastic waste
Hamburg-ABB	*University of Hamburg (D), Asea Brown Boveri*	*Bubbling fluidized bed*	***High-temperature pyrolysis** (600–800°C) in a BFB, fluidized with liquid-free pyrolysis gas or inert (steam + N_2) gas*	*I: shredded plastic wastes (having as low as possible Cl content)* *O: high yield of olefins, BTX-rich oil*	*Pilot (40 kg/h) at the Univ. of Hamburg.* *Demonstration (5,000 t/y) operated in Ebenhausen (D) 1986–1989*

Mazda	Mazda Motor Corp.	Fixed bed	**Catalytic cracking** in a fixed bed reactor that uses a $AlCl_3$+HCl catalyst at 250–450°C	I: ASR O: 60% oil (petrol, kerosene)	Pilot (400 t/y)
Mitsui R21	Mitsui Eng. and Shipbuilding (J), Mitsui Babcock Energy Ltd (J)	Rotary kiln, indirectly heated	Two-stage process that starts with a **low-temperature pyrolysis** (<450°C) in a rotary kiln and is followed by a **high-temperature combustion** (1300°C) of the gaseous and solids products in an ash-melting furnace. The process derives from Siemens Schwel-Brenn Process (D)	I: MSW and municipal commercial waste, plastic waste, sludge. O: energy, ferrous and non ferous metals, glass granulate	Operational: 2 × 110 t/d, Yame Seibu (J) 2 × 200 t/d, Toyohashi City (J) 2 × 70 t/d, Ebetsu City (J) 2 × 130 t/d, Koga Seibu (J) 2 × 105 t/d, Nishi Iburi (J) 2 × 105 t/d, Kyohoku (J)
Nikon	Nikon Rikagaku		**Catalytic cracking** at 200–250°C and 1bar with metal catalyst	I: plastic wastes of 10 mm particle size O: 80% oil	Pilot
Noell-KRC	Noell-KRC Energie und Umwelttechnik GmbH(D)	Externally heated rotary kiln + entrained flow reactor	**Low-temperature pyrolysis** (550°C) in a rotary kiln. Subsequent **gasification** with pure oxygen (at flame temperature of 1400–2000°C and at a pressure of 2–50 bar) of dedusted gas, cooled condensates and water-quenched, screened and pulverized coke-like residues. Recovery of obtained syngas or its **combustion** in a boiler, gas turbine or engine	I: MSW, industrial waste slurries, dried sewage sludges O: syngas, energy	Pilot (0.5 t/h) in Freiberg (D) Demonstration (116,000 t/y) in Northeim (D) for MSW and dewatered sludges

(*continued overleaf*)

Table 16.1 (*continued*)

Process	Actors involved	Technology	Process description	Input/output	Technical status
NKT	NKT Res.Center (DN), Danish EPA		**Low-temperature pyrolysis** (375°C) with subsequent metal extraction. Light plastics are sorted out in the pretreatment section together with sand and metals	I: PVC wastes (cables, flooring, etc.) or MPW to be treated to obtain almost pure PVC O: Metal concentrate (up to 60% lead) for recycling; calcium chloride; coke and organic condensate to be used as fuel	Pilot (200 t/y) since 1998
PKA	PKA Umwelttechnik GmbH&Co. KG (D); PEC-Product en Energie Centrale (NL)	Rotary kiln, indirectly heated	**Drying** followed by **low-temperature pyrolysis** (500–550°C) in a rotary kiln for about 1 h. **Gasification** of produced gas at 1000°C to obtain CO/H_2-rich gas; char fines are separately gasified by oxygen at 1500°C	I: MSW, ASR, industrial plastic wastes, spent tires, contaminated soil O: energy	Pilot (24 000 t/y) in Aalen-Goldshöfen (D) Operational: 3 × 4 t/h, Delfzijl (NL)
Pyropleq	Mannesmann, Technip (F), WasteGen (UK)	Rotary kiln, indirectly heated	**Low-temperature pyrolysis** (450–470°C) in a rotary kiln, with internal blades, indirectly heated by hot gases at 550°C. **Combustion** of the product gas at 1200°C after a high-temperature particulate collection	I: MSW O: energy	Operational: 2 × 3 t/h, Burgau (D) 2 × 6.7 t/h Dortmund (D) under construction

Veba Oel	Veba Oel AG in Gelsenkirchen (Veba Pyrolyse anlagen)	Rotary kiln, indirectly heated	**High-temperature pyrolysis** (650–800°C) of plastic waste, fed into the rotary kiln via a screw feeder. Solid cokes and pyrolytic vapours are sent to further treatments in gasification or hydrogenation plant	I: ASR + vulcanized elastomers O: coke (~80%), oil, gas	Operational: 0.5 t/h, Gelsenkirchen (D) 12.5 t/h, Ruhr area (D)
Takuma SBV	Takuma Corp. (J)	Indirectly heated rotary kiln + ash-melting system	**Drying** of crushed waste followed by **low-temperature pyrolysis** (500–550°C) in a rotary kiln for about 1 h. **Combustion** of the pyrolysis gas in a high temperature combustion chamber. The process derives from Siemens Schwel-Brenn Process (D)	I: MSW, ASR, sewage sludge O: energy, iron, aluminium	Demonstration (7,000 t/y) in Fukuoka (J) Operational: 90 t/d, Kanemura (J) ASR 2 × 81 t/d, Kokubu (J) MSW 2 × 63 t/d, Oshima (J) MSW
Toshiba	Toshiba (J), Yamanaka		Pyrolysis + gasification + gas cracking	I: ASR	Operational: 20 000 t/y (J)
Von Roll RCP	Von Roll Umwelttechnik AG (CH)	Reciprocating grate + circulating fluidized bed	**Pyrolysis** in a Von Roll forward reciprocating grate. Gas and solids residue are sent to a smelting reactor and then to a CFB furnace operated at less than 1000°C	I: ASR, plastic wastes, MSW O: energy	Operational: 6 t/h, Bremerhaven (D)

MPW = mixed plastic waste; MSW = municipal solid waste; ASR = auto shredded residue; BFB = bubbling fluidized bed; CFB = circulating fluidized bed. Rows in italics are related to fluidized-bed processes. Data have been mainly obtained from [9, 20–24] plastic waste pyrolysis. This comes from several reasons. The very good heat and material transfer, and the consequent almost constant temperature, provide for uniform products (that are not constrained in their application) and allow short residence times at moderate temperatures; the suppression of side reactions as cyclization increases the process controllability; the absence of moving parts in the hot region reduces the maintenance time and cost; the possibility to apply the process on a relatively small scale increases the range of investment alternatives. Moreover, the pyrolysis process in a fluidized-bed reactor appears really flexible, as demonstrated by the pilot-plant and demonstration-scale investigations that several companies and research groups are carrying out. The aim is assessing the possibility to obtain different products by operating the reactor at different temperatures and with different fluidizing gas. Table 16.2 proposes a taxonomy of different plastic waste pyrolysis processes that the flexibility of the fluidized-bed reactors makes possible. On the other hand, the disadvantages that are not yet completely eliminated are the necessity to limit the chlorine content in the inlet stream, the risk of fluidization worsening as a consequence of solid agglomeration in the bed and the lack of reliable assessments on the scale and operating conditions under which the full economic convenience of the fluidized-bed pyrolysis process is obtainable.

Table 16.3 sketches a comparison between the main gas–solid reactors utilized in the industrial (and demonstration) processes listed in Table 16.1. It again shows the great potentiality of bubbling and circulating fluidized-bed reactors, particularly when the process aims to obtain very valuable products.

2 DIFFERENT STAGES IN THE FLUIDIZED-BED PYROLYSIS OF A PLASTIC WASTE

2.1 AN OVERVIEW OF PHYSICAL AND CHEMICAL PHENOMENA

The yields of the products obtained from a pyrolysis process in a fluidized-bed reactor are due to two contributions. The first, called primary cracking, is that of raw material degradation, i.e. the cracking of molten polymer, which occurs in the dense bed. The second contribution, referred to as secondary and ternary reactions, is that of reactions involving the primary volatiles, which can occur partially inside the bed and partially along the freeboard [16, 19]. These processes are only two of a series of physical and chemical steps that polymer particles undergo after their feeding into a pyrolyser. The sequence of steps strongly depends on the reactor type. In a fluidized-bed reactor, the interactions between the injected polymer particles and the bed material define the peculiar mechanisms of a series of these steps. Figure 16.1 provides a list of them as deduced by batchwise and continuous experiments [32, 33], highlights the region of a bubbling bed where each of them mainly occurs and indicates the paths by which the carbon, under its different forms of fixed carbon (FC), volatile (V) and elutriable fines (F), moves inside the reactor.

Figure 16.2 visualizes the same series/parallel sequence of steps, but by following the fate of a single polymer pellet just after its injection into the hot fluidized-bed pyrolyser. The pellet is fast heated up by a high-rate heat transfer mechanism that leads external surface up to the softening temperature (step 1 in Figure 16.2). Several sand particles

Table 16.2 Different pyrolysis processes that can be carried out in a fluidized-bed reactor

Process	Temperature range (°C)	Plastic waste	Fluidizing gas	Output	References
Low-temperature pyrolysis for monomer recovery	450–580	PMMA, PS	Nitrogen	MMA (98% at 450°C); Styrene (61% at 515°C)	[9, 13, 25, 26]
Low-temperature pyrolysis for feedstock recovery	500–600	Single or mixed polyolefins (HDPE, LDPE, PP, PS, PVC), SB rubber	Nitrogen; liquid-free pyrolysis gas	Broad spectrum of products (C_1–C_{50}). The gas yield is generally low with respect to waxes and oils	[9, 14, 16, 26, 27, 28]
High-temperature pyrolysis for feedstock recovery	650–800	Polyolefins (HDPE, LDPE, PP, PVC), SB rubber, ABS, PA, PTFE, . . .	Nitrogen; steam	Gas yield is generally high High content of olefins	[8, 9, 16, 19, 28, 29, 30, 31]
	600–800	Mixed polyolefins (HDPE, LDPE, PP, PS)	Liquid-free pyrolysis gas	Generally high yield of gases with a high heat-content. High content of BTX-rich oils	[9, 10]
Catalytic pyrolysis	370–550	PE, PS, PP	Nitrogen	Product spectrum strongly depends on the catalyst. Silica–alumina produces high yield of liquids from PE and PP. FCC promotes high gas yield even for PS and PE (waxes fraction decrease from 90 to 1%)	[18, 25]

Table 16.3 Comparison of different gas–solid reactors for plastic pyrolysis

	Fixed bed	Bubbling fluidized bed	Circulating fluidized bed	Rotary kiln	Melting vessel	Extruder
Temperature profile	Large temperature gradients can occur. Frequent presence of hot spots	Temperature is almost constant in vertical direction. Limited variation in radial direction	Temperature gradients in direction of solid flow can be limited by high solid flow rate circulation	Longitudinal as well as transversal gradient may be large and not easy to control	Severe temperature gradients are difficult to control	Two zones are recommended: one at <150°C to remove the volatile fractions and one at >250°C to extract HCl gas
Temperature range (°C)	400–800	500–850	750–850	450–800	300–480	200–520
Heat exchange and transfer	Inefficient exchange. Necessity of large surface of exchanger	Very efficient exchange. Large heat transfer activated by solids circulation	Efficient exchange, particularly along longitudinal direction	Very poor exchange. Then there is often the necessity of long cylinder kilns	Poor exchange	Degradation occurs by exposure to thermal and mechanical work (shear forces)
Particle size	Generally fairly large. Due to the poor temperature control, there is risk of sintering	Wide size distribution. Mean particle diameter between 0.08 and 3 mm. Attrition of bed particles and the consequent entrainment may be severe	Fine solids for the bed particles (generally the mean particle diameter is 0.05–0.5 mm). Plastic waste must be not larger than 10 cm	No problem for size. Any size can be treated, from fines to large lumps	Feeding problems can arise (air lock). The particle size needs to be <1 cm^3 and the bulk density >300 kg/m^3. Agglomerated polymer feedstock must respect severe specifications	The plastics waste must be shredded to the size of side-plates

Residence time		Particles spend substantial time (minutes or hours) in the bed. Gas residence time depends on gas velocity that is below 2 m/s	Particles pass repeatedly trough the circulation loop: residence time for each circuit is few seconds. Gas velocity is 3–15 m/s	Very long (1–2 h)	Long (20 min)	
Conversion	Very high conversion is possible with plug flow of gas and proper temperature control	Mixing of solids and gas bypassing can determine performance poorer than other reactors	High conversion is possible	Conversion can be high	The conversion efficiency of the process is over 90%	Mainly used as a pretreatment before feedstock recycling processes
Process flexibility	Very limited. Any change in process variables (temperature, type of catalysts, etc.) needs a new reactor design	Excellent. It can be used for low- and high-temperature pyrolysis, in presence or not of a catalyst. Different plastic wastes can be treated	Excellent. The reactor can be operated in either a co-current upward flow mode or fast fluidization mode, depending on gas velocity and solid circulation rate. Moreover different reactants can be add at different heights of the riser	Limited. The operating parameters (residence time, temperature, etc.) can be varied in a narrow range. Generally used to produce fuel gas for energy recovery	Limited	Allows highly diverse mixed-plastics stockpiles to be homogenized, sterilized, compacted, chemically modified and converted into a form fit for transport

(*continued overleaf*)

Table 16.3 (*continued*)

	Fixed bed	Bubbling fluidized bed	Circulating fluidized bed	Rotary kiln	Melting vessel	Extruder
Noncatalytic pyrolysis	Unsuitable for continuous operation	Excellent for continuous operations, yielding a uniform product	Excellent for continuous operations	Widely used. Suitable for solids, which may sinter or agglomerate	Suitable for solids, which may sinter or melt	Not used
Catalytic pyrolysis	Can be used for very slow or nondeactivating catalyst	Excellent temperature control allows large-scale operations	Attrition of catalyst is serious	Not used	Not used	Degradation is supported by catalytic effect of added or sprayed-in chemical agents (metal oxides) or by exposure to reactive gas (air, oxygen, steam, hydrogen)
Value of obtained products	Quality of the oil products is equal to that of conventional gasoline, kerosene and diesel oils	Can be high, particularly in process for monomer recovery and in high-temperature pyrolysis	Can be high taking in mind the high flexibility of the reactor	Generally low, since the poor temperature control leads to a wide spectrum of products	Liquid product yields are strongly dependent on feed type, temperature and residence time. The oil products require further purification. The liquid yields and their quality are not as high as that produced by fluidized-bed pyrolysis	The heterogeneous commingled plastics waste is converted into a homogeneous liquid or granulated at the exit of the extruder or heated up so much at the end of the extruder (>520°C) that it volatilizes

Scale-up problems	Serious temperature control problems limit the size of the units	Must be carefully considered. A pilot plant is often necessary	As for BFB	Generally not relevant	No information	The experiments have been performed on different sized equipment (screw diameter 30–90 mm)
Costs	High costs and risk of poisoning/deactivation of catalyst	Moderate. The possibility of small-scale plants makes the investment alternatives wider. Low costs of maintenance	Capital costs higher that those for BFB. Generally convenient for large-scale plants	Moderate cost of investments. Large costs of maintenance due to moving parts and the fouling and erosion of inner walls	A full-scale plant needs about 300 000 t/y of plastic waste to be convenient. Low capital investment, but processing costs that exceed the value of the crude oil product obtained. Maintenance costs can be high for several reasons (e.g. fouling of inner walls)	Single-screw extruders have low price and operating costs. Co-rotating twin screws are more expensive. Counter-rotating twin screws occupy an intermediate position

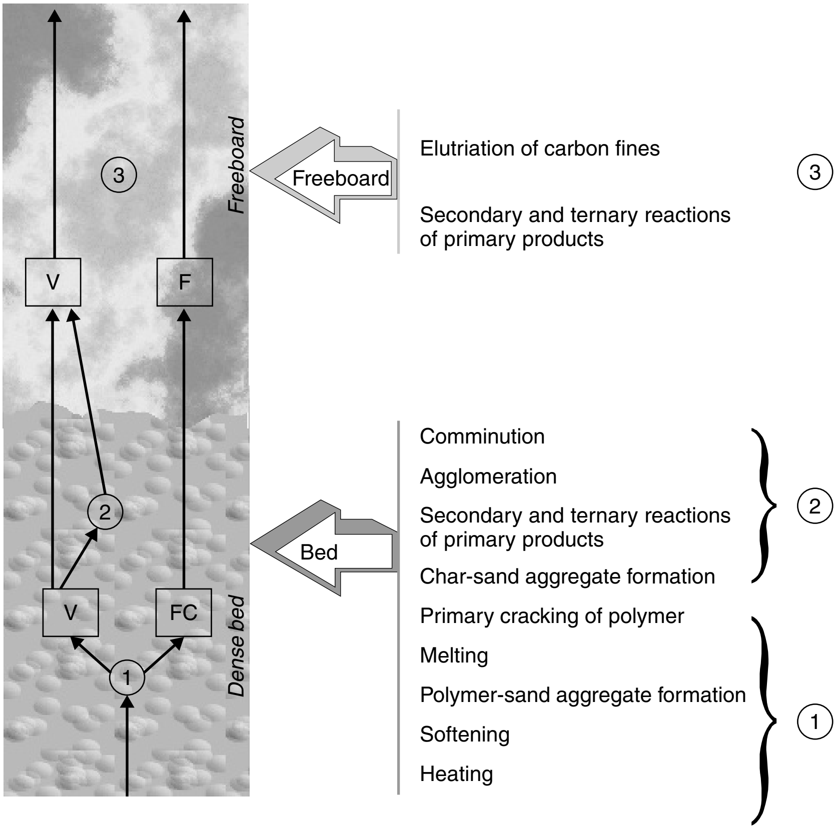


Figure 16.1 Different steps that a polymer particle undergoes after the injection into a fluidized-bed pyrolyser. The graph indicates the carbon paths inside the reactor (adapted from [19]). (Reproduced with permission from Elsevier)

stick on the plastic surface, forming a polymer–sand aggregate that has the external shell made of sand particles and the internal core made of polymer not yet molten. When the temperature further increases, the surface of the pellet reaches the melting temperature and the polymer flows throughout the bed particles of the external shell, so forming a uniform coating over and between them (steps 2–4). The peculiar features of fluidized beds [1] make this heating and coating process very fast, so that the beginning of the pyrolysis, i.e. the cracking of the weak carbon–carbon bonds of the polymer chain, starts when the polymer has already covered the bed particles. The primary cracking (step 7) is then not related to the whole molten pellet, but to a layer of polymer, which coats and adheres on the external surfaces of single sand particles [32, 34, 35]. The thickness of this coating layer grows with a rate that mainly depends on temperature and degradation kinetics as well as on polymer feed rate: in any case, measurements under different operating conditions showed that its value is always of the order of 10 μm, therefore making the physical resistances negligible (i.e. mass and heat transfer rates related to the polymer mass) when compared with the chemical kinetics. As a consequence, whatever the initial size of the plastic pellet, the primary reactions occur on the external surfaces

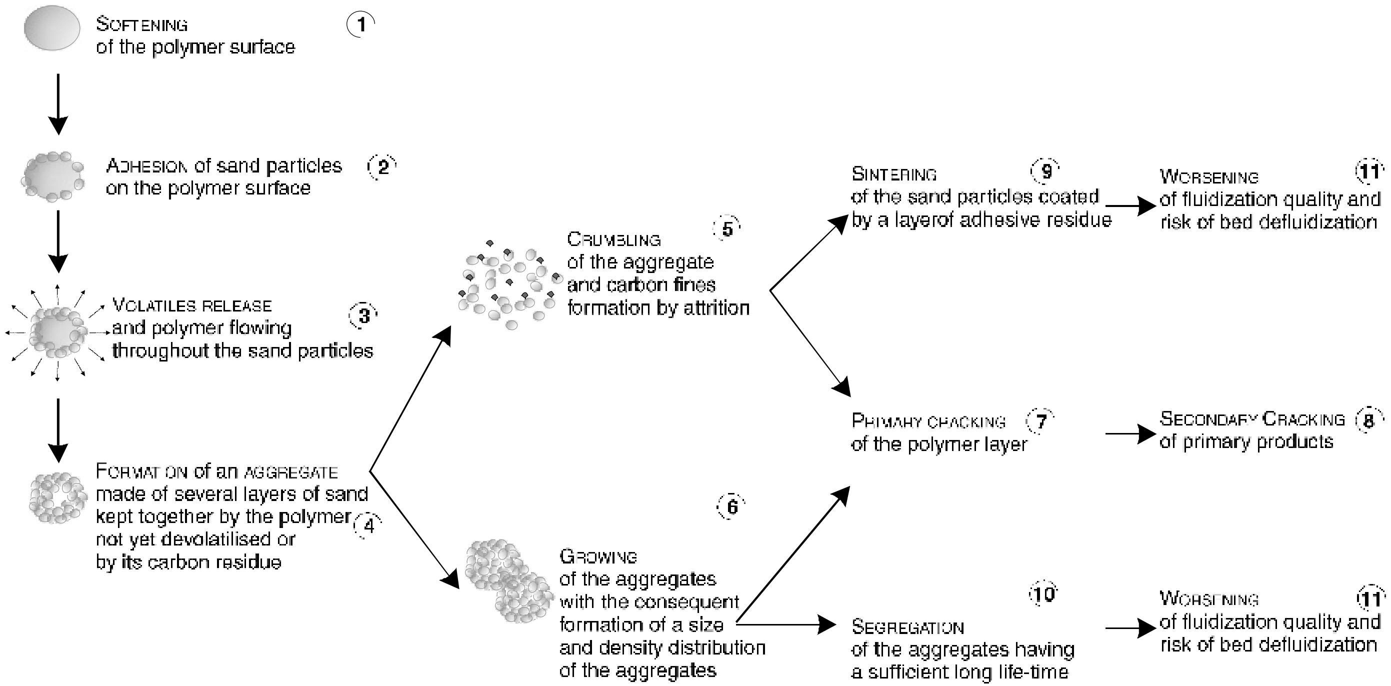


Figure 16.2 Sequence of steps that can occur after the injection of a polymer particle into a fluidized bed pyrolysers (adapted from [35]). (Reproduced with permission from Elsevier)

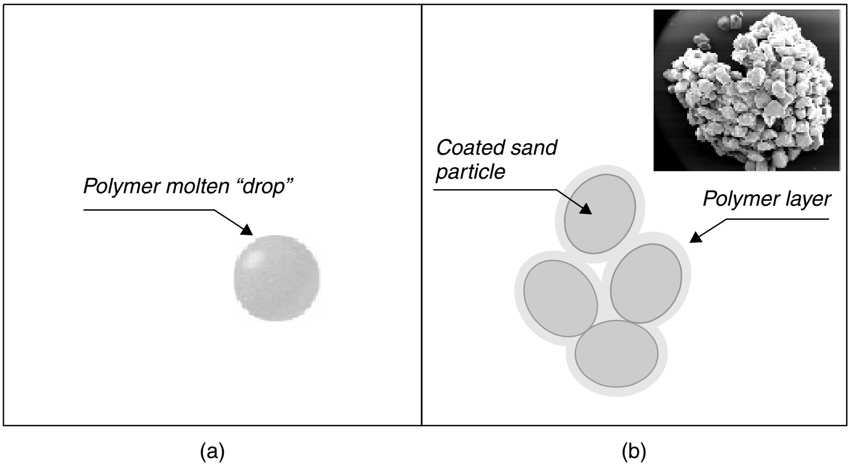


Figure 16.3 *Molten drop* and *Coated particle* approaches for modelling of primary cracking of polymers in a fluidized-bed reactor [5]. (Reproduced by permission of Rapra Technology)

of particles having the same size and shape of the sand particles (Figure 16.3 B and step 7 in Figure 16.2). This aspect is peculiar to the fluidized-bed pyrolysis and must be taken into account in the modeling of process as well as in the definition of design and operating criteria of the reactor. It allows considering a uniform temperature not only in the fluidized bed, but even throughout the polymer layer, so that the solution of mass loss rate equation can be strongly simplified [5]. The time for primary cracking as evaluated by means of this *coated particle* approach is remarkably different (up to few orders of magnitude) from that calculated by means of the *molten drop* approach [36] that considers the reactions occurring throughout the whole molten polymer drop for which the internal resistances are not negligible (Figure 16.3).

2.2 THE POLYMER DEGRADATION PROCESS

Just after the heating, melting and coating process the polymer undergoes a radical scission of the chain that leads to the production of *primary products*. Depending on the operating conditions of the reactor (temperature, gas residence time and type of fluidizing gas), secondary and ternary reactions can become predominant. Figure 16.4 proposes a scheme of possible reactions that lead to different products: it can help to explain the effect of the operating parameters on the products of the process, specially with reference to the different yields and composition of gas, liquids and waxes obtained, for a fixed polymer, under different conditions (see Table 16.2).

The primary products are involved in a series of successive gas-phase reactions in the different regions of the reactor. In a bubbling fluidized-bed pyrolyser, it is possible to distinguish three different regions, dense bed, splashing zone and freeboard, having a relative extension that depends on the main design and operating variables [1]. Figure 16.5 indicates the zones of the fluidized bed where reactions take place and that are characterized by different hydrodynamic and thermodynamic conditions (and, as a consequence, by

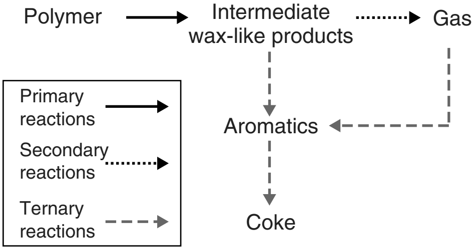
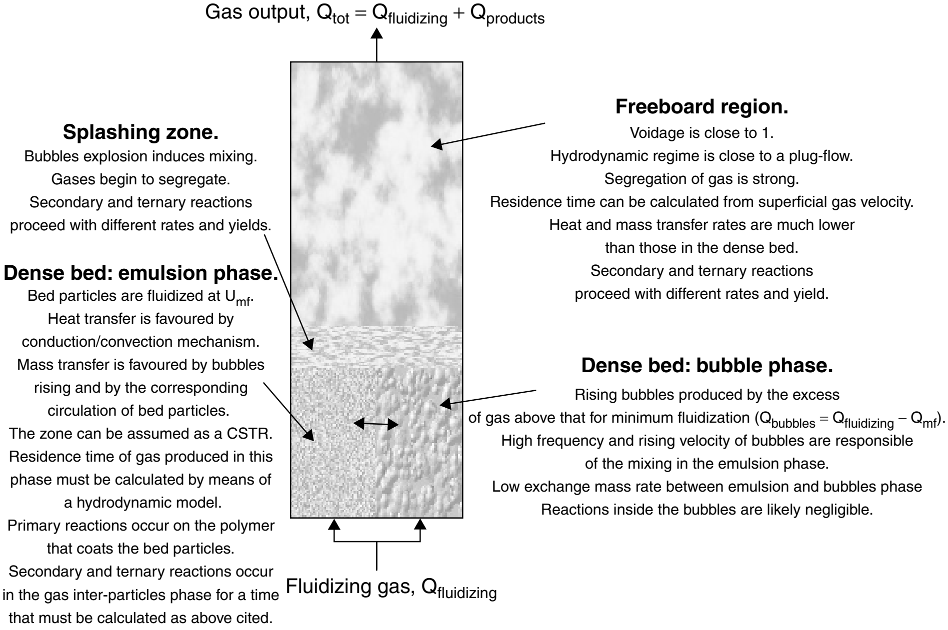


Figure 16.4 Reactions scheme for pyrolysis of polyolefins (adapted from [43]). (Reproduced by permission of the American Chemical Society)



Splashing zone.
Bubbles explosion induces mixing.
Gases begin to segregate.
Secondary and ternary reactions proceed with different rates and yields.

Dense bed: emulsion phase.
Bed particles are fluidized at U_{mf}.
Heat transfer is favoured by conduction/convection mechanism.
Mass transfer is favoured by bubbles rising and by the corresponding circulation of bed particles.
The zone can be assumed as a CSTR.
Residence time of gas produced in this phase must be calculated by means of a hydrodynamic model.
Primary reactions occur on the polymer that coats the bed particles.
Secondary and ternary reactions occur in the gas inter-particles phase for a time that must be calculated as above cited.

Freeboard region.
Voidage is close to 1.
Hydrodynamic regime is close to a plug-flow.
Segregation of gas is strong.
Residence time can be calculated from superficial gas velocity.
Heat and mass transfer rates are much lower than those in the dense bed.
Secondary and ternary reactions proceed with different rates and yield.

Dense bed: bubble phase.
Rising bubbles produced by the excess of gas above that for minimum fluidization ($Q_{bubbles} = Q_{fluidizing} - Q_{mf}$).
High frequency and rising velocity of bubbles are responsible of the mixing in the emulsion phase.
Low exchange mass rate between emulsion and bubbles phase
Reactions inside the bubbles are likely negligible.

Figure 16.5 The different zones of a bubbling fluidized-bed pyrolyser where reactions take place, with the indication of the specific hydrodynamic and thermodynamic features

different overall rates). These are maximized in the dense bed, due to the high quality of contact and the good level of mixing; on the contrary, the gas stream segregation in the freeboard implies a strong reduction of heat transfer and contact efficiency.

3 OPERABILITY RANGE OF FLUIDIZED-BED PYROLYSERS

3.1 THE PHENOMENOLOGY OF BED DEFLUIDIZATION

Stable, long-term operations of fluidized-bed reactors can be compromised by bed material-to-polymer interactions, which can generate worsening of fluidization quality. Several investigations carried out with monopolymeric feeds of packaging wastes (PE, PP, PET and PVC) as well as with mixtures of these wastes showed that, under conditions typical of low-temperature pyrolysis processes (Table 16.2), there is a considerable risk of worsening in the bed fluidization quality [32–35] that can eventually lead to the whole bed defluidization. The phenomenon can occur in different ways, depending on the polymer type, and with different rates, depending on the reactor temperature and other operating conditions as the polymer feed rate and the bed amount and type. The sequence of steps that can lead to segregation and defluidization phenomena is schematically sketched on the right-hand side of Figure 16.2. For operation with polyolefins waste (such as PE and PP), the bed defluidizes as a consequence of sintering between sand particles (sequence 1-2-3-4-5-9-11 in Figure 16.2). Some aggregates surely form (step 4) at early instants but, since the polyolefins do not produce a sticky carbon residue, they crumble rapidly (step 5) so setting several free sand particles. These are covered by a layer of polymer that, at certain waste feed rates, has no time to completely devolatilize, so becoming progressively larger. The polymer coating the particle surface can be seen as a viscous liquid that completely wets the sand particles. When two of these particles collide, their relative velocity could be too low to overcome the viscous adhesion of the bridge between the surfaces [19, 37]. On the contrary, for operations with PET and PVC wastes, a large formation of polymer-sand aggregates is observed. These, under a range of temperatures between 450 and 650°C have a lifetime long enough to generate accumulation, as a consequence of the presence of a sticky carbon residue. They take a large fraction of the bed (up to about 25% at the lowest temperature) and have very high minimum fluidization velocities. These aggregates are responsible for the beginning of segregation, with the consequent worsening of the fluidization quality, and contribute to determine the occurring of defluidization (sequence 1-2-3-4-6-10-11 in Figure 16.2), as confirmed by the evidence of experiments carried out in hot and cold models. Some sintering between sand particles however occur, probably promoted by the reduced momentum of bed material that, in turn, is determined by the segregation effect [34, 35]. The behavior of plastic waste mixtures, in particular those substantially made of polyolefins and PET, shows a synergistic interaction between these two mechanisms: the presence in the mixture of just a small fraction of PET (or of another polymer having a sticky carbon residue) induces a faster defluidization of the bed while, when the PET content is gradually increased, the measured defluidization time becomes substantially equal to that of tests with only PET [35].

Experimental and theoretical studies [32, 33, 35, 37] showed that, for different plastic waste feeds (PE, PP, PET, their mixtures) and under a fixed reactor temperature, the time of occurrence of defluidization for a bed of a given material is linearly related to the value of the ratio between the bed solids hold-up and the polymer feed rate. The latter is a key parameter of the process. Diagrams in Figure 16.6 summarize all the data obtained in these experiments under different operating conditions and report the linear relationships that fit the data very well for the specific temperature and plastic waste feeding.

3.2 PREDICTIVE DEFLUIDIZATION MODELS AND OPERABILITY MAPS

The considerations and the experimental evidence just described suggest that the reactor design as well as the definition of process conditions need a tool, able to provide reliable predictions for the on-set of fluidization worsening and bed defluidization. Mastellone and Arena [37] proposed a predictive defluidization model valid for low-temperature pyrolysis

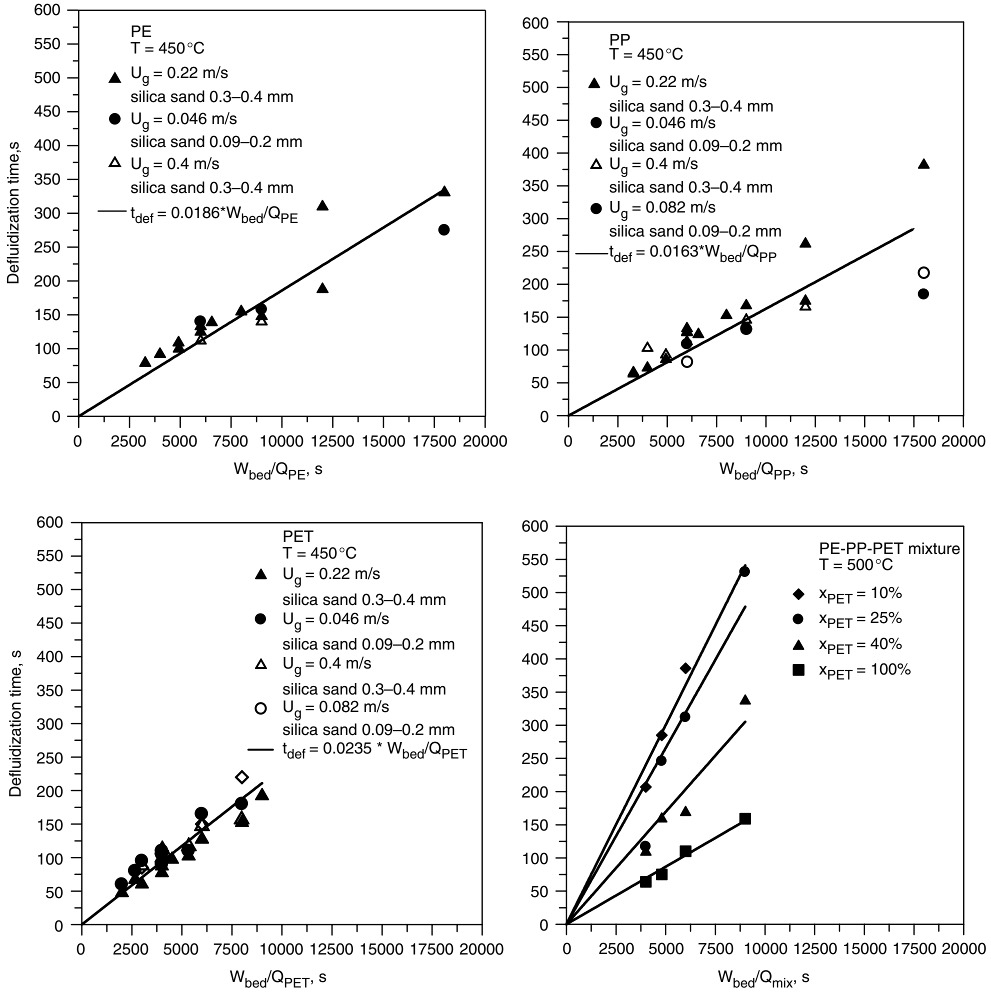


Figure 16.6 Experimental defluidization times of different plastic wastes as a function of ratio between bed amount and polymer feed rate [32, 33, 35]. (Reproduced with permission from Elsevier)

of polyolefins, based on observed defluidization mechanisms and fluidization engineering principles. It allows construction of an operability map that indicates if, for given reactor geometry and on the basis of the main operating variables and of physical and chemical properties of plastic waste, stable or unstable operations will be established inside the pyrolyser. For the latter case, it is also able to provide the time at which defluidization will occur, if no actions are managed by the plant operator. Figure 16.7 shows one of these maps that, for fixed reactor geometry, can be used for PP pyrolysis. Since the operating conditions (essentially, reactor temperature, plastic waste feed rate, fluidization velocity, bed amount) cannot be considered as completely ‘free variables’ due to the constraints that process and throughput requirements could impose, it might be possible

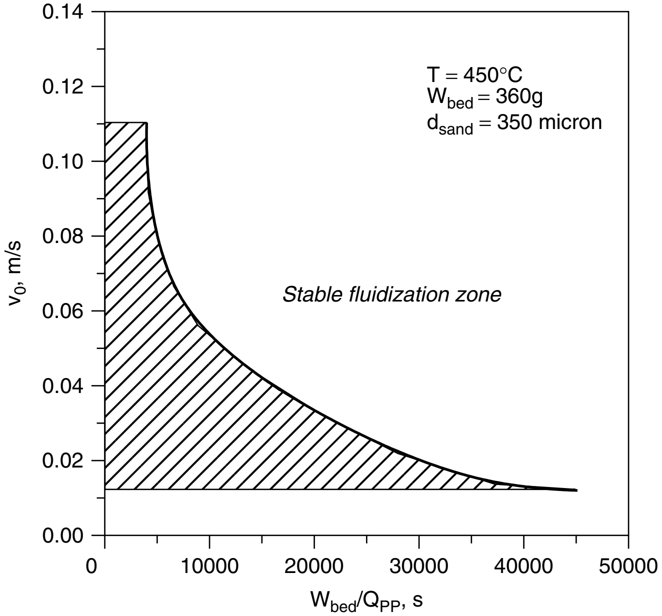


Figure 16.7 The operability map of PP pyrolysis at 450°C, showing the zone of stable fluidization and that of defluidization. v_0 is the particle collisional velocity, which can be evaluated as reported in [37]. (Reproduced by permission of AICHE)

that a process operation will be localized in the 'unstable region' of the map. In this case, it is however possible to operate without defluidization risk by adopting a specific design solution, adequately defined by means of a defluidization model. The solution imposes that a continuous make-up of fresh particles has to be realized, together with simultaneous withdrawal of a part of the bed. The feed rate of fresh material must be equal to that of bed drain in order to avoid any increase of bed hold-up [32], and its value must be determined by the defluidization model in order to avoid an excessive accumulation of agglomerates in the bed or (for the sintering mechanism) to maintain the thickness of polymer coating in a range of values limiting the adhesion forces. Defluidization models have also been recently proposed for other polymers, such as PET and PVC [32, 38].

4 THE EFFECT OF THE MAIN PROCESS VARIABLES ON THE YIELD AND COMPOSITION OF PYROLYSIS PRODUCTS

Thermal polymer degradation is determined by the chemical structure and length of the polymer chain, by the presence of unstable structures (such as impurities or additives) and by the temperature level inside the reactor, which must be high enough to break the weakest, primary chemical bonds. Madorsky and Straus [39] found that some polymers (such as PMMA and PTFE) mainly revert to their monomers upon heating, while others (such as PE) yield a great many decomposition products. These two types of dominant thermal polymer degradation are called *end-chain scission* and *random-chain* *scission*, respectively. Chain scission, or depolymerization, is the successive release of monomer units from chain-end or at a weak link, which is essentially the reverse of chain polymerization; it is often called *depropagation* or *unzipping*. Random-chain scission (or degradation) occurs by chain rupture at random points along the chain, giving a disperse mixture of fragments which are usually larger than the monomer unit. The two types of thermal degradation may occur separately or in combination; in the latter case, which is rather normal, the chain depolymerization is often dominant [40, 41].

The main experimental results recently obtained in the field of fluidized-bed pyrolysis of different plastic wastes are summarized in Table 16.4. All these studies utilize a bubbling bed type as experimental fluidized-bed apparatus, probably due to its easier design and operating criteria. The information related to circulating fluidized-bed pyrolysers (or to some other types, like the internally revolving fluidized beds commercialized by Ebara) is limited and usually covered by industrial secrecy. Moreover, it is difficult to deduce general considerations about the reactor behavior and the process performance under different operating conditions since information about reactor geometry, bed material, hydrodynamic variables as well as that related to procedures for sampling and chemical analyses is often deficient or sometimes completely missing. This, together with the already mentioned scale-up difficulties in fluidized-bed reactor engineering, reduces the relevance of the recalled experimental studies and the possibility of an immediate transfer to the industrial scale.

Table 16.4 also lists the operating conditions used in the cited experiments, i.e. polymer type, reactor size, reactor temperature, bed material type and size, fluidizing agent, fluidization velocity, as these are reported in the papers. A strong difficulty has been found in deducing reliable data about gas residence time in the reactor, which is a crucial parameter to characterize the spectrum of reactions and of possible products. The difficulty comes from the complete absence of gas residence time data and/or of their calculation procedure, as already complained of by other authors [43]. Due to the complex hydrodynamics of bubbling fluidized beds (see [1] for the simple two-phase model or Kunii and Levenspiel model) is in fact not straightforward the evaluation of an average residence time of gas: first, it is necessary to take into account the gas fed from the bed bottom and that produced along the bed as pyrolysis product; then, it could be important to estimate the gas fraction which is exchanged between the emulsion and bubble phases inside the bed; finally, it is necessary to distinguish between the time spent along the bed and that along the freeboard (these usually have different temperature profiles). This lack of information (that probably means different residence times in different experimental studies), together with the wide differences in reactor type and geometry, bed and freeboard temperature profiles, sampling and analytical procedures, make it quite difficult, or often impossible, to achieve a critical comparison of reported data.

The influence of the applied reaction conditions (temperature, residence time, concentrations of reactants and products) on the product spectra obtained from pyrolysis of different plastic wastes could be estimated under the hypothesis of thermodynamic equilibrium, as shown by Westerhout *et al.* [43]. They evaluated the maximum achievable yield of valuable products during the pyrolysis of PE and PP, with the validation of experiments carried out under conditions of controlled temperature and residence time. In large-scale reactors the residence time and temperature control are difficult and certainly

Table 16.4 Main studies on plastic pyrolysis reported in the recent scientific literature

Plastic feed; bed material	Apparatus	Operating conditions	Main results	Reference
HDPE; sand	Bubbling fluidized bed, 69 mm ID	Batch feeding $U = 0.036$ m/s $T = 500, 600{,}700, 800, 900$°C	Gas yield progressively increases from 5.7 to 96.5%. Methane, benzene, toluene formation is favoured by high residence times. Gas yield reaches maximum at 800°C	[16]
Mixed plastics, HDPE; quartz sand	Bubbling fluidized bed, 154 mm ID	Fluidizing gas: nitrogen; nitrogen/steam $U = 0.17$ m/s $T = 600, 700, 800$°C $Q = 1.1-1.4$ kg/h	Pyrolysis with steam as fluidizing gas demonstrates that the olefins yield is increased due to water–gas reaction. Mixed plastics pyrolysis does not allow optimization of process temperature since styrene production from PS requires low temperatures while olefins production from PE and PP requires high temperatures	[8]
Mixed plastics; quartz sand	Bubbling fluidized bed, 154 mm ID	Fluidizing gas: pyrolysis gas $U = 0.2$ m/s $T = 730$°C	Pyrolysis of mixed plastics lead to aromatics without chlorine yield of 48%. Chlorine is present, together with heavy metals, in the solid fraction	[10]
Polyolefins; quartz sand	Bubbling fluidized bed, 154 mm ID	Fluidizing gas: steam $T = 605, 655, 690, 700, 750, 805$°C $Q = 1-3$ kg/h	With the exception of experiments at 605°C, the gas fraction is the main product (58–71%), having a maximum yield at a temperature of about 700°C. BTX-aromatics increase from 1.6% at 605°C up to 16% at 805°C. Distillation residue is higher at lower temperature (at which heavier hydrocarbons are produced) and at the highest (since more condensed aromatics are present). Chlorine is present in the water and in the solids	[29]

Mixtures of LDPE, HDPE, PP, PS, PVC, PET; silica sand	Bubbling fluidized bed, 100 mm ID	Batch feeding. Fluidizing gas: steam $U = 0.072$ m/s $T = 500–700$°C	Liquid and gas phase composition is given. Gas yield reaches its maximum value at 650°C	[27]
Mixed plastics from DSD; quartz sand	Bubbling fluidized bed, 154 mm ID	Fluidizing gas: nitrogen $T = 685, 710, 716,$ 730°C $Q = 0.4–0.9$ kg/h	Two different mixtures of plastics having different PVC content have been pyrolysed in order to evaluate aromatics and light gas yields. BTX represent the 20% of input, gases the 44%. Chlorine is absent in the aromatics compounds due to reaction with $CaCO_3$	[12]
PS, PE; FCC catalyst	Bubbling fluidized bed, 154 mm ID	Fluidizing gas: nitrogen $T = 370–515$°C $Q = 1$ kg/h	Effect of FCC catalyst on pyrolysis of PE and PP is studied. The catalyst allows the use of low-temperature for pyrolysis. The catalyst induces a strong decrease in aromatics yield (1–7% styrene instead of 59–61%) for PS pyrolysis, and in waxes yield (from 90 to 1%) for PE pyrolysis	[25]
HDPE, PP (0.1 mm); silica-based catalysts (Sio_2:Al_2O_3:Na_2O)	Bubbling fluidized bed, 25 mm ID	Fluidizing gas: nitrogen $U = 0.4, 0.6$ m/s $T = 400–550$°C	Two different catalysts were used for pyrolysis of PE and PP. The SA (SiO_2–Al_2O_3) catalyst increases the liquids yield	[18]
PE/PP/PS, alone and mixed; quartz sand	Bubbling fluidized bed, 130 mm ID	Fluidizing gas: nitrogen $T = 510$°C $Q = 1–3$ kg/h	Composition of gas, liquids and waxes obtained with pyrolysis of PP, PE, PS mixtures are reported. Composition and yield of gases do not change for a mixture of the three polymers	[26]

(*continued overleaf*)

Table 16.4 (*continued*)

Plastic feed; bed material	Apparatus	Operating conditions	Main results	Reference
HDPE; silica sand	Bubbling fluidized bed, 48 mm ID	Fluidizing gas: air/nitrogen ER = 0.06–0.07 $U = 0.11, 0.18$ m/s $T = 640, 700, 730, 780, 850$°C	The gas yield reaches the maximum value at 780°C. The oxygen increases the reactivity of degradation. Comparison between aromatics yield with the two processes is reported	[28]
Filled or not PMMA; quartz sand	Bubbling fluidized bed, 154 mm ID	Fluidizing gas: nitrogen $T = 450–480$°C $Q = 0.3–3$ kg/h (lab. scale) $Q = 30$ kg/h (pilot plant)	PMMA with and without filler has been pyrolysed at low temperature (450 and 480°C). High monomer recovery has been obtained (98%). The experiments were carried out also in a pilot plant 20 times larger than the lab-scale	[13]
SBR (styrene-butadiene-rubber); quartz sand	Bubbling fluidized bed, 154 mm ID	Fluidizing gas: nitrogen, steam $U = 0.12, 0.28$ m/s $T = 500, 550, 600$°C $Q = 1–3$ kg/h	Low temperature pyrolysis (500–600°C) of tires produces a high carbon black yield (40% at 600°C), styrene and butadiene. Butadiene yield increases if nitrogen is used instead of pyrolysis gas due to suppression of secondary and ternary reactions	[14]
Recycled PE; silica sand	Bubbling fluidized bed, 55 mm ID	Fluidizing gas: nitrogen $U = 0.15, 0.28$ m/s $T = 550–750$°C	The effect of bed temperature appears to play a crucial role in defining yield and composition	[19]

HDPE; silica sand	Bubbling fluidized bed, 48 mm ID	Fluidizing gas: air/nitrogen ER = 0, 0.06 U = 0.11, 0.17 m/s T = 640, 700, 730, 780, 850°C Q = 3–4 g/min	High yield of waxes and oils found at 640 and 700°C. The presence of an incharacterized char is highlighted	[30]
Waste tire powders; not specified	Bubbling fluidized bed, 100 mm ID	Fluidizing gas: air/nitrogen ER = 0.07–0.41 T = 350–900°C Q = 2–4 kg/h	Calorific value of gas increases if ER decreases. Oil and char content decreases if ER increases	[42]
Recycled PP; quartz sand	Bubbling fluidized bed, 55 mm ID	Fluidizing gas: nitrogen U = 0.13, 0.28 m/s T = 550–750°C	A specific procedure is adopted to change gas residence time inside the bed and along the freeboard. The bed temperature remarkably affects the composition of gaseous products	[31]

ER = equivalent ratio; Q = plastic feed rate; T = bed temperature; U = fluidizing velocity far from ideal: this may lead to excessive cracking of the desired intermediate products to undesired side products [43]. The estimation of the ultimate, maximum achievable, yield and the influence of different reaction conditions can then be utilized to optimize the product spectrum in industrial-scale reactors. On the other hand, the differences between the results of ultimate yields and those of laboratory- or pilot-scale experiments reported in Table 16.4 can be related to the actual reaction conditions and, in particular, to the limited residence time, even though the doubtful purity of many polymers may also be responsible for many of conflicting results reported [41]. In the following, the results of some of the main experimental studies listed in Table 16.4 are described, by using the following distinction for the pyrolysis product fractions [26]: gases (up to C_4); oils (boiling point <300°C, n-C_{5-17}, i-C_{5-20}); light waxes (bp 300–500°C, n-C_{18-37}, i-C_{21-50}); heavy waxes (bp >500°C, $> n$-C_{37}, $> i$-C_{50}); soot, carbon black.

4.1 FLUIDIZED-BED PYROLYSIS OF MONOPOLYMERIC WASTE

Polyethylene (PE). Pyrolysis of PE proceeds via a random degradation mechanism that initiates by C–C bond scission at the weakest points in the chain and propagates via decomposition of the macroradicals to produce smaller fragments and, depending on temperature and residence time, lighter hydrocarbons, aromatics and coke (i.e. aromatic compounds with two or more benzene rings). Table 16.4 reports related recent papers, which include interesting observations about the effect of small fraction of oxygen in the fluidizing gas, that of temperature and residence time and that of catalyst used as bed material. Again, the differences in the operating conditions do not allow a coherent comparison, but it is possible to say, accordingly to some fundamental previous papers [8–10], that the gas and aromatics yield increases with temperature and residence time. An analysis of studies carried out at temperatures between 450 and 750°C [16, 19, 28] shows in fact that: at 450°C, the main product is a wax-like fraction (as that shown in Figure 16.8); at 500°C, the solid fraction is substantially negligible and gas and liquid products are obtained; in the range 650–750°C, different studies found the maximum yield of gases (its value moving from about 40% [16] to 65% [19] until 100% [28]). In order to achieve the same gas yields at lower temperatures, it is not sufficient to increase the gas residence time (the typical range for fluidized-bed reactors is about 0.5–5 s) and an intervention on the dissociation energy is necessary. Mertinkat *et al.* [25] studied the effect of a catalyst on PE pyrolysis and indicated that an advantageous product spectrum could be gained by using a FCC catalysts in a temperature range 370–450°C: C_3 and C_4 gases, together with BTX and ethylbenzene, can be produced in large quantities with an energy demand much lower than that of a noncatalytic process.

Polypropylene (PP). Pyrolysis of PP is favored by the branched structure of the polymer: the thermal degradation also proceeds in this case via a random-chain scission, but the influence of the temperature on the product spectrum is more pronounced than in the case of PE [43, 31]. At temperatures as low as 515°C, Predel and Kaminsky [26] found that PP pyrolysis leads to the production of 6.8% of gases, 36.7% of oils, 21.6% of light waxes and 34.6% of heavy waxes. At these low temperatures the main compounds in the gas fraction are propene and butenes (about 51 and 17% in [26]), but at higher temperatures these products are converted into others [43]. Ponte *et al.* [31] found a remarkable

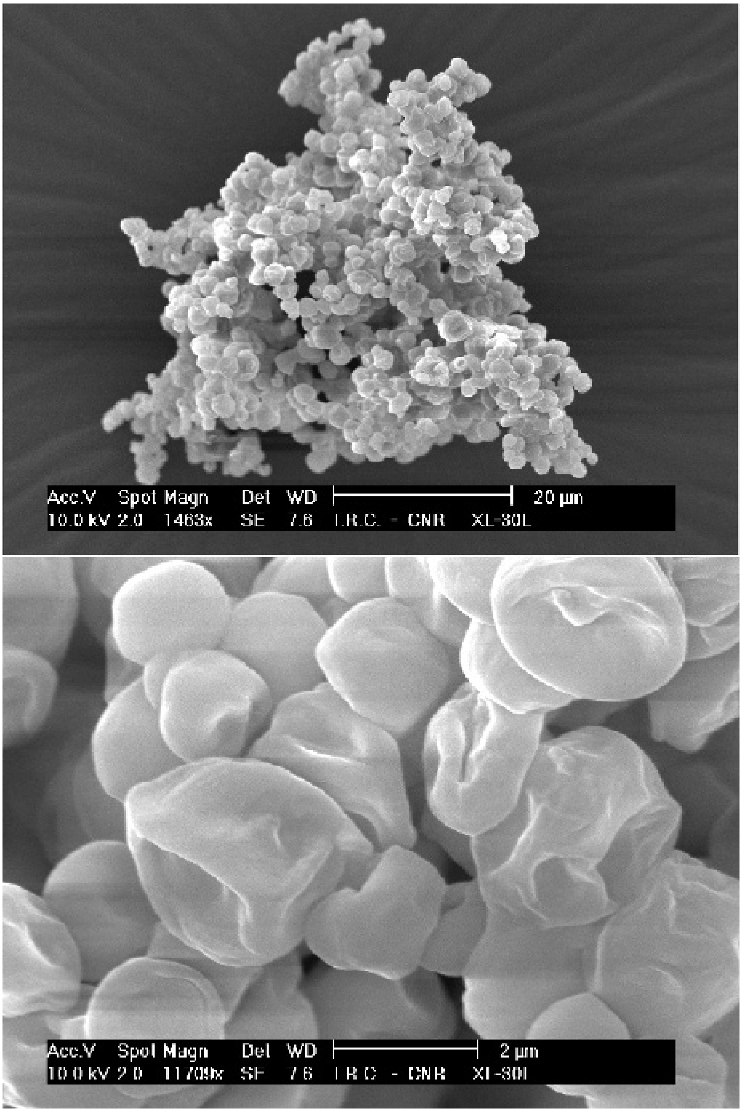


Figure 16.8 Scanning electronic microscope pictures of degraded PE as obtained at 450°C and $U = 0.2$ m/s (see [19] for details). (Reproduced with permission from Elsevier)

effect of temperature in the range 500–750°C, both on the yield in gaseous products and on their composition: at higher temperatures the highest values of solid yields and methane content were measured. This is in agreement with the finding [43] that, at the equilibrium state (i.e. at very long residence time and/or at very high temperatures), PP degradation yields methane and coke as the main reaction products. As already observed, the discrepancy in the cited values of experimental results can be partly justified by considering the differences in reactor size and geometry, temperature and residence time.

The effect of gas residence time in the different region of the reactor has been recently investigated, by means of experiments with different bed hold-up (to change the bed residence time) and with different fluidizing velocity (to change the freeboard residence time) [31]. Results suggest that a longer residence time inside the bed increases the gas yield, while a longer residence time along the freeboard does not substantially modify the gas yield, but affects the gas composition, with increased methane and hydrogen contents and reduced percentages of heavier hydrocarbons.

Fluidized-bed pyrolysis of virgin or recycled PP has been recently proposed [44] as an innovative and low-cost production process of carbon nanotubes (CNTs). It is known that the very high aspect ratio and extraordinary mechanical, electrical and thermal properties of CNTs can be extremely useful in several fields of application, but the high cost of production currently limits wider industrial utilization [45]. The new technique uses fluidized-bed reactors to obtain high heating rates of the injected polymers, high heat and material exchange coefficients and a reliable control of gas and solids residence time in the bed and the freeboard [44]. The process, which is still in the development state, has also been successfully carried out with recycled PE and PET and with their mixtures [46]. It should allow a continuous and low-cost production of CNTs, having a degree of purity compatible with most of the applications already known for this type of nanostructured material (Figure 16.9): this could largely extend the potential market of CNTs in a number of applications as, for instance, those of composite materials.

Polystyrene (PS). The thermal degradation proceeds again by C–C scission, which is then followed by a complex radical chain reaction. In the early stages of reaction and at low temperatures (290°C), the primary products are styrene, diphenylbutene, and triphenylhexene. At higher temperature or longer residence times, the final stable products are toluene, ethylbenzene, cumene, and triphenylbenzene [47]. Fluidized-bed pyrolysis was applied successfully to pure PS: more than 60% of monomer and 25% of other aromatics were obtained at a pyrolysis temperature of 515°C [25, 26].

Polyethylene terephthalate (PET). At temperatures above 300°C PET pyrolysis proceeds via a random-chain scission of the ester links to yield a mixture of terephthalic acid monomer and vinyl ester oligomers [47]. The presence in the monomer of oxygen and a benzene ring implies that the decomposition products contain aromatic and oxygenated carbon compounds, like CO_2, ketones and aldehydes [27].

4.2 FLUIDIZED-BED PYROLYSIS OF MULTIPOLYMERIC WASTE

In the last decade several studies focused on the pyrolysis of plastic mixture in BFB reactors, operated under different conditions of temperature, fluidizing gas, bed material, reactor size and geometry [10, 12, 26, 27, 48]. Particular attention has been devoted to the effect of PVC presence on the determination of yield of chlorinated aromatics [10, 12, 27]. The effect of temperature, which has been also well studied [12, 27, 48], appears to be in accordance with that described for single polymer feeding: an increase of temperature leads to an increase of yields in gas and aromatics and to a decrease of waxes. It is however noteworthy that the temperature value has to be selected on the basis of mixture composition, in order to optimize the desired products. In fact, most of polymers produces aromatics at higher temperatures and residence times (PE, PP) while others (like PS) do so at lower temperatures.

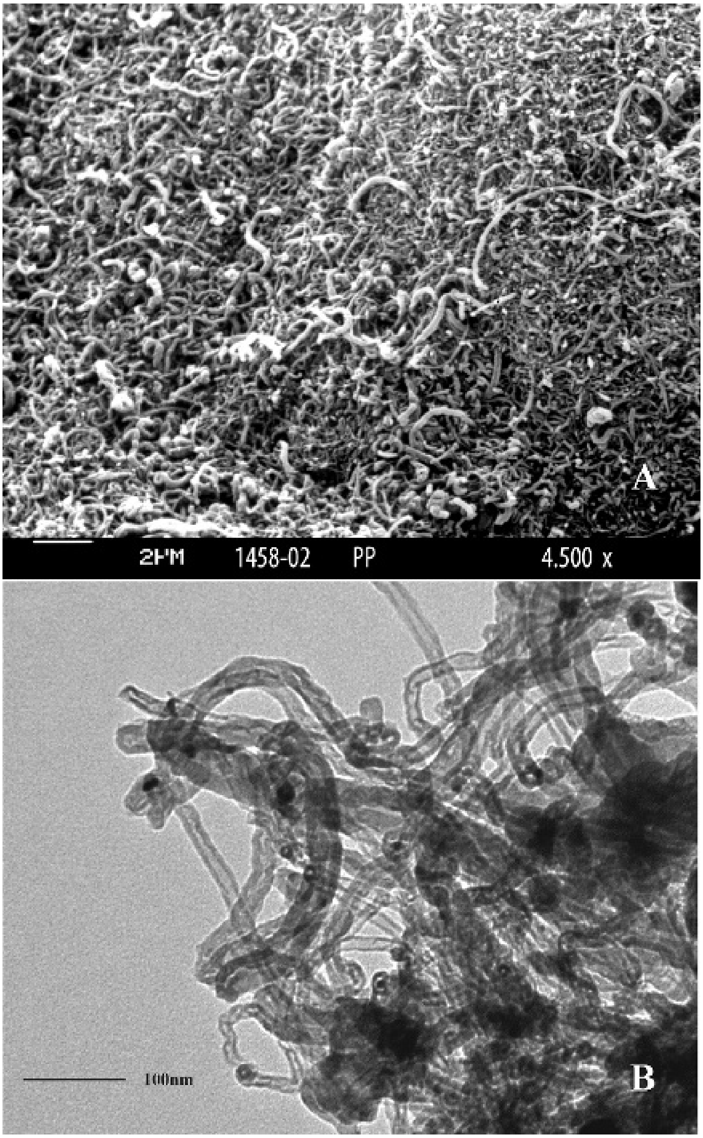


Figure 16.9 (A) Scanning electronic microscope picture of CNTs as obtained from PP (B) Transmission electronic microscope picture of CNTs as obtained from PE

The interaction between pyrolysis products coming from different polymers present in the mixture has been also investigated [26, 43, 48]. The pyrolysis of polymer mixtures appears to have no significant mixing effect on the product spectrum in comparison with the spectra obtained from the pyrolysis of pure polymers. This finding is contradictory to other pyrolysis methods (see, for instance, [49]) and is another indication that predominantly unimolecular reactions determine the product spectrum since the presence of other components does not influence it [43]. In particular, Predel and Kaminsky [26] found that adding 10% PS to either PE or PP or a PE–PP mixture does not change significantly the distribution of products fractions, apart from additional PS degradation products. The compositions of the products also remain substantially similar, even though when PS is added to PP the peak distribution of the waxes changes significantly, although its amount remains constant.

4.3 FLUIDIZED-BED PYROLYSIS OF OTHER POLYMERIC WASTES

Fluidized-bed pyrolysis of rubber tires has been carried out over a temperature range from 500 to 740°C. A recent study [14] indicates that operation between 500 and 600°C leads to a production of a large amount of solid phase (>60%), made of carbon black and distillation residue, together with a remarkable amount of distillate (25–30%) and a limited amount of gases (3–9%). The most valuable fraction is the carbon black: its yield and quality being an important criterion for the economic evaluation of the process. The carbon black yield increases from about 30% at 500°C to about 40% at 600°C. The use of steam instead of nitrogen as fluidizing gas does not significantly affect yield and quality of the carbon black nor the yields of the other product fractions. The main product in the gas fraction is 1,3-butadiene, the monomer of the original rubber. In the steam experiment, there are also significant yields of CO_2 and CO, resulting from the reaction of carbon black with water to carbon oxides and hydrogen. The latter appears to increase the degree of oil desulfurization due to the production of H_2S [14].

Waste from electrical and electronic equipment (WEEE) has an absolutely remarkable, total amount considering that several millions tons are produced only in the European Union. In a mixed WEEE stream about 75% is made of metals, glass and wood that can be mechanically recycled while the plastic fraction accounts for 15–20%. This fraction contains some minor flame retardants additives (such as polybrominated diphenyl ether) that can form toxic compounds when incinerated. This aspect, together with the presence of various polymeric materials (both thermoplastic and thermoset), makes pyrolysis a viable recycling solution. WEEEs are first shredded and then pyrolysed at temperatures in the range 700–900°C, with some interesting advantages. The metals are not oxidized and thus they can be separated and recovered from further use; the flame retardant additives are split off in the form of hydrohalogen gas during the process and then removed. Limited information about technical and economical feasibility of processing of WEEE by means of thermal processes is available, even though a recent study [50] made a careful assessment of available processes. Six criteria (energy efficiency, bromine and antimony recovery, emissions, quality of residues, operational experiences and profit expectations) were utilized to score all the examined technologies. The composition of plastic fraction of WEEE has comparable aspects to that of automotive shredder residue (ASR), except for high metals content. Therefore, in identifying processes for WEEE treatment, operational experiences with ASR, particularly by means of fluidized-bed reactors [51, 22] give a good indication of possible performances. Table 16.1 gives information about some of the processes suitable for pyrolysis of WEEE and ASR (Akzo, Compact-Power, Ebara TwinRec, Hamburg, Mazda, NKT, PKA, Veba Oel, Takuma, Toshiba, Von Roll): those carried out by means of fluidized-bed reactors are the well-known Hamburg process and the Akzo and Ebara TwinRec processes, described in the following paragraph.

5 OPERATING EXPERIENCE WITH INDUSTRIAL FLUIDIZED-BED PYROLYSERS

Table 16.1 reports an up-to-date list of the main pyrolysis processes that can be utilized for material and energy recovery from different type of plastic wastes. In the following, brief descriptions are given of three of them, having a different commercial status, and involving a bubbling, a circulating and an internally revolving bed, respectively. The aim is to give an essential summary about the technical process, its environmental and economic performance and its current commercial status.

5.1 THE BP CHEMICALS POLYMER CRACKING PROCESS

BP Chemicals has led promotion of a fluidized-bed cracking process that could be used to convert plastic waste into petrochemicals. The Polymer Cracking Process was first tested on a laboratory scale and then on a continuous pilot scale (having a nominal 400 t/yr capacity) at BPs Grangemouth site in the UK.

Description of the process. Prepared mixed waste plastics, oxygen free and with a maximum of 5% of nonpolymeric impurities, are introduced into a bubbling fluidized-bed reactor, where the low-temperature cracking reaction takes place (Figure 16.10). The bed is made of sand and is fluidized in an inert atmosphere by nitrogen and/or recycled light hydrocarbons and heated at about 500°C by fired tubes which provide the endothermic heat of reaction. As the plastics enter the reactor, they quickly melt and coat the sand particles with a thin layer of polymer. This undergoes thermal cracking and produces lighter hydrocarbons that leave the bed with the fluidizing gas [21, 32]. The gaseous products are purified first in a cyclone, which removes the bulk of the entrained fines (made of a mixture of coke, sand and residual plastic additives) and then in a successive guard bed, which catches the chloride content coming from PVC destruction by the reaction of CaO with HCl. The main result is a spent $CaO/CaCl_2$ that has to be landfilled. The gas exiting the guard bed is purified via cyclones and a collection hopper to remove the $CaO/CaCl_2$ fines. An intermittent withdrawal of material from both fluidized-bed reactor

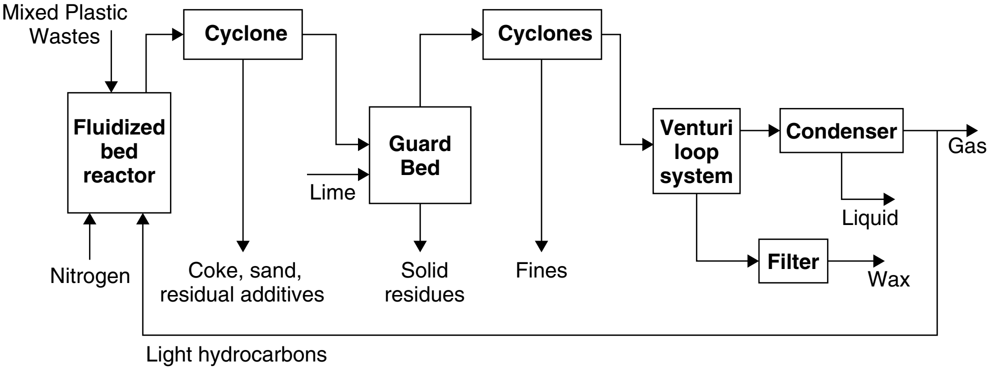


Figure 16.10 Flowchart for the BP Polymer Cracking process

and guard bed is necessary to purge the bed from accumulated unwanted materials. The gas resulting from the process is collected in a two-stage process. A Venturi loop system partially condenses the gas to give a waxy hydrocarbon product. This is condensed first and filtered to remove remaining fine solid particles: its high degree of purity allows the mixing with naphtha at levels up to 20% so that the resulting mixture can be directly utilized in a steam cracker to give classic petrochemical products. The noncondensed gas stream is compressed, reheated and returned to the cracking reactor as fluidizing gas: excess gas is continuously removed as a product to keep the process operating at a pressure of about 4 barg and partially used as fuel for indirect heating of the fluidized reactor [47, 21, 52].

Process performance and commercial status. The Polymer Cracking Process has an efficiency of approximately 80% conversion of plastic waste to petrochemical products with an additional 10–15% utilized as fuel gas in the process itself [21]. The hydrocarbon feedstock obtained is of high quality while the waxy product can be used as feedstock material for steam crackers or can be fed into refinery units (such as the FCC unit). It is not easy to give reliable data about environmental and economic performances since the process is still in the development stage [53]. However all the emissions should be very low and should comply with local regulations. Total solid waste products (which include both feed plastic and the solids used as make-up) are typically up to 0.2 kg/kg of total solids feed [23]. The overall environmental performance of the process has been also evaluated and compared with those of alternative options for waste plastics management in a couple of life-cycle analyses [52, 54]. Both the LCAs highlighted that, in particular with reference to energy consumption, the BP process has a performance worse than those of mechanical recycling, monocombustion and of a couple of alternative feedstock recycling processes. The recent process developments seem to work in the direction of an improved energy efficiency that could change the results of the above-mentioned comparison [53]. The economic performance of the process will depend on many factors (plant scale, preparation stages, location, etc.). Some information has been produced by BP Chemicals and indicated an investment of €23–30 million for a 25 000 t/yr plant in Western Europe (1998 prices), which implies a gate fee of about 260 €/t. These figures have an uncertainty of ±30% and include product values but exclude collection and preparation [23].

5.2 THE AKZO PROCESS

Akzo Nobel is an important producer of chlorine, vinyl chloride and PVC, strongly interested in a process for feedstock recycling of MPW containing PVC. Since 1994 they have chosen a fast pyrolysis process in a circulating fluidized-bed reactor, based on the technique developed by the Battelle Memorial Institute (CO, USA) for biomass gasification.

Description of the process. The process involves the utilization of two separate CFBs, both operated at ambient pressure (Figure 16.11). The first is a flash pyrolysis reactor in which waste is converted with the addition of steam, at a temperature between 700 and 900°C, into product gas and tar. The reducing atmosphere avoids the dioxins formation. The product stream, made of fuel gas and HCl in a composition strongly dependent on feed/steam ratio, is quenched to recover HCl, which is then further purified. The second CFB is a combustor that provides heat for flash pyrolysis by burning the residual tar: the

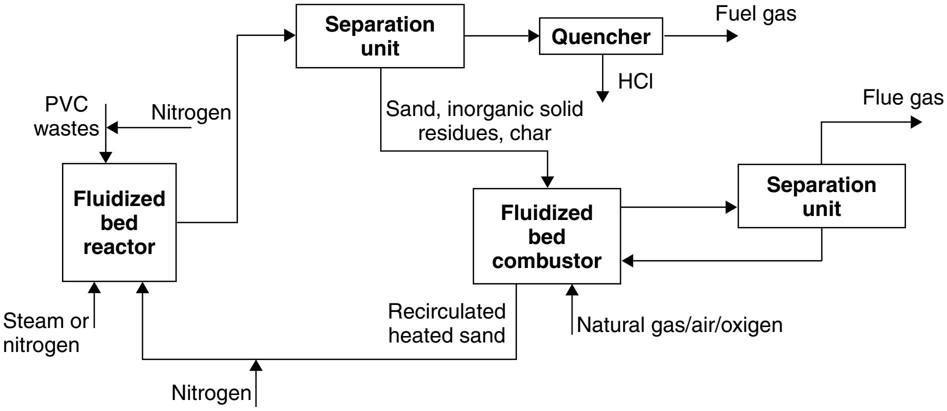


Figure 16.11 Flowchart for the Akzo–Nobel process

heat transfer between the two units occurs by the circulation of heated sand. The choice of CFB technology allows high PVC waste throughputs [23].

Process performance and commercial status. The Akzo process was investigated on a pilot scale (30 kg/h) with PVC cable and pipe scrap. Some tests with mixed PVC waste were carried out on a larger scale (300 kg/h) with the support of the European Council of Vinyl Manufacturers, giving promising results. At the moment the project is on hold, even though there is a plan to realize an industrial-scale plant, with a capacity of about 50 000 t/yr. On the other hand, Akzo Nobel has stopped all activities on HCl recycling from PVC [50]. The process is still at pilot-scale status, so that large uncertainty exists about its technical, environmental and economic performance.

5.3 THE EBARA TWINREC PROCESS

Ebara Corporation developed the TwinRec process as an innovative combination of two existing waste-to-energy technologies: the twin internally revolving fluidized bed (IRFB) combustion technology and the Meltox combined combustion and ash melting technology. The name TwinRec emphasizes the combined recovery of energy and material from different wastes, in particular those coming from dismantling and shredding process of vehicles (ASR). The former license agreement with ALSTOM Power (CH) was terminated in 2002 and now Ebara provides the technology on their own.

Description of the process. The simplified process flow diagram is shown in Figure 16.12. The shredder waste (ASR, plastic and electronic waste as well as MSW) is fed in an IRFB, which operates in a reducing atmosphere and at temperatures as low as 500–600°C, allowing easy control of the process. The IRFB reactor separates the combustible portion and the dust from the inert and metallic particles of the fed waste: the obtained mixture of metallic and inert particles is sent to a mechanical metal separation while fuel gas and carbonaceous particles are burnt in a cyclonic combustion chamber for energy production and fine ash vitrification. Metals such as aluminium, copper and iron can be recycled as valuable products from the bottom off-stream of the IRFB as they are neither oxidized nor sintered with

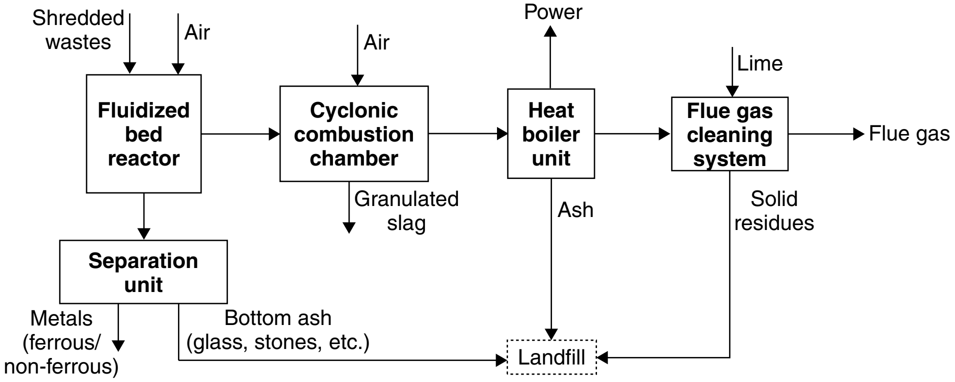


Figure 16.12 Flowchart for the Ebara TwinRec process

other ash components. After metal recovery, the bottom ashes, which are about the 7–10% of the waste throughput and have a low carbon and heavy metals content, are sent to landfill [51, 20, 22] or can be recycled directly, similar to stocker grate bottom ash, or even be upgraded by vitrification in the existing ash melting furnace [55]. The combustor operates at 1350–1450°C with secondary air addition but without auxiliary fuel. The furnace operates as a slag tap, with the ash encouraged by the cyclonic action of the air to adhere to the refractory walls and to flow as a molten slag through the slag tap at the furnace bottom: the molten slag is then quenched with water and obtained as granulate that can be sold to the construction industry. The process involves a reduced flue-gas flow rate, which allows for a size reduction of steam boiler and pollution control units.

Process performance and commercial status. The process can be integrated into existing recycling schemes by the co-operation with shredding plants, specialized nonferrous separation plants, the construction industry and the district heat and/or electricity off-taker. This possibility of integration, together with the avoidance of intermediate pretreatments, gives attractive environmental and economic performance to the process. In particular, each recoverable component of the shredder residues has a chance of recovery (metals are recycled, inert minerals are separated from organics and dusts and recycled, mineral dusts and metal powders are bound into the glass granulate and recycled) while organic pollutants are destroyed and the final amount to landfill is reduced. The Ebara process also shows a wide flexibility on the input wastes, being possible the operation with ASR and MSW as well as that with plastic waste of electrical and electronic equipment (WEEE). A TwinRec plant with electrical energy production achieves a net efficiency of 17–25%; if electricity and heat are produced, the net efficiency can be raised to 70%. As already mentioned, the economic performance depends greatly on the specific project (plant scale, location, required standards, combinations with existing structures, etc.). As a rough indication, for ASR the investment cost is between 600 and 1100 €/(t/y of installed capacity) with a gate fee (2004 prices) between 100 and 230 €/t [55]. The TwinRec process has full commercial operation status. Two pilot plants (1.5 and 5 MWth, respectively) operated in Japan since 1995, with different wastes, including ASR and WEEE. At the beginning of 2004, 20 commercial lines were in operation. The Aomori (J) plant has a capacity of 2 × 10 t/h (about 2 × 40 MW thermal input) and is fed with 70% shredder residues and 30% mechanically dewatered sewage sludge. Other plants are at Kawaguchi (3 × 21 MWth), Kurobe (7.4 MWth), Sakata (2 × 12.3 MWth), Ube City (3 × 9.5 MWth) and Chuno Union (3 × 7.3 MWth). Recently, Ebara received an order from Malaysian government for a very large plant (1500 t/d) for MSW treatment to be built in Selangor Province and one more from Tokyo Rinkai Recycle Power Co. for a 550 t/d plant for treatment of nonhazardous industrial waste to be located on an island in Tokyo Bay.

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17

The Hamburg Fluidized-bed Pyrolysis Process to Recycle Polymer Wastes and Tires

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1 INTRODUCTION

After the first oil crisis in 1975, there was great interest in feedstock recycling of polymers to recover oil and gas from this hydrocarbon source. Another goal was to protect the environment from landfilling of plastic materials that decompose very slowly.

The problem for cracking plastics into oil was the low heat transfer, the high heating energy needed for cracking and the different impurities such as inorganic fillers, food residues, and paper. Under the leadership of H. Sinn it was decided to build at the University of Hamburg a process which was able to use filled and dirty plastics in a fast pyrolysis process [1]. We used an indirectly heated fluidized-bed process to avoid mixtures of incineration exhaust gases with the pyrolysis products, but with the advantage of an excellent heat transfer. Up to this time, only a few fluidized-bed had been described processes for plastics cracking in Japan using air as fluidizing gas and partial incineration by oxygen to cover the cracking heat.

Polystyrene bottles were pyrolyzed by the Japan Fluid Cracking process (JFC) in a fluid sand bed reactor of 500 mm diameter and with a capacity of 1 t/day [2]. The oily products were contaminated by oxidized compounds.

In the years from 1973 to 2005, different size fluidized-bed reactors were built at the Institute for Technical and Macromolecular Chemistry, continuously working with plastics throughput of 50 g/h (LWS 1), 500 g/h (LWS 2), 2 kg/H (LWS 3 + 4), 3 kg/h (LWS 5), a small pilot plant of 10–30 kg/h (TWS1) for plastics, and a pilot plant of 100–200 kg/h for whole tires (TWS2) [3–5]. All reactors were heated indirectly, the small laboratory sizes electrically from the outside, and the pilot plants by heating tubes with incineration

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of gas (at first propane, later in a run by pyrolysis gas). A flow scheme of a laboratory plant is shown in Figure 24.1 in a later chapter in this book.

The experiments at the University of Hamburg led to the building of three pilot plants by companies. The first was built in 1982 in Ebenhausen, Bavaria by DRP/ABB using a fluidized-bed reactor with a diameter of 1800 mm and a capacity of 800 kg/h of mixed plastics and whole tires. The second plant was built in Grimma, GDR in 1984 for whole tires with a capacity of 5000 t/yr. BP also carried out preliminary experiments 1992 at the University of Hamburg and then built a pilot plant in Grangemouth, Scotland with a capacity of about 5000 t/yr to obtain waxy products from mixed plastics, mainly polyolefins. These waxy products could be used as feedstock for naphtha-crackers. All pilot plants ran for only a few years, mainly because economically operation was not possible due to decreasing crude oil price.

The Hamburg process can be varied by some simple process parameters such as pyrolysis temperature, type of fluidizing gas (nitrogen, steam, cycled pyrolysis gas), residence time to produce different products from plastic waste (Table 17.1).

The Hamburg process was also used for oil and gas recovery from oil shale, oil sand, and biomass such as wood (flash pyrolysis), lignin, bark, oil seed, and fat [6–8].

2 PILOT PLANT DESCRIPTION

The scheme of the pilot plant is shown in Figure 17.1. At the heart of the plant is a fluidized-bed reactor with an inside diameter of 450 mm and a height of 900 mm. This bed part is followed by a 1075-mm-long freeboard zone in which there is no sand fluidizing. The height of the sand bed (fluidized bed) is 650 mm. The sand has a particle size of 0.3–0.7 mm. The reactor is heated by four steel heating tubes which use propane or the excess gas of the pyrolysis products (Figure 17.2). For feeding, there are three possibilities: a screw conveyor, a tube for liquid feed from the side, and a lock with two flap valves for material from the top of the reactor. The feeding system consists of a screw conveyor nearer to the hooper which controls the amount of the feed and a fast-moving screw conveyor directly at the reactor which brings the feed into the fluidized bed very rapidly to avoid the formation of glue and congestion. This screw conveyor is cooled by a water double jacket. The lock with the two flap valves is used for big pieces of plastics or for material with a high viscosity. The capacity of the pilot plant is between 10 and 30 kg feed per hour.

Table 17.1 Variation of the Hamburg pyrolysis process feeding polyolefins by different temperatures and fluidization gases

Temperature (°C)	Fluidizing gas	Products
400–550	Nitrogen, steam, cycled pyrolysis gas	70–90% waxy products/oil, 2–9% gas
550–700	steam	60–70% oil and aliphatics, 30–40% gas
700–800	Nitrogen, steam	70–80% gas, mainly ethylene and propene, 20–30% oil
700–800	Cycled pyrolysis gas	30–50% aromatics, 30–55% gas, 1–10% soot

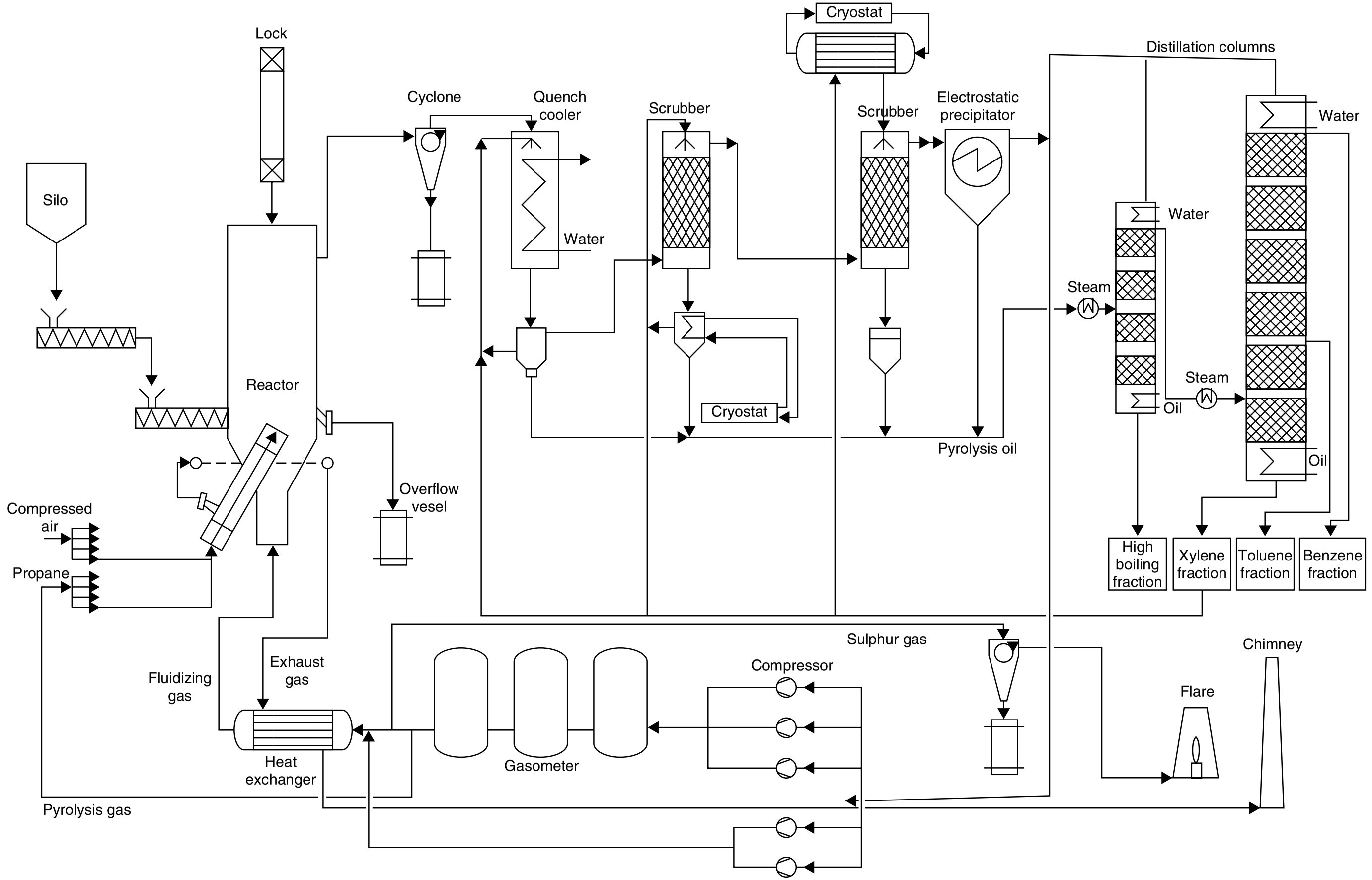

Figure 17.1 Scheme of the pilot plant TWS of the Hamburg process for pyrolysis of 30 kg plastics per hour in a fluidized-bed reactor

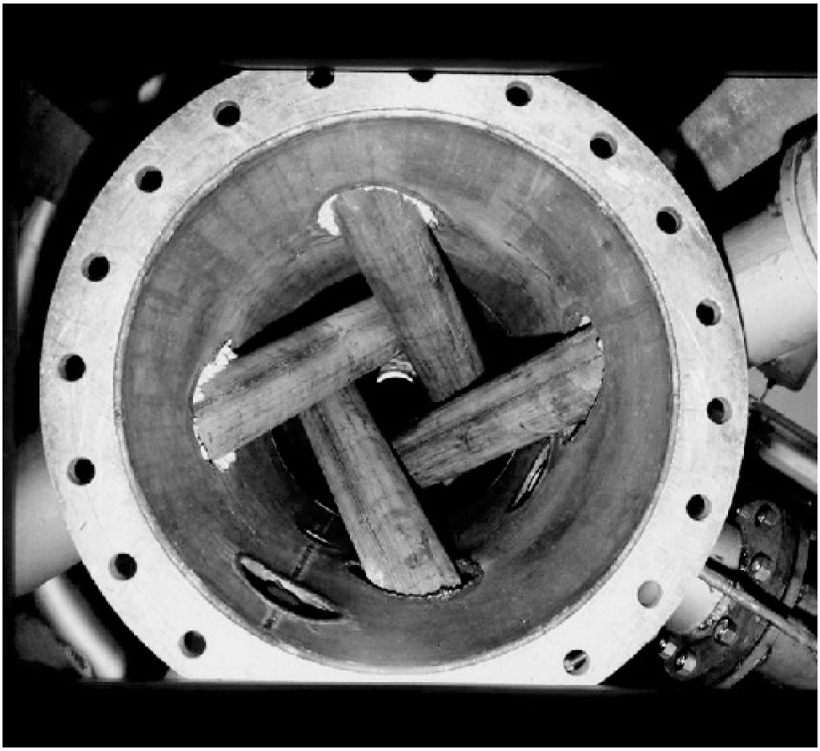

Figure 17.2 View inside the fluidized-bed reactor from the bottom with four fire tubes and the hole for feeding

The bottom of the fluidized bed has an incline of about 15° and carries the bent gas-inlet tubes. These tubes are movable vertically so that their distance from the bottom of the fluidized bed can be varied. With this arrangement, there is a variable settling zone for small metal pieces and stones which occur as impurities of the plastic waste.

Behind the fluidized bed reactor there follows a cyclone for separation of solids. Then the product gases pass a washing cooler; in this cooler, xylene is cycled and used as cooling medium and solvent. It washes the cooler free from waxes and other high-boiling products. Heat transfer occurs in a tube heat exchanger. After this, the cooled product gases pass two packed columns in which xylene is used as quenching medium. This solvent is cooled down to −5°C by a cryostat running with ethanol. Before the gas is compressed, it is cleaned up from fog by an electrostatic precipitator (electrofilter). Compression is effected by five membrane compressors. Two of them transport the gas directly into the fluidized bed. The other three press the gas into three steel gasometers. From this, a part of the gas is used for fluidizing the bed; it can be controlled and is mixed with the other gases. The correct flow gas rate is the sum of both gases. If a high flow gas rate is necessary, three membrane compressors can directly pump the gas into the fluidized bed. The capacity of a compressor is higher if the pressure is less. The excess gas of the pyrolysis can be burned in the fire tubes or in a flare on top of the building.

In a separate room (in case of explosion) the distillation and quenching columns are installed. In the two distillation columns, four distillation boiling cuts can be obtained from the pyrolysis oil. In the first column with a diameter of 150 mm and a length of 10.5 m, the fraction with a boiling point of more than 180°C is split off from the distillation residue. In the second column with a diameter of 80 mm and a height of 8 m cuts of 80°C, 110°C, and 140°C (xylene) are obtained. The xylene is used as quenching oil also in the coolers.

The plant is controlled by a process computer (ABB-Hartmann and Braun) and equipped with numerous data-collecting instruments. Surveillance is carried out by continuous analysis of the room air as well as by explosion-limit controls. The pyrolysis gas is analyzed automatically by a gas chromatograph. All data obtained are registered to enable calculation of energy and mass balances. Some basic components are continuously monitored by infrared spectroscopy, i.e. ethylene in the pyrolysis gas, sulphur dioxide and oxygen in the exhaust gas.

The heating of the fluidized bed by fire tubes was necessary to up-scale the plant. The Ebenhausen plant and the Grimma plant used fire tubes, for heating. A scheme of the fire tube is shown in Figure 17.3.

The fire tube consists of two tubes. The outer tube is closed in front, while the inner tube is open. The flame is started at the burner lead and the exhaust gases passes between the inner and outer tubes. They are collected outside the reactor and go through a heat exchanger in which the incoming gas for fluidizing is heated up. There is no mixing of exhaust and product gas. The whole reactor is shown in Figure 17.4, isolated by rock wool.

In one run, 200–500 kg of plastic materials are pyrolyzed and 50–150 L of oil and 20–290 kg gas are obtained. The products are analyzed by GC and GC-MS with four different separation columns.

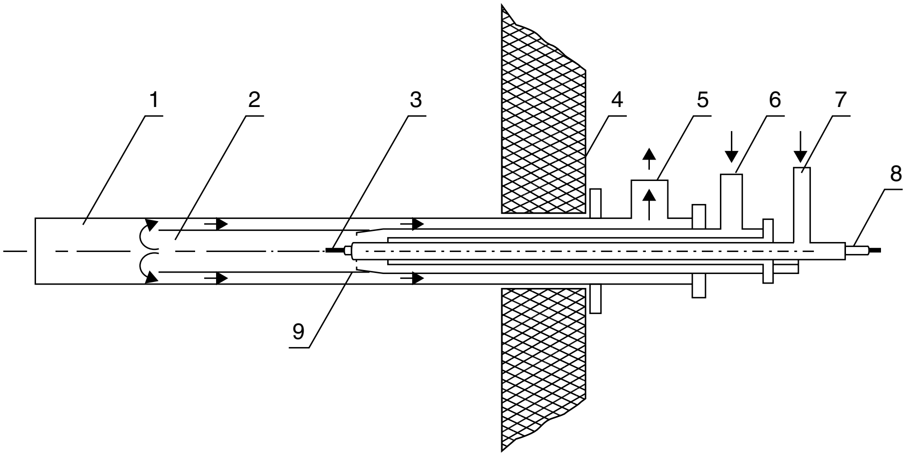

Figure 17.3 Fire tube for heating of the fluidized bed. 1 closed outer tube; 2 open inner tube; 3 ignition; 4 reactor wall; 5 outlet for exhaust gas; 6 inlet for air; 7 inlet for propane or gas; 8 spark plug; 9 burner head

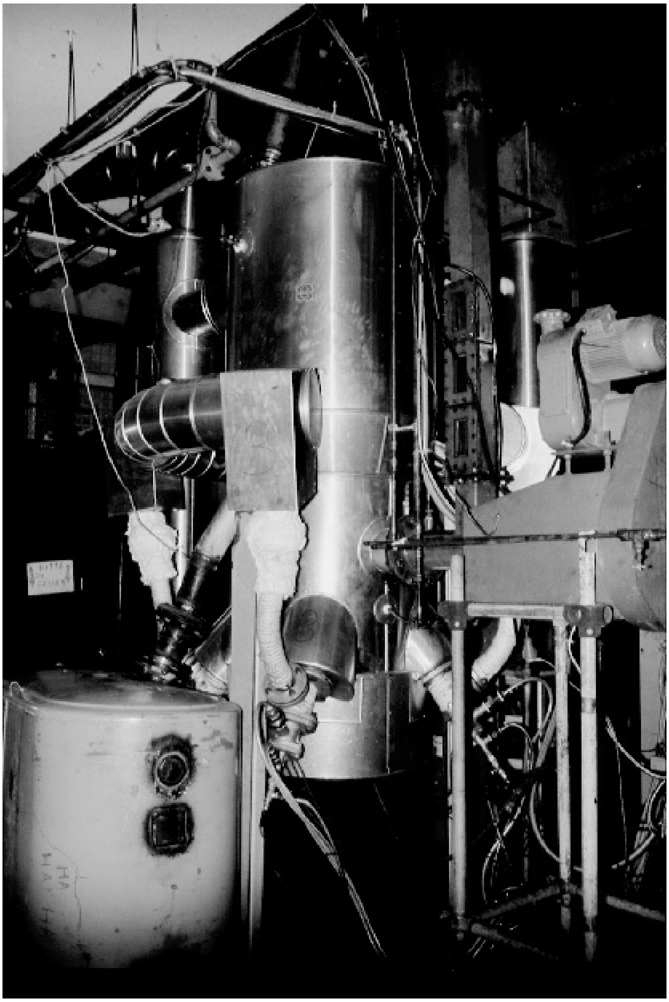

Figure 17.4 Isolated fluidized-bed reactor with the outside fire tubes (middle), the screw conveyor for feeding (right) and the drump for inorganic fillers from the overflow (left)

2.1 PYROLYSIS OF WHOLE TIRES

Fluidized sand beds are surprisingly insensitive to the unit size of the feed material. Pieces of scrap tires up to a weight of 2.7 kg each were fed and quantitatively pyrolyzed. These results offer the perspective for a pyrolysis process for scrap tyres without prior size reduction. Most pyrolysis processes use feed crushed to a 200–20 mm size which involves considerable expense [9]. Successful pyrolysis experiments in an indirectly heated rotary kiln have been conducted by Kobe Steel [3].

In cooperation with the Hamburg company C.R. Eckelmann, a pilot plant fluid-bed reactor (TWS 2) for a 1.5–2.5 t/day throughput of scrap tires has been built at the University of Hamburg (Figure 17.5). Its particular construction shows horizontal, fluidizing-gas inlet

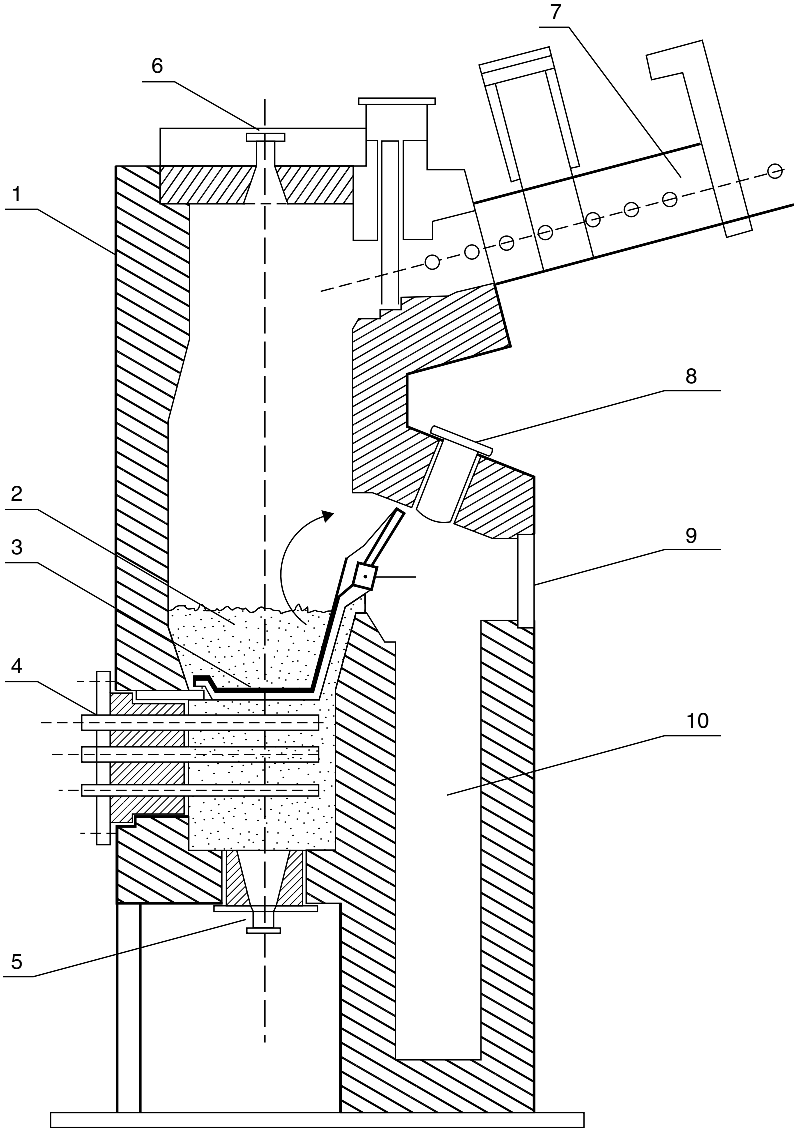

Figure 17.5 Scheme of the pilot plant for the pyrolysis of whole scrap tires. 1 steel wall with fireproof walling; 2 fluidized bed; 3 tiltable grate; 4 radiation fire tubes, two layers, third layer inlet tubes for fluidizing gas; 5 nozzles to remove sand and metal; 6,8, and 9 flanges for observation and repairs; 7 gas-tight lock; 10 shaft for steel cord

tubes. The fluidized-bed reactor has a square inner size of 900 × 900 mm and a height of 3200 mm [10].

The pyrolysis zone itself, i.e. the fluidized sand bed, indirectly heated by seven fire tubes in two layers, has a fireproof wall. The whole tires roll through a gas-tight lock into the reactor. A tiltable grate is extended into the fluidized sand to remove the steel cord from the pyrolyzed tires. On top of the tiltable grate, the fluidized bed extends to a size of 1000 × 1000 mm to form a freeboard and to provide sedimentation of the sand.

The pyrolysis products, together with the fluidizing gas (i.e. the noncondensable pyrolysis gases), leave the reactor via a cyclone, where dry carbon soot and filler materials are precipitated. A cooling system and an electrostatic precipitator condense the liquid fraction of the pyrolysis products. The waste heat is used to heat up the fluidizing gas. A stream of pyrolysis products is branched off the main product cycle and refined in the rectification unit described for the smaller test plant.

The investigations up to now suggest that this fluidizing technique allows the formation of a stable fluid bed with a minimum of coagulations, independent of the size of the feed, which, of course, causes a significant viscosity change inside the bed. In addition, this construction allows the use of the inclined bottom of the reactor as a settling zone for the metal pieces.

The throughput of the plant is definitely limited by the capacity of heat radiation of the commercial fire tubes. The prototype reactor allowed a space-time yield of 1.3 t/m^3 fluid bed per hour. The heating value of the pyrolysis gas produced was sufficient to balance the heat demand of the process.

3 PYROLYSIS PRODUCT COMPOSITION

Tables 17.2–17.5 show some detailed product composition of different plastic feeds, pyrolyzed in a laboratory or pilot plant [11, 12].

It can be seen that under these conditions high amounts of aromatics are produced. The benzene content is 12.2 wt% at a pyrolysis temperature of 740°C and 24.75 at 780°C. Other main components of the PE pyrolysis (780°C) are methane, ethylene, and propene as gas and toluene, naphthalene as aromatics. The amount of carbon soot is low. Tire pyrolysis produces mainly carbon black (filler), gas, and aromatics. Steel cord is one of the other main products if whole tires are fed.

The pyrolysis of polypropylene gives similar results to the pyrolysis of polyethylene (Table 17.3). The amount of methane and oil is slightly higher, the amount of aliphatics is lower. The feedstock recycling of polyolefins is easy. Up to 50 wt% can be obtained as aromatics if the pyrolysis gas is cycled and used as fluidizing gas. The other 50% are gas components. Benzene and toluene reach 25 wt%.

A real plastic waste collected by the German Dual System (DSD) from municipal packaging waste was pyrolyzed in the laboratory plant as well as in the pilot plant. The composition of the mixed plastic wastes is shown in Table 17.4.

Beside polyolefins it contains polystyrene, polyesters, and PVC up to 4% and others. Table 17.5 gives a detailed composition of the obtained pyrolysis products.

The results are similar to those with polyolefins as feedstock, but the amount of styrene is higher because of the high amount of polystyrene in the feed. The HCl coming out from PVC was quantitatively absorped by calcium oxide which was added in 5% weight to the feed. The $CaCl_2$ formed was separated in the cyclone after the fluidized-bed reactor.

No chlorine was found in the gas fraction. The oil (run at 728°C) contains 15 ppm chloroorganic compounds, mainly chlorobenzene, the soot separated by the cyclone contains 18.4 wt% $CaCl_2$. There were no chlorinated dibenzodioxines (TCDD) or furane (TCDF) found in the oil (detection limit 0.01 ng/g).

Table 17.2 Pyrolysis of polyethylene (PE), used syringes, and tires by the Hamburg Pyrolysis process in a fluidized-bed using pyrolysis gas as fluidizing gas. Products in wt%

Reactor Feed Material Temperature (°C)	LWS PE 740	TWS1 PE 780	TWS1 Used syringes 720	TWS1 Tire pieces 750	TWS2 Whole tires 700
Hydrogen	0.5	0.17	0.49	1.30	0.42
Methane	16.1	20.27	19.09	15.13	6.06
Ethane	5.3	4.33	6.64	2,95	2.34
Ethylene	25.4	16.89	15.44	3.99	1.65
Propane	+	0.80	0.12	0.29	0.43
Propene	9.03	5.35	9.93	2.50	1.53
Butene	0.5	0.08	3.03	1.31	1.41
Butadiene	2.8	1.28	1.38	0.92	0.25
Isoprene	+	0.09	0.31	0.34	0.35
Cyclopentadiene	1.0	2.63	2.08	0.39	0.25
Other aliphatic compounds	13.3	0.69	3.13	0.36	1.07
Benzene	12.2	24.75	13.62	4.75	2.42
Toluene	3.6	5.94	4.20	3.62	2.65
Xylene	1.1	+	+	+	+
Styrene	1.1	1.46	0.45	0.17	0.35
Indan, Indene	0.3	1.27	0.46	0.31	0.48
Naphthalene	0.7	3.73	2,48	0.85	0.42
Methylnaphthalene	0.15	0.84	0.92	0.83	0.67
Diphenyl	0.02	0.34	0.33	0.49	0.39
Fluorene	0.01	0.29	0.15	0.15	+
Phenanthrene	0.02	0.59	0.47	0.29	0.19
Pyrene	+	0.22	+	0.21	0.06
Other aromatic compounds	5.1	5.40	8.24	8.50	13.67
Carbon monoxide				3.80	1.48
Carbon dioxide				1.95	1.74
Water				0.10	5.11
Hydrogen sulfide				0.23	0.02
Thiophene				0.15	0.25
Carbon soot, fillers	0.9	1.50	5.80	40.59	40
Steel cord				1.62	11.30

LWS laboratory-scale reactor; TWS1 pilot plant; TWS2 pilot plant for whole tires; + trace detection

To recover a maximum of olefins and butadiene from recycling polyolefins, it is necessary to have a short residence time of the product gases in the fluidized bed zone to avoid no secondary reactions. The pyrolysis gas should not be circulated and used as fluidizing gas. For the experiments, steam was used as fluidizing gas [13, 14]. An easy separation of the hydrocarbon products is possible by condensation to water in a cooler. The results are shown in Table 17.6. As feedstock a light plastic fraction from household waste separation was used which contains 95.8% of PE and PP, 3% of PS, and 0.2% of PVC.

In all experiments, the pyrolysis products are rich in olefins. The highest yields are produced at 690 and 700°C. The yield of ethylene is 29–31 wt%, of propene 14–18

Table 17.3 Pyrolysis of polypropylene (PP) and mixtures of PP and PE in the pilot plant (TWS1) using pyrolysis gas as fluidized gas. Products in wt%

Temperature (°C)	740	760	710	720
Feed	PP	PP	PP:PE(1:1)	PE:PP(5:1)
Throughput (kg)	435	330	355	325
Hydrogen	0.63	0.74	0.28	0.46
Methane	20.60	28.21	17.17	15.25
Ethylene	13.32	13.90	15.36	18.31
Ethane	4.43	4.01	5.91	7.85
Propane	0.16	0.09	0.08	0.19
Propene	7.09	3.69	9.71	8.01
1-Butene	2.32	0.17	1.06	0.62
2-Butene	0.11	0.21	1.29	0.22
1,3-Butadiene	0.96	0.41	1.90	1.75
Pentene	0.28	0.10	0.69	0.35
Isoprene	0.08	0.21	0.53	0.04
Pentadiene	0.05	0.11	0.36	0.26
Cyclopentene	0.11	0.15	0.55	0.36
Cyclopentadiene	0.50	0.23	1.11	1.11
Dicyclopentadiene	0.96	0.62	1.01	1.50
Hexene	0.02		0.15	0.09
Hexadiene	0.03		0.03	0.08
Methylcyclopentane	0.02	0.01	0.05	0.05
Methylcyclopentene	0.05		0.002	0.02
Cyclohexene		0.01	0.19	0.11
Cyclohexadiene	0.04	0.01	0.08	0.09
Other aliphatics	0.08	0.05	0.23	+
Benzene	18.12	18.23	15.28	19.31
Toluene	6.67	6.64	6.08	4.93
Styrene	0.08	0.99	0.79	0.71
Vinylbenzene	0.11	0.11	0.12	0.12
α-Methylstyrene	0.11	0.13	0.08	0.01
Indane	0.19	0.20	0.22	0.31
Indene	0.62	0.82	0.52	0.83
Methylindane	0.11	0.06	0.14	+
Methylindene	0.36	0.30	0.32	0.45
Naphthaline	3.15	3.48	2.52	3.22
Dimethylindene	0.04		0.02	0.02
2-Methylnaphthaline	0.60	0.56	0.47	0.46
1-Methylnaphthaline	0.42	0.35	0.32	0.35
Diphenyl	0.38	0.35	0.29	0.56
Ethylnaphthaline	0.12	0.08	0.07	0.04
Dimethylnaphthaline	0.10	0.09	0.04	0.06
Acenaphthylene	0.22	0.23	0.14	0.16
Acenaphthene	0.02	0.04	0.03	0.04
Fluorene	0.25	0.30	0.16	0.22
Methylfluorene	0.12	0.07	0.07	0.11
Phenanthrene/anthracene	0.60	0.68	0.43	0.44
1-Phenylnaphthaline	0.01	0.01	0.02	0.01
2-Phenylnaphthaline	0.01	0.02	0.02	0.01
Methylphenanthrene	0.10	0.12	0.10	0.05
Fluoranthene	+	0.04	0.03	0.01
Pyrene	0.09	0.22	0.09	0.08
Other aromatics	13.61	10.73	12.48	9.62
Carbon soot, fillers	1.61	1.70	1.41	1.85
Total gas (H_2, C_1–C_4)	46.62	51.43	52.76	52.66
Total oil > C_4	46.94	45.87	44.68	44.92
Total aromatics	44.52	44.27	39.49	40.86

Table 17.4 Different compositions (A and B) of the mixed plastic wastes used in wt% collected by the DSD system

Fraction (feed)	A	B
Polyolefins	65	65
Polystyrene	14	25
PVC	3.8	1.2
Polyester/paper	7.2	1.5
Other plastics	2.0	1.3
Water	4.0	4.1
Fillers, metals	4.0	1.9

Table 17.5 Mass balance of the pyrolysis of mixed plastics (different fractions A and B see Table 17.4) in a fluidized bed with different feedstocks and plants using pyrolysis gas for fluidization

Plant	LWS5	LWS5	LWS5	LWS5	TWS1
Throughput (g)	1185	1165	1230	2800	212 kg
Feed	A	A	A	B	B
Temperature (°C)	685	710	716	738	730
Gases (total)	41	44	43	38	35
Hydrogen	0.4	0.5	0.6	0.7	0.4
Carbon monoxide	4.6	5.5	6.0	1.3	1.3
Carbon dioxide	2.0	2.5	1.7	0.6	0.4
Methane	10.9	12.3	16.2	20.5	11.9
Ethylene	8.6	8.9	10.1	10.3	8.9
Ethane	4.0	3.9	3.3	2.2	3.9
Propene	6.3	6.0	3.2	1.0	5.0
Propane	0.5	0.6	0.2	0.1	0.6
n,*i*-Butane	0.08	0.08	0.05	0.19	0.03
n,*i*-Butene	2.1	2.3	0.7	0.1	1.6
Butadiene	0.8	0.9	0.7	0.5	0.7
trans-2-Butene	0.2	0.2	0.1	0.1	0.2
cis-2-Butene	0.2	0.2	0.1	0.1	0.1
Other gases	0.1	0.1	0.1	0.3	0.1
Oils (total)	48	44	45	50	51.8
Paraffins C_5–C_6	5.7	4.9	2.2	0.7	3.1
Paraffins C_7–C_9	2.3	1.6	0.5	0.2	0.5
Benzene	9.5	10.8	14.	17.4	9.1
Toluene	6.7	6.1	4.8	3.9	7.6
Xylene	0.6	0.6	0.5	0.2	0.8
Ethylbenzene	0.9	1.0	0.9	0.2	2.5
Styrene	9.0	7.9	6.8	8.7	10.8
C_3-Benzene	0.6	0.5	0.5	0.5	1.2
Methylstyrene	1.4	1.1	1.5	0.2	1.6
C_4-Benzene	0.1	0.1	0.1	0.3	1.1
Indene	0.6	0.8	2.1	2.5	1.2
Methylindene	0.4	0.3	0.5	0.3	0.7
Naphthalene	0.8	1.2	4.2	7.2	2.3
Methylnaphthalene	0.3	0.4	0.5	0.1	1.0
Diphenyl	0.1	0.1	0.2	0.1	0.4
Fluorene	0.04	0.07	0.05	0.18	0.1
Phenanthrene/anthracene	0.01	0.02	0.04	0.63	0.2
Other aromatics	0.7	0.6	0.6	0.5	2.5
Oxygen compounds	0.1	0.3	0.01	0.01	0.01
Nitrogen compounds	0.02	0.1	0.01	0.01	0.01
Other compounds	8.1	5.8	5.0	6.2	5.1
Distillation residue	5.8	5.6	6.3	6.5	11.0
Soot/fillers	5.2	6.4	5.7	5.5	2.2

Table 17.6 Feedstock recycling of polyolefin mixtures to high amounts of olefins using steam as fluidizing gas by different pyrolysis temperatures

Temperature (°C)	655	690	700	700	750	805
Residence time reactor (s)	2.7	1.8	2.3	3.2	2.9	3.1
Products (wt%):						
Gases	68	75	72	72	69	58
Hydrogen	0.4	0.6	0.6	0.6	0.9	1.3
Carbon monoxide	1.3	1.3	1.0	1.4	0.8	1.4
Carbon dioxide	0.6	0.9	1.4	1.3	1.6	2.2
Methane	5.4	8.9	11	8.8	13	13
Ethylene	24	29	31	30	36	30
Ethyne	0.08	0.3	0.3	0.4	0.8	1.3
Ethane	2.9	3.3	3.4	2.8	0.8	1.7
Propene	18	18	14	15	8.4	3.2
Propane	0.6	0.7	0.5	0.5	0.2	0.07
n/*i*-Butene	6.7	4.7	2.2	310	0.6	0.2
cis/*trans*-2-Butene	0.7	0.9	0.6	0.7	0.3	0.08
Butadiene	7.1	6.9	5.4	6.4	4.0	2.2
Aliphatics	9.8	7.2	3.7	4.5	1.5	0.7
C_5-Hydrocarbons	6.9	4.6	2.8	3.4	1.5	0.7
C_6-Hydrocarbons	2.4	1.2	0.5	0.6	0.03	0.01
BTX-aromatics	5.9	9.8	13	9.9	14	16
Benzene	3.9	6.8	9.4	7.4	11	13
Toluene	1.9	2.7	3.2	2.4	2.8	2.4
Other aromatics	2.6	4.6	6.0	4.6	7.7	7.7
Styrene	1.0	1.6	1.8	1.4	2.1	2.1
Indene	0.2	0.5	0.7	0.6	1.0	1.1
Naphthalene	0.2	0.7	1.4	0.8	2.7	2.9
Total oil	18	22	23	19	24	24
Distillation residue	13	3.4	4.7	8.5	6.4	18
Soot	0.6	0.4	0.6	0.9	0.8	0.7

wt%, of butanes 2–5 wt%, and of butadiene 5–7 wt%, a total of more than 59 wt%. This is even higher than naphtha crackers produce (55%). The other components produced are pyrolysis benzene 24–26 wt%, methane 9–11 wt%, and styrene 1.4–1.8 wt% because of the small amount of PS in the plastic feed. Similar results can be obtained if nitrogen is used instead of steam as the fluidizing gas. Steam reduces the formation of soot.

As shown, it is possible to recover directly high amounts of olefins similar to that of a naphtha crackers from polyolefin wastes. For selling, the olefins have to be cleaned up in distillation plants. To avoid problems with HCl from unexpected PVC fractions, it is safer to produce from polyolefins a waxy material which can be analyzed and, if free from HCl and chloroorganic compounds, mixed with naphtha and used as cracker feed. This was the concept of BP Chemicals. The test runs were made in our Hamburg laboratory plant (LWS3) [15]. Detailed material balances for experiments are provided in Table 17.7

To obtain low amounts of gas and aromatics, the pyrolysis temperature was mild and varied from 450 to 530°C. Only 1–8 wt% of gas is produced. With a heat of combustion of some 47 MJ/kg, it can be used for the indirect heating of the fluidized bed. The waxes

Table 17.7 Pyrolysis of polyolefins in a fluidized bed (LWS3) using nitrogen as fluidizing gas at low temperatures to recover oily and waxy products; products in wt%

Temperature (°C)	530	510	510	510	510	450
Material	HDPE	HDPE	LLDPE	PP	Mix	LLDPE
Input (kg)	1.6	2.7	5.5	4.9	4.6	1.8
Throughput (kg/h)	0.9	0.9	1.1	1.0	0.9	1.0
Methane	0.8	0.3	0.4	0.6	0.4	0.1
Ethylene	2.0	0.6	0.8	0.5	0.6	0.2
Ethane	0.8	0.3	0.6	1.0	0.5	0.2
Propene	1.8	0.7	0.8	3.0	1.5	0.2
Propane	0.7	0.3	0.3	0.4	0.3	0.2
Butenes	1.1	0.3	0.5	0.7	1.0	0.2
Total gas	**7.6**	**2.6**	**3.4**	**6.3**	**4.7**	**1.1**
Pentenes	0.1	0.2	0.3	0.5	1.0	0.1
Pentanes	0.03	0.1	0.1	1.2	1.7	0.1
Pentadienes	0.1	0.1	0.1	0.1	0.2	0.04
Hexenes	0.9	1.0	1.0	1.7	2.3	0.4
Hexanes	0.2	0.2	0.2	0.2	0.4	0.1
Hexadienes	0.1	0.1	0.1	0.5	0.4	0.03
Heptenes	0.8	0.6	0.6	0.6	1.0	0.3
Heptanes	0.3	0.4	0.3	+	0.3	0.2
Heptadienes	0.01	+	+	0.5	0.2	0.01
Octenes	0.6	0.4	0.5	0.3	0.4	0.3
Octanes	0.2	0.2	0.2	0.3	0.4	0.2
Octadienes	0.03	0.01	0.02	0.2	0.01	0.01
Nonenes	0.7	0.4	0.4	7.8	4.2	0.2
Nonanes	0.2	0.2	0.2	0.3	0.4	0.2
Nonadienes	0.1	0.1	0.04	0.1	0.1	0.02
Decenes	1.0	0.7	0.7	0.8	0.8	0.4
Decanes	0.2	0.2	0.2	+	0.1	0.2
Decadienes	0.1	0.1	0.1	+	0.03	0.04
Total C_5–C_{10}	6.9	5.2	5.6	15	14	3.4
Total C_{11}–C_{20}	9.9	6.9	6.7	13	5.7	6.1
Total $> C_{20}$	34	24	24	35	37	18
Total BTX-aromatics	0.3	0.05	0.05	0.02	0.1	0.03
Total waxes bp < 500°C	51	36	37	64	57	28
Total waxes bp > 500°C	42	61	60	30	38	71

Mix PP/LLDPE/HDPE: 40/15/45, wt%; + detected, but not quantified

are made of hydrocarbon groups forming a homologous series when pure polyethylene is used as feedstock. The alkenes, alkanes, and alkadienes of each group are their main components. The total amount of waxes reaches 93–99 wt%, while the total amount of aromatics is less than 0.5 wt%.

Beside the polyolefins described polystyrene (PS), polymethylmethacrylate (PMMA), polytetrafluoroethylene (PTFE) (see Chapter 24) and polyester (PET) [16], polyamide (PA) [17], polyurethane (PUR) [17], and polyepoxides [18] were used as feedstock for the Hamburg process. The fluidized-bed process is very flexible for different feeds and process parameters.

3.1 INDUSTRIAL PILOT PLANTS

The first industrial pilot plant using the Hamburg pyrolysis process was built in 1983 at Ebenhausen/Ingolstadt by Deutsche Reifen und Kunststoff-Pyrolyse (DRP) and later operated by Asea Braun Bovery (ABB). The plant contains two fluidized-bed reactors, each with a diameter of 1800 mm. A scheme is shown in Figure 17.6 [19]. The heating tubes are in contact from the top of the reactor to the fluidizing sand bed (Figure 17.7). Impurities such as metal particles and stones, glass and sand can be removed at the bottom by a water cup to avoid the loss of gases.

One reactor was used for the feedstock recycling of plastics and the other for tires. The feedstock passes a lock and then is transported by a screw conveyor into the fluidized bed. Exhaust gases from the heating tubes are used to render the feedstock inert.

The product gas is cleaned up from solids by hot-working cyclones, and then cooled down. In the first step, high-boiling oil is obtained. After compression and cooling, low-boiling oil is separated. The oil-free gas is used as heating gas for the heating tubes and for fluidization. The capacity of the plant was 800 kg plastics per hour in one reactor. In this time, scrap material from cable dismantling (cross-linked polyethylene), polypropylene carpet wastes, and mixed plastics from household waste separation were used as feedstock. The most valuable light-oil fraction reached 40 wt%. The composition is shown in Table 17.8.

The necessary electrical power for 1 ton of plastic operation was measured to be between 200 and 280 kW. The heating tubes consumed 19 wt% of the plastic products as

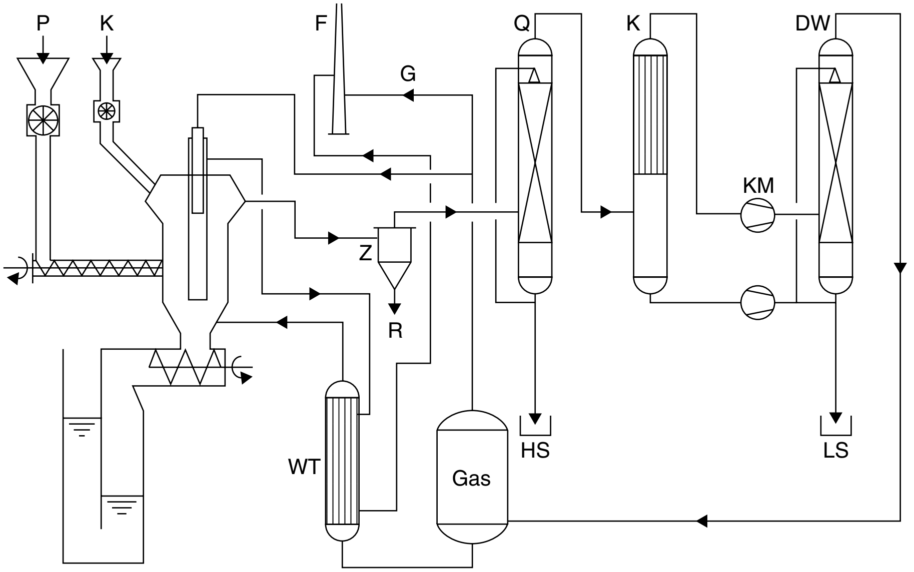

Figure 17.6 Scheme of the industrial pilot plant for the pyrolysis of 5000 t/yr plastics or tires. Z cyclone; Q quench cooler; K cooler; DW high-pressure quench cooler; KM compressor; WT heat exchanger; F flare; G excess gas; R carbon black; P plastic feed; K: calcium oxide, LS low-boiling oil; HS high-boiling oil

Figure 17.7 View of the top of the fluidized-bed reactor, DRP plant with the inlet of the 12 fire tubes

Table 17.8 Composition of pyrolysis light oil obtained at the DRP plant in Ebenhausen, compared with pyrolysis benzene (PBC) from a cracker

Feedstock	PBC	CPE	CPP	MPW
Benzene	40	43.7	18.6	17.5
Toluene	20	15.9	14.6	12.5
Xylene	8	2.9	12.2	9.0
Styrene		8.1	16.3	15.0
BTX + styrene	68	70.6	71.7	54.0
Others	32	29.4	28.3	46.0

Fluidized bed temperature 700°C. CPE cross-linked polyethylene; CPP: carpet polypropylene waste, MPW: mixed plastic waste

gas. There is more gas produced (40–50 wt%) than needed for the heating and electrical power. The composition of the gas can be seen in Table 17.9.

The heating value of the gas varies between 10.3 to 13.5 kW h/m^3. The plant ran for two years from 1984 to 1985. It was then closed because the crude oil price decreased and this small plant of about 5000 ton plastics per year and 5000 ton tires per year was uneconomic.

The industrial pilot plant built up in Grimma, Germany for the pyrolysis of 5000 whole tires per year has a similar structure to that of the university plant, shown in Figure 17.5. There was only one reactor with a size of 2000 × 3600 mm. A picture of the plant is shown in Figure 17.8. The plant ran until the reunification of Germany in late 1989 and

Table 17.9 Composition of the pyrolysis gas in the DPR plant in Ebenhausen, obtained from different feedstocks (see Table 8) at 700°C in volume%

Feedstock	CPE	CPP	MPW
Hydrogen	18.8	14.4	30.0
CO_2	1.9		1.4
CO	5.7	2.1	7.2
Methane	58.2	45.5	51.8
Ethylene	10.2	13.2	5.7
Ethane	3.0	7.7	1.2
Propene	1.2	7.7	0.1
Others	1.0	9.4	2.6

Figure 17.8 View of the Grimma plant for feedstock recycling of whole tires, in front two cyclones to separate the carbon black

was then closed down. The plant required too many workers for recycling only 5000 tons of tires a year. The most valuable compound was carbon black which was reused again for tire production.

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18

Liquefaction of PVC Mixed Plastics

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1 INTRODUCTION

In today's modern world, plastics make a fundamental contribution to all activities such as agriculture, the automobile industry, electricity and electronics, building materials, packing and so on. Recently, plastics have shown rapid and visible growth compared with other materials. This is primarily because of substitution of other materials with plastics as well as their applications in new areas, and material's durability and versatility. Plastics are low-cost materials and widely used, they can be easily processed into light but durable materials with low thermal and electrical conductivity. The rapid growth in plastics consumption is increasing and subsequently plastic waste is accumulated, and poses serious problems to the environment due to their non-biodegradable nature. The world's annual consumption of plastic materials has increased around 5 million tons in the 1950s to nearly 150 million tons today. Due to the world's limited reserve of coal, crude oil and natural gas, it becomes very urgent to preserve the existing non-renewable materials. Various recycling methods have been developed and being used now. However, reduction or minimizing the consumption of raw materials through the novel design of products may allow the reduction of wastes generated.

Recovery can be classified as material recycling and energy recovery. Material recycling can be performed using two approaches such as mechanical recycling and feedstock recycling. In general, recycling must be applied only when the amount of energy consumed in the recycling process is lower than the energy required for the production of new materials. Mechanical recycling is performed in the following manner. The waste plastics are collected, sorted, washed to remove contaminants, baled, shredded into flakes and then placed into an extruder by heat and reprocessing into new plastic goods. This technique is limited to thermoplastics and not applicable to thermosets; compatibility between the different types of polymers also poses problems. Another difficulty with mechanical recycling is the presence of plastic waste products made of the same resin, but with

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different colors, which usually impart an undesirable grey color to the recycled plastic. Finally, the recycled polymers usually exhibit lower properties and performance than the virgin material, and are useful only for undemanding applications. Mechanical recycling can be performed solely on single-polymer plastic waste because a market can be found only if the recycled products match the original products as closely as possible in quality. Feedstock recycling is the process for conversion of waste plastics into chemicals and fuels. The detailed discussion on feedstock recycling will be provided in the following sections.

If neither secondary market nor feedstock recycling is possible, incineration can be applied to produce energy from the waste plastics combustion. Plastic wastes greatly contribute to the energy production in incineration plants, as plastics are materials of high calorific value. They can be used in cement kilns, industrial furnaces or power plants. However, there are problems with the halogen-, i.e. chlorine- and bromine-containing plastics due to the possible formation of dioxins during the incineration. Incineration of plastic waste to produce heat may be a possibility, but its organic content would totally be destroyed and converted into CO_2 and H_2O. The nonavailability of proper landfill sites and opposition from the public can make landfilling difficult.

On the other hand, plastic waste has a high content of organic materials and energy that is totally lost by disposal or is recovered only in a very small amount by incineration. Due to the world's limited reserve of coal, crude oil and natural gases it becomes very urgent to preserve the existing non-renewable materials and to find other carbon sources as feedstock materials or as fuels. Pyrolysis is one of the best methods to recover the material and energy from polymer waste, as only about 10% of the energy content of the waste plastic is used to convert the scrap into valuable hydrocarbon products. This is obtained by breaking down polymers at high temperatures into petrochemical feedstock components from which they originate while the additives in the polymer materials (e.g. metals, inorganic fillers and supports) remain in the pyrolysis residue. New pathways in plastic recycling and status of plastics recycling have been recently highlighted by Kaminsky and Hartmann [1]. The development of different viable recycling technologies for plastic waste materials is becoming increasingly important. There is growing interest in thermolysis and catalytic polymer degradation as methods of producing various fuel fractions from polymer wastes. Pyrolysis is one of the best methods for preserving valuable petroleum resources in addition to protecting the environment by limiting the volume of nondegradable waste. Pyrolysis of waste plastics is favored because of the high rates of conversion into oil. The gaseous products coming from the pyrolysis process with high caloric value may be used as fuel in the process. Recycling by pyrolysis has high potential for heterogeneous waste materials, which cannot be economically separated.

There has been a plethora of research work published on the pyrolysis of waste plastics into fuel. Pyrolysis involves the thermal degradation of organic matter in an oxygen free environment. Kastner and Kaminsky [2] studied the thermal cracking of PE in a fixed-bed reactor over the temperature range 500–600°C. At temperatures below 550°C, high yields of useful products with low yields of gas and aromatics were obtained. Ding *et al.* [3, 4] have studied hydrocracking of PE using HZSM-5 and metal-loaded hybrid catalysts prepared from HZSM-5 and silica–alumina. HZSM-5 produced more aromatic hydrocarbons, whereas hybrid catalysts (especially Ni-loaded) showed higher hydroisomerization ability. An interesting result was that the liquid products obtained over hybrid catalysts were clean and white or light yellow with a gasoline-like smell, while the liquids produced from thermal cracking and over HZSM-5 were brown red with a strong unpleasant smell. Aguado *et al.* [5] investigated the effect of β-zeolite on the degradation of PP, LDPE and HDPE at 400°C in a batch reactor. It was observed that degradation of HDPE affords a high selectivity of C_5–C_{12} products (70 wt%) whereas in the cracking of LDPE and PP, selectivity to gasoline is reduced (64 wt%) and higher proportions of lighter products C_1–C_4 are obtained. Dehydrochlorination of plastic mixtures was studied by Bockhorn *et al.* [6–7]. They explained how stepwise low-temperature pyrolysis mixtures of PVC, polystyrene and polyethylene have been separated into hydrogen chloride, the monomer of polystyrene and aliphatic compounds from polyethylene decomposition. The degree of conversion of chlorine from PVC into hydrogen chloride in the low temperature (330°C) is about 99.6% [7]. Sen and Pifer reported the chemical recycling of plastics to useful organic compounds by oxidative degradation [8]. The new procedure for the oxidative degradation of polythene to valuable α,ω-diacids under fairly mild conditions [9].

Pyrolysis of plastic wastes and the effect of plastic waste composition on product yield [10], and the effect of catalyst on product yield have been discussed in detail [11]. The liquefaction of waste plastics into fuels have been studied by various researchers using the model mixed plastics and real waste plastics. Novel tertiary plastics recycling method for the production of fuel over microporous catalysts were reported by Gobin and Manos [12a]. They reported that the US-Y is the most active catalyst, but produced the highest amount of coke, due to its strong acidity. Whereas, the presence of ZSM-5 increased the yield to gaseous products and decreased the coke content, due to their small pores (shape-selective catalysts). Pyrolysis of individual plastics and plastic mixtures in a fixed-bed reactor was performed by Williams and Williams [13]. Production of harmful compounds such as PAHs were produced during the pyrolysis of polyvinyl chloride, polyvinyl benzyl chloride or polychloro styrene [14]. Hydrogen chloride formed by elimination from PVC depresses the formation of PAHs more effectively in the presence of iron. Chlorine from polyvinyl benzyl chloride increased the production of PAHs in the presence of copper. The effect of carbon black on the thermal decomposition of vinyl polymers were studied by Jakab and Blazso [15]. In our earlier studies [16–18], we have reported on the catalytic degradation of PP and PE by silica–alumina catalyst in a semi-batch reactor and showed that silica–alumina was effective in increasing the degradation rate and yield of oil products. The studies [18–21] on the effect of catalyst type on polymer degradation indicated that the catalysts with strong acid sites such as zeolite accelerated the degradation of PP and PE into gases, which resulted in low liquid yields.

Pyrolysis of non-halogenated polymers such as polyethylene, polypropylene, and polystyrene is simple and the liquid products obtained by thermal degradation can be used as fuel oil or as a feedstock. However, municipal waste plastics or commingled waste plastics from packaging and other sectors contain chlorine plastics such as polyvinyl chloride or polyvinylidene chloride. The pyrolysis of PVC-containing mixed plastics produce corrosive mineral acid (HCl) and chlorinated organic compounds in the liquid products. The presence of such chlorine compounds in the liquid products is not desirable to use as a fuel or feedstock. The key technology for the utilization of valuable organic content from PVC-containing mixed plastics is the dehalogenation of liquid products. Compared with studies, on non-halogenated plastics pyrolysis halogen-containing plastics pyrolysis and dehalogenation studies are few in the literature. The thermal and catalytic degradation of individual PE/PVC, PP/PVC, and PS/PVC by silica–alumina catalysts and dechlorination by iron oxides (FeOOH and Fe_3O_4 sorbents) has been studied [20–22]. The halogen-free liquid products can be produced in two stages, i.e. degradation and dehalogenation or simultaneous degradation and dehalogenation (single stage) of PVC-containing plastics. The following sections will address the detailed information on the development of various catalysts, sorbents for dechlorination, dechlorination of plastic-derived oil with chlorine compounds (plastic-derived oil obtained in first step of a two-stage process), simultaneous degradation and dehalogenation of various commingled plastics, and finally application of this process to the real municipal waste plastics.

2 EXPERIMENTAL AND ANALYTICAL METHODS

2.1 PREPARATION OF IRON AND CALCIUM COMPOSITES

Calcium carbonate, iron oxide carbon composites were cooperatively prepared with Toda Kogyo Corporation, Hiroshima, Japan. Briefly, about 90 wt% of calcium carbonate is mixed with 10 wt% phenol resin by mechanical kneading, during the kneading process 20% of water is added to the mixture and pellet formation is achieved by extrusion. The prepared sorbent was calcined at 500°C for 1 h in a nitrogen atmosphere and in the calcination process the phenol resin was converted into carbon. The addition of phenol resin and calcination gave good mechanical strength and loss of hygroscopic nature of the sorbent, which are important parameters for the successful use in pilot plant. The finished sorbent designated as Ca-C [calcium carbonate carbon composite]. In a similar way with the same weight ratios of active component to the carbon material, the iron oxide carbon composite sorbent with α-FeOOH was prepared. The physical properties such as surface area (BET), and pore volume were obtained from nitrogen adsorption analysis and they are as follows:

Sorbent	BET surface area (m^2/g)	Pore volume, (mL/g)
Ca-C ($CaCO_3$)	40	0.11
Fe-C (Fe_3O_4)	83	0.44

2.2 EXPERIMENTAL PROCEDURE

A schematic diagram of the experimental set-up is shown in Figure 18.1. Pyrolysis of PP/PE/PS mixed with PVC was carried out in a glass reactor (length 350 mm; id 30 mm) under atmospheric pressure by batch operation with identical experimental conditions and temperature program. Briefly, 10 g of mixed plastics (weight ratio: PVC/PP/PE/PS = 1/3/3/3) was loaded into the reactor for degradation in vapor phase contact with Ca-C. The fresh PP/PE/PS and PVC grains were well mixed and used for degradation. The Ca-C (1 mm average diameter) was loaded into another reactor (dechlorination reactor) and the sorbent bed temperature was kept at 350°C. In a typical run, after setting the reactor, the reactor was purged with nitrogen gas at a flow rate of 10 mL/min and held at 120°C for 60 min to remove the physically adsorbed water from the sorbent and plastic sample. The reactor temperature was increased to the degradation temperature (430°C)

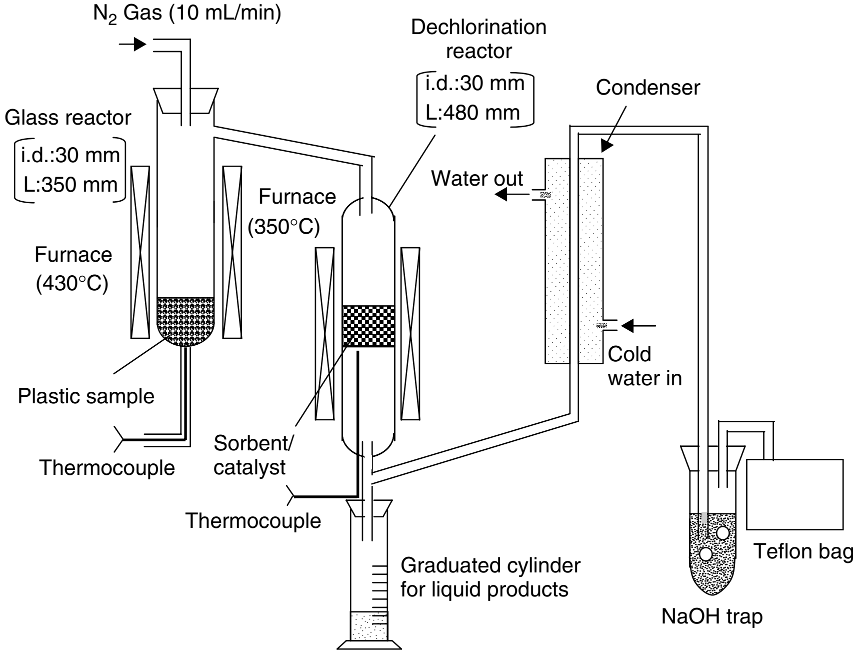


Figure 18.1 Schematic experimental set-up for pyrolysis of plastics and dehalogenation process. (Reproduced with permission from the American Chemical Society)

at a heating rate of 3°C/min (degradation reactor temperature program: room temperature, rate 3°C/min → 120°C, rate 3°C/min; hold 60 min → 430°C). The dechlorination reactor temperature (350°C) was increased linearly at a heating rate of 5°C/min (dechlorination reactor temperature program: room temperature → 350°C, rate 5°C/min). In a similar way, the thermal degradation of plastics was carried out in the absence of sorbent. The waste plastic bed temperature was taken as the temperature of the degradation and the sorbent bed temperature was taken for the dechlorination process (Figure 18.1). The gaseous products were condensed (using a cold water condenser, Figure 18.1) into liquid products and trapped in a measuring jar. 80 mL of 1 M NaOH was used for NaOH trap (container capacity 100 mL). The weight of a reactor including the mixed plastics was measured before and after the degradation process. The weight difference Δ before and after degradation was taken as a measure of liquid and gas yields. The residue (plastic feed, 10 g −Δ) was the difference between plastic feed and liquid and gas yields. There is very small amount of liquid products on the reactor walls and on side arm. In a similar way, other combinations of mixed plastic samples pyrolysis were performed.

2.3 ANALYSIS PROCEDURE

The quantitative analysis of the liquid products (collected once at the end of the experiment) was performed using a gas chromatograph equipped with a flame ionization detector (FID; YANACO G6800; column, 100% methyl silicone; 50 m × 0.25 mm × 0.25 μm; temperature program, 40°C, hold 15 min → 280°C, rate 5°C/min; hold 37 min) to obtain the quantity of hydrocarbons and carbon number distribution of the liquid products. The distribution of chlorine compounds and the halogen content (organic) in liquid products were analyzed by a gas chromatograph equipped with an atomic emission detector (AED; HP G2350A; column, HP-1; cross-linked methyl siloxane; 25 m × 0.32 mm × 0.17 μm). 1,2,4-Trichlorobenzene was used as the internal standard for the quantitative determination chlorine content using the GC-AED analysis. The amount of Cl content in NaOH trap (Figure 18.1) was analyzed using an ion chromatograph (DIONEX, DX-120).

The main liquid products were also analyzed by a gas chromatograph with a mass-selective detector (GC-MSD; HP 5973; column, HP-1; cross-linked methyl siloxane, 25 m × 0.32 mm × 0.17 μm; temperature program, 40°C, hold 10 min → 300°C, rate 5°C/min, hold 10 min) for the identification of various chlorinated hydrocarbons in liquid products. The composition of the liquid products was characterized using C-NP gram [23] (C stands for carbon and NP from normal paraffin) and Cl-NP gram (Cl stands for chlorine). The curves were obtained by plotting the weight percent of Cl, which was in the liquid products against the carbon number of the normal paraffin determined by comparing the retention times from GC analysis using a nonpolar column. The analysis of various degradation products are given in Figure 18.2.

2.4 HCl ADSORPTION CAPACITY

Reaction of hydrogen chloride with various composite sorbents was carried out using a fixed-bed microreactor (diameter 8 mm, length 470 mm). About 2 g of sorbent was loaded into the reactor in between two quartz wool plugs and reactor temperature was increased linearly (5°C/min) to 350°C in a nitrogen atmosphere (50 mL/min) and kept for an hour for the pretreatment (removal of moisture content) of sorbent. For low-temperature hydrogen chloride reaction process, the sorbent was pretreated at 350°C in N_2 atmosphere for an hour and cooled to the required adsorption temperature (100, 200, and 270°C). A high-temperature (400°C) reaction was carried out by pretreating the sorbent at 400°C for an hour in N_2 atmosphere followed by hydrogen chloride sorption. A known concentration of hydrogen chloride gas mixed with nitrogen gas was fed to the reactor and the outlet of reactor gases (not adsorbed HCl gas) was trapped using ion-exchanged water (600 mL). The ion-exchanged water trap was changed with a 1-h interval during all the sorption experiments. The quantity of inlet HCl concentration fed into the reactor over 1 h was determined in a separate experiment. The quantitative analysis of hydrogen chloride evolved from the reactor and trapped in ion exchanged water trap was carried out by an ion chromatograph (DIONEX: DX-120). The isothermal adsorption break through curves were plotted against reaction time (h) on the x-axis and the quantitatively estimated outlet HCl concentration (ion chromatograph) on the y-axis. The cylinder containing 2% (v/v) hydrogen chloride balance nitrogen was used.

3 FUNDAMENTAL STUDIES ON THE DECOMPOSITION OF PVC

3.1 PRODUCT DISTRIBUTION AND MECHANISM OF PVC DECOMPOSITION

Poly (vinyl chloride) (PVC) is essentially a linear polymer with a head-to-tail configuration. Theoretical calculations and model compound studies predicted that PVC of ideal

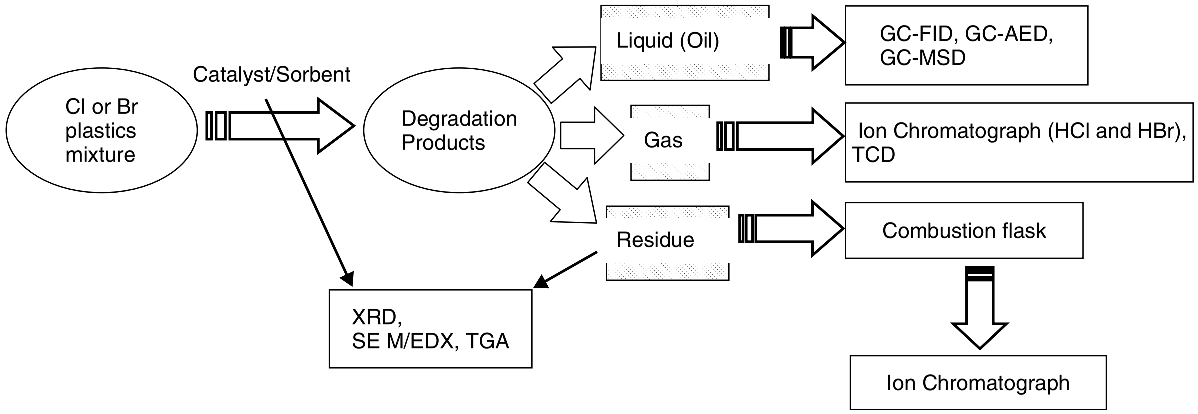


Figure 18.2 Analysis of degradation products and catalyst/sorbent

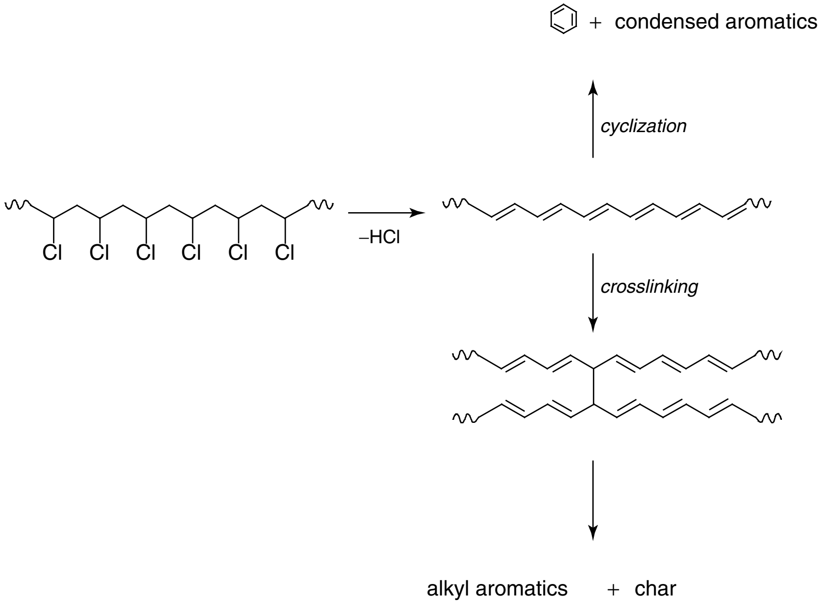
structure should be thermally stable. Nevertheless, pristine PVC has very low thermal and photo-oxidative stability. Thermoplastic processing requires elevated temperatures; however, PVC undergoes thermal degradation, oxidation and mechanochemical chain scission already above 100°C. In spite of the low thermal stability, PVC has become one of the most widely used plastics because the stabilization technology has developed greatly over the last 40 years and PVC is compatible with various plastic additives (stabilizers, plasticizers, fillers, etc.) [24].

The combustion of PVC leads to the formation of harmful polychlorinated dibenzodioxins, dibenzofurans and diphenyls; therefore, other recycling methods are necessary for the elimination and utilization of PVC-containing plastic wastes. The thermal decomposition of PVC begins with dehydrochlorination of the polymer chains. Long-term heat-treatment leads to HCl release already above 100°C. When PVC is heated at a 10°C/min heating rate in a helium atmosphere, the decomposition commences above 220°C. The DTG curve reveals three maxima. In earlier studies, the first two maxima were not well separated or were considered as one decomposition stage [25–27], while later studies identified three decomposition stages [28, 29]. The dehydrochlorination is a two-stage process. In the first step, benzene is evolved in addition to HCl at about 300°C. The second decomposition step is dominated by the release of HCl, which can be attributed to the dehydrochlorination of the irregular structures. From the irregular structures (branching, etc.), HCl can be eliminated at some what higher temperatures than from the regular polymer segments, and benzene formation is restricted. The third decomposition step takes place between 400 and 500°C and is dominated by the release of toluene, and other alkyl substituted aromatics. Methane was also detected by TG/MS, indicating the occurrence of charring reactions. In helium, 5% char is produced after the decomposition of PVC. The char yield strongly depends on the experimental conditions (e.g. atmosphere, sample size, heating rate) and can even reach 15% by analytical techniques.

The detailed product distribution of PVC pyrolysis can be studied by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), where the samples are heated at a high heating rate in helium atmosphere. At a lower temperature (400°C), unsubstituted aromatic compounds (benzene, naphthalene, anthracene and diphenyl) are detected in addition to HCl. However, the formation of benzene is dominant among the aromatic products. At higher pyrolysis temperature (550°C), the formation of substituted aromatic products (toluene, styrene, methyl indene, methylnaphthalene, etc.) and indene becomes significant besides the formation of low-temperature products. Alkenes, alkadienes and cyclic dienes are also formed during the third stage of degradation [30].

The formation of the major products can be described by the following mechanisms (Scheme 18.1). After initiation, HCl elimination takes place from the adjacent monomer units and conjugated double bonds are formed in the polymer chains. The average polyene sequence length is about ten double bonds. The formation of more extensive polyene chain segments is prevented by the defect sites in the polymer chains or by the subsequent degradation pathways. The polyene segments undergo cyclization accompanied by chain cleavages [31] resulting in the evolution of benzene and smaller amount of condensed aromatic compounds (naphthalene, anthracene, etc).

At low temperatures, PVC pyrolysis yields only traces of volatile chlorinated hydrocarbons. The main chlorine-containing hydrocarbons reported are methyl chloride, vinyl chloride, ethyl chloride and chlorobenzene. Heating PVC at 10°C/min up to 500°C in



Scheme 18.1 Major routes of the thermal decomposition of PVC

vacuum results in the evolution of several chlorinated organic compounds. Chlorinated alkenes, alkanes and alicyclic hydrocarbons as well as chlorobenzene and alkyl chlorobenzenes have been detected by McNeill *et al.* [27] The chlorinated compounds detected account for 0.14 wt% of the polymer and 1.75 wt% of the liquid fraction. Lattimer and Kroenke[12b] established that most chlorine-containing compounds are formed by secondary reactions of HCl with the products or polyenic segments of PVC as well as with the compounding ingredients of PVC. Direct scission of the PVC chains to form chlorine-containing products is a very minor degradation pathway.

3.2 DEGRADATION OF PVC – POLYMER MIXTURES

Recently the pyrolysis of polymer mixtures has become a focus of interest due to the increasing role of plastics recycling. Many researchers have investigated the thermal decomposition of various polymers in the presence of PVC. Knümann and Bockhorn [25] have studied the decomposition of common polymers and concluded that a separation of plastic mixtures by temperature-controlled pyrolysis in recycling processes is possible. Czégény *et al.* [31] observed that the dehydrochlorination of PVC is promoted by the presence of polyamides and polyacrylonitrile; however, other vinyl polymers or polyolefins have no effect on the dehydrochlorination. PVC generally affects the decomposition of other polymers due to the catalytic effect of HCl released. Even a few per cent PVC has an effect on the decomposition of polyethylene (PE) [32], HCl appears to promote the initial chain scission of PE. Day *et al.* [33] reported that PVC can influence the extent of degradation and the pyrolysis product distribution of plastics used in the electronics industry (acrylonitrile–butadiene–styrene polymer, polycarbonate, and polyoxymethylene). PVC promotes the hydrolytic decomposition routes of polyamides and the product distribution is changed significantly in the presence of PVC [34, 35]. Macropyrolysis of PVC and poly(ethylene terephthalate) (PET) mixtures results in the formation of a series of chloroorganic compounds including chloroesters of terephthalic and benzoic acids [36]. It was concluded that PET will reduce the efficiency of dehydrochlorination during the pyrolytic recycling process in an autoclave. The yield of liquid products decreased with increasing reaction pressure during the PVC degradation, whereas the yield of residue increased, reaching maxima at 9.8 MPa (400°C) and 22.4 MPa (440°C) [37]. The pressure dependences of the product distribution and atomic ratio of hydrogen to carbon (H/C) imply that some of the liquid products were polycondensed with the dehydrochlorinated PVC and were retained in the residue under high pressure. Some of the polyene chains underwent hydrogenation to form linear paraffins under high pressure [37]. The decomposition of polyvinyl chloride using supercritical water was also performed by Sato *et al.* [38].

4 LIQUEFACTION WITH COMMINGLED PLASTICS AND DECHLORINATION

4.1 PYROLYSIS OF PE, PP OR PS WITH PVC

Degradation of plastic samples can be performed in two different catalyst contact modes (Figure 18.3): (i) the catalyst is mixed with the plastic samples (catalyst with liquid phase contact); (ii) the catalyst is kept away from the plastic samples and the gas/vapors produced during the heat treatment contact the catalyst (catalyst with vapor phase contact). There has been extensive research work on the degradation of PVC mixed waste plastics into plastic-derived oil and dechlorination of plastic-derived oil by various catalysts/sorbents by Lingaiah *et al.* [39–42]. In the later stages, it was found that the simultaneous degradation and dehalogenation was found to be effective and can be performed successfully. The degradation of PE (8 g)/PVC (2 g) at 430°C, PP (8 g)/PVC (2 g) at 380°C and PS (8 g)/PVC (2 g) at 360°C into fuel oil was performed in a glass reactor (Figure 18.1) under atmospheric pressure by batch operation without any catalysts (thermal degradation). Table 18.1 shows the yield of products obtained from the degradation of PVC mixed plastics, and Table 18.2 shows the distribution of chlorine in products and chlorine content (both organic and inorganic) of oil. Liquid yield was highest (73 wt%) for PP/PVC and lowest (60 wt%) for PS/PVC degradation. The residue, which consists of both carbonaceous materials and heavier hydrocarbons, was highest in the case of PS/PVC degradation. From chlorine balance, 91–96 wt% of the chlorine content of the sample was evolved as gaseous HCl, 3–12 wt% as liquid, and less than 0.5 wt% as residues. The organic chlorine content of the oil from PP/PVC degradation was 12 700 ppm, which was the highest among the PVC mixed plastics. The oil obtained from PE/PVC mixed plastics degradation contained 2800 ppm.

Figure 18.4 shows the composition of the liquid product: (a) for hydrocarbons and (b) for organic chlorine compounds. The liquid products from both PE/PVC and PP/PVC are distributed broadly in the range C_5–C_{25}, and the distribution of products from PS/PVC had a sharp peak at C_9, which is mainly due to styrene monomer. The organic chlorine

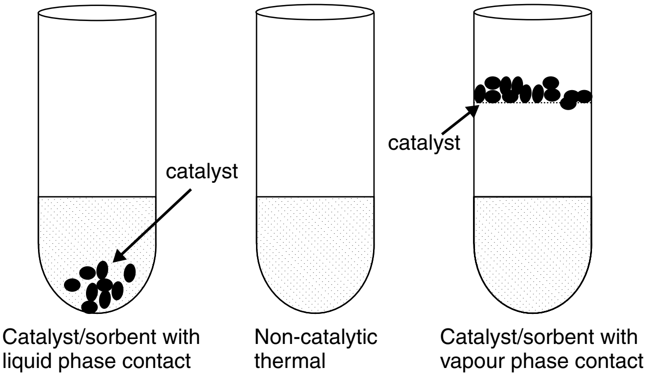


Figure 18.3 Schematic diagram of catalyst/sorbent contact mode during the liquefaction of plastics. (Reproduced with permission from the American Chemical Society)

Table 18.1 Yields of the products obtained from the degradation of (PE or PP or PS)/PVC[a] into fuel oil. (Reproduced with permission from the American Chemical Society)

	Degradation temperature (°C)	Product yield (wt%)			d^c (g/mL)	Cnp[d] (−)
		Liquid (L)	Gas $(G)^b$	Residue (R)		
PE/PVC	430	67.9	17.5	14.6	0.76	13.4
PP/PVC	380	73.2	12.8	14.0	0.78	13.0
PS/PVC	360	60.4	12.3	27.3	0.89	9.2

[a] Cl content of PVC polymer is 56.8 wt%;
[b] $G = 100 - (L + R)$;
[c] liquid density;
[d] average carbon number of liquid

Table 18.2 Distribution of Cl in the products obtained from the degradation of (PE or PP or PS)/PVC into fuel oil. (Reproduced with permission from the American Chemical Society)

	Degradation temperature (°C)	Cl distribution (wt %)						Cl content in oil (ppm)	
		Liquid		Gas	Residue				
		Organic	Inorganic	Inorganic	Organic	Inorganic	Total	Organic	Total
PE/PVC	430	1.8	1.1	96.6	0.1	0.1	99.7	2800	4500
PP/PVC	380	8.8	3.4	89.4	0.1	0.0	101.7	12700	17600
PS/PVC	360	4.2	1.8	91.8	0.5	0.0	98.3	7400	10500

compounds were distributed in the boiling point range 36–174°C (equivalent to the boiling points of n-C_6 to n-C_{10}) for PE/PVC and PP/PVC and 174–195°C for PS/PVC. The main chlorine compounds from PE/PVC and PP/PVC liquid products were identified as 2-chloro-2-methylpropane and 2-chloro-2-methylpentane, and from PS/PVC degradation were α-chloroethylbenzene and 2-chloro2-phenyl propane. Ivan *et al.* [43] have reviewed

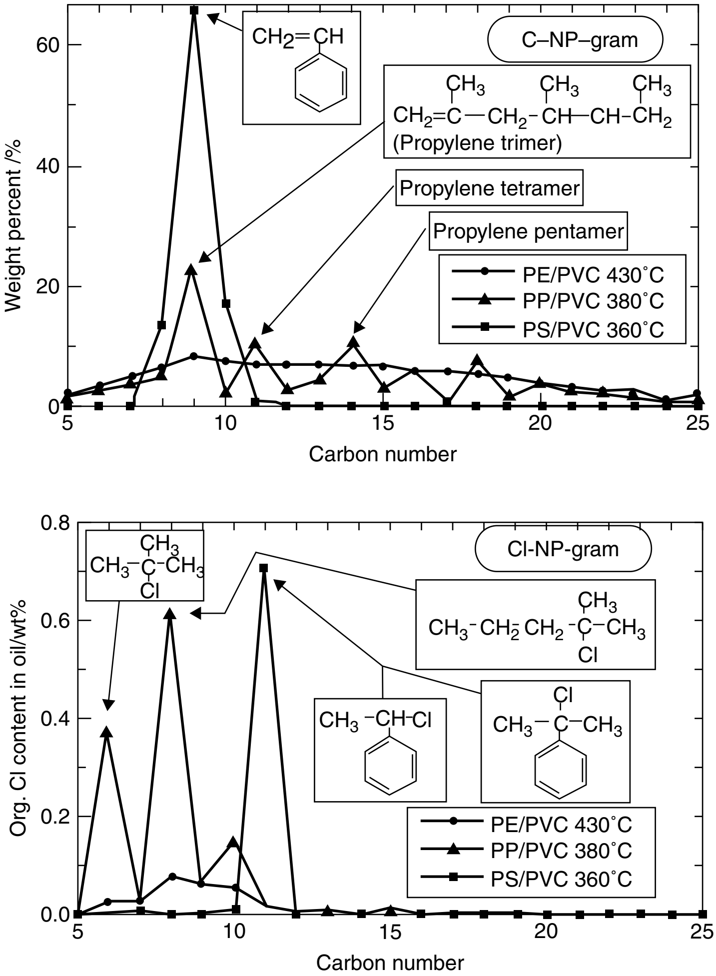


Figure 18.4 (a) C-NP gram of liquid products from thermal degradation of (PE or PP or PS)/PVC (8/2) mixture (10 g); (b) Cl-NP gram of liquid products from thermal degradation of (PE or PP or PS)/PVC (8/2) mixture (10 g). (Reproduced with permission from the American Chemical Society)

the mechanism of dehydrochloriantion of PVC. The degradation of PP/PVC mixture was carried out at 380°C in the presence of a silica–alumina (SA1) catalyst, which is known as an effective catalyst for the degradation of hydrocarbons. Figure 18.5 shows the C-NP gram of liquid products obtained from the PP/PVC at 380°C in the presence and absence of SA1 catalyst. The initial slope of the cumulative volume curve represents the initial recovery rate of oil. As can be seen, by the use of solid acid catalyst, the rate of oil recovery is increased and the weight fraction of heavier hydrocarbons decreased. Therefore, the solid acid catalyst accelerated the rate of oil recovery and lowered the boiling point distribution of products.

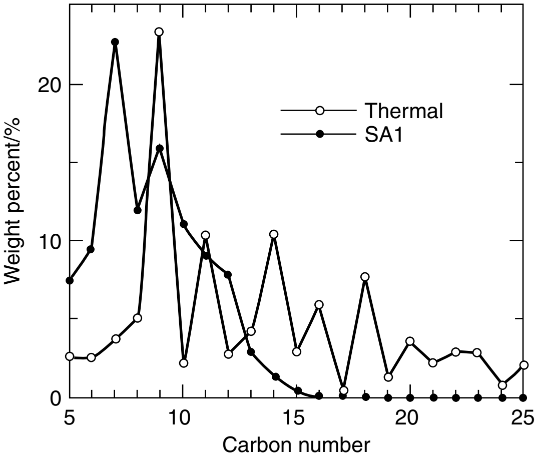


Figure 18.5 C-NP gram of liquid products from thermal and catalytic (SA1) degradation of PP/PVC (8/2) mixture (10 g) at 380°C. (Reproduced with permission from the American Chemical Society)

4.2 THERMAL DEGRADATION OF PP/PVC BY SOLID ACID CATALYSTS AND DECHLORINATION WITH IRON OXIDES

The effect of iron oxides such as FeOOH, Fe_2O_3, and Fe_3O_4 as chlorine sorbents were examined for the degradation of PP/PVC at 380°C. Table 18.3 shows the product yield and chlorine content of oil obtained from the thermal degradation of PP/PVC. As mentioned earlier, the oil from the thermal degradation of PP/PVC contained 12 700 ppm of organic chlorine compounds. When only the solid acid catalyst SA1 was used in both liquid (No. 2) and vapor phase contact (No. 3), the chlorine content of oil decreased slightly; however, when FeOOH was used in both liquid (No. 4) and vapor phase contact (No. 5), the chlorine content of oil decreased significantly (3000–4000 ppm). The best result, i.e. the lowest content of chlorine (1100 ppm) in oil was obtained when both FeOOH and SA1 were in the vapor phase (No. 7).

Figure 18.6 shows the C-NP gram of the liquid products obtained from PP/PVC with different catalysts and mode of contact and Figure 18.7 shows the Cl-NP gram of the liquid products obtained from PP/PVC. It is evident that when SA1 was used in liquid phase contact the amount of higher molecular-weight products decreased and the lower-molecular-weight products increased. FeOOH had no effect on the nature of the degradation products. When FeOOH was used as chlorine sorbent, the organic chlorine compounds identified in the products were the same as the thermal degradation, but the amount decreased significantly.

The effect of type of iron oxides on the removal of chlorine from the PP/PVC-derived oil was investigated using Fe_2O_3, Fe_3O_4, and FeOOH in vapor phase contact. The distribution of chlorine in the gases (inorganic only), liquids, residues, catalysts and sorbents of the products are shown in Figure 18.8. As can be seen, the distribution of chlorine in FeOOH and Fe_3O_4 was more than 90%, which indicates that these iron oxides are very effective for fixing chlorine in their structural framework. However, in the case of Fe_2O_3, the

Table 18.3 Degradation of PP/PVC = $\frac{8}{2}$(10 g) into fuel oil at 380°C. (Reproduced with permission from the American Chemical Society)

No.	Contact mode	Catalyst	Degradation yield (wt %)			d^c (g/mL)	Cnp^d (−)	Cl content in oil (ppm)	
			Liquid (L)	Gas (G)^a (HC^b/HCl ratio)	Residue (r)			Organic	Total
1	Thermal		73.2	12.8 (24.1/75.9)	14.0	0.78	13.0	12700	17600
2	Liquid phase	SAl	59.2	21.0 (52.4/47.6)	19.8	0.71	8.6	7000	8600
4	Liquid phase	FeOOH	73.4	9.7 (81.2/18.8)	16.9	0.78	12.9	4100	5400
6	Liquid phase	FeOOH, SAl	60.6	17.0 (88.5/11.5)	22.4	0.73	8.7	18100	23100
3	Vapor phase	SAl	68.4	14.5 (35.5/64.5)	17.1	0.74	10.1	11400	13900
5	Vapor phase	FeOOH	62.6	8.9 (92.4/7.6)	28.5	0.75	10.9	3200	4100
7	Vapor phase	FeOOH, SAl	63.9	16.4 (98.4/1.6)	19.7	0.73	9.8	1100	1700
8	Vapor phase Liquid phase	FeOOH SAl	60.5	13.6 (97.8/2.2)	25.9	0.72	8.8	5600	14900
9	Vapor phase Liquid phase	SAl FeOOH	63.1	17.5 (92.2/7.8)	19.4	0.77	10.4	4900	6200

[a] $G = 100 - (L + R)$;
[b] gaseous hydrocarbon;
[c] liquid density;
[d] average carbon number of liquid

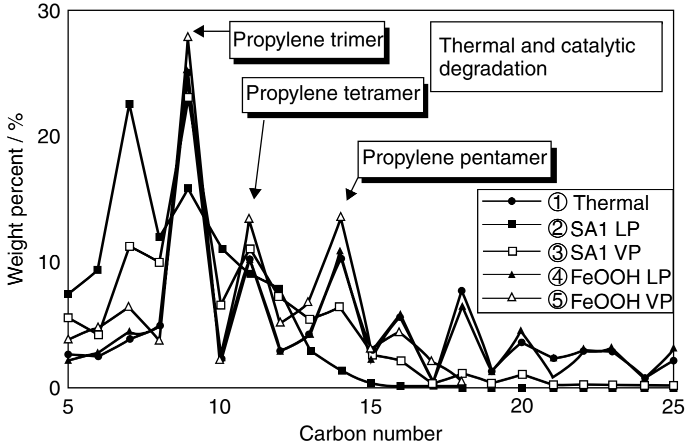


Figure 18.6 C-NP gram of liquid products from thermal and catalytic degradation of PP/PVC (8/2) at 380°C. (Reproduced with permission from the American Chemical Society)

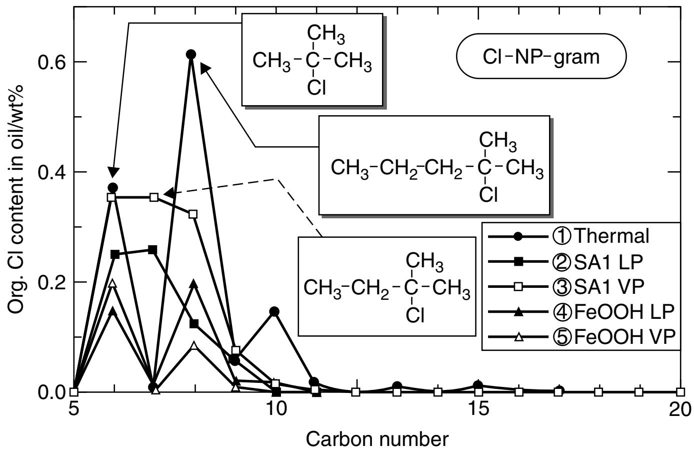


Figure 18.7 Cl-NP gram of liquid products from thermal and catalytic degradation of PP/PVC (8/2) at 380°C. (Reproduced with permission from the American Chemical Society)

distribution of chlorine in the sorbent was less than 50%, and gaseous products were about 40%. Furthermore, the chlorine content in oil (Figure 18.8) was almost the same as the thermal degradation. This indicates that Fe_2O_3 is not as effective as FeOOH and Fe_3O_4. The crystalline structure of used iron oxides was determined using an X-ray diffractometer. The crystalline structure of both FeOOH and Fe_3O_4 was Fe_3O_4 after use in the PP/PVC degradation. However, no crystalline phase of iron chloride was observed. The formed $FeCl_2$ can be present as a monolayer on iron (II) oxides, and no crystalline peaks of $FeCl_2$ are observed under these conditions [44]. Although the data on chlorine removal from PE/PVC and PS/PVC degradation using solid sorbents are not shown, they

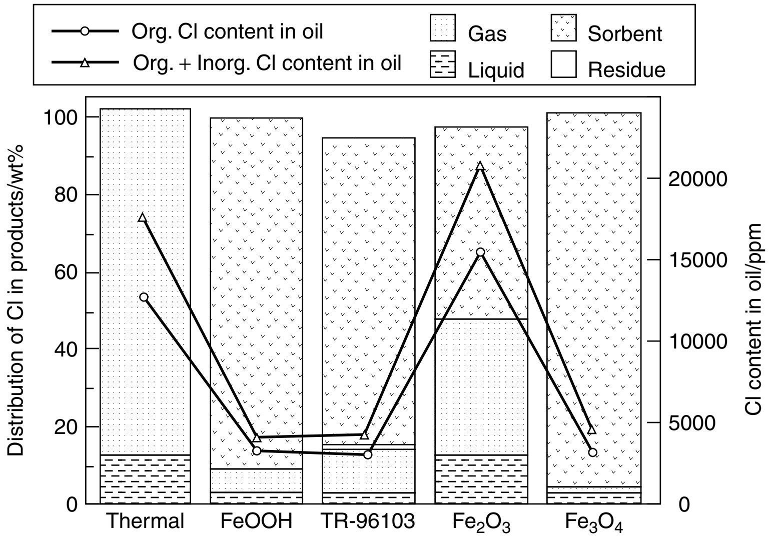


Figure 18.8 Distribution of chlorine in products and sorbents from thermal and catalytic degradation of PP/PVC (8/2) at 380°C. (Reproduced with permission from the American Chemical Society)

showed similar effects to those in PP/PVC, i.e. the content of chlorine in the oil products was decreased by the use of chlorine sorbents. Detailed discussion on the effect of various other iron oxides is given elsewhere [21].

4.3 THERMAL DEGRADATION OF PE MIXED WITH PET

The thermal degradation of PE mixed with polyethylene terephthalate (PET) and PE only degradation were compared. The presence of small amounts of PET is quite possible with the mixture of PE, PP, and PS, which is generally considered as municipal waste plastics. The yields of product gases, liquids and residues from the degradation of PET and the mixtures of PET and PE in ratios of 1:9 and 2:8 are shown in Table 18.4. Unlike PE or PVC, no liquid products could be obtained from the degradation of PET. The decomposition of PET proceeds with the production of a large amount of pale yellow

Table 18.4 Product yields for thermal degradation of PET and mixtures of PE and PET at 430°C. (Reproduced with permission from Elsevier)

Samples	PE/PET (wt ratio)	Product yield[a]			Average density of liquid product (g/cm^2)
		Liquid (L) (wt%)	Gas (wt%)	Residue (R) (wt%)	
PE(10 g)	10:0	69.2	8.5	22.3	0.76
PET(1 g) + PE(9 g)	1:9	52.2	11.2	36.6	0.77
PET(2 g) + PE(8 g)	2:8	32.7	15.3	52.0	0.76
PET(10 g)	0:10		33.4	66.6	

[a] $G = 100 - (L + R)$.

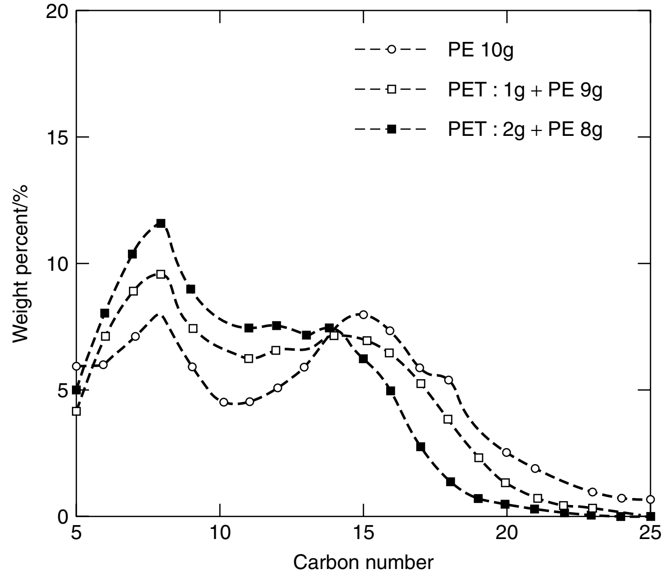


Figure 18.9 C-NP gram of the liquid products from degradation of mixtures of PE and PET at 430°C. (Reproduced with permission from Elsevier)

particles, most probably consisting of benzoic acid and terephthalic acid, which eventually blocked the outlet of the reactor. Carbonaceous residues were also obtained inside the reactor. Total yield of residues (both carbonaceous compound and yellow particles) was 66.6 wt% and the yield of gaseous products was 33.4 wt%. The gaseous products were mainly carbon monoxide and small amount of hydrocarbons (C_1–C_3). As was the case with the mixture of PE and PVC, the addition of PET to PE affected the product yields of gaseous product and residues increased compared with the product yields of PE degradation.

Figure 18.9 shows the NP grams of liquid products obtained from the degradation of the mixture of PE and PET, and is compared with the NP gram of liquid products from PE. Due to the addition of 10% PET to PE,, the weight fraction of higher-molecular-weight components decreased in the liquid products and those of low-molecular-weight components increased compared with the degradation products (liquid) of PE. Addition of 20% PET further enhanced the degradation of PE into low-molecular-weight products. These results suggest that the presence of the residues from PET decomposition may promote the degradation of PE. Visual inspection of the inside of the reactor during the thermal degradation of plastics such as PE, PVC and mixtures of PE with PVC, and PE with PET have been discussed in detail [45].

4.4 LABORATORY EVALUATION OF VARIOUS CARBON COMPOSITES AS HCl SORBENTS

Calcium-, iron- and potassium-based carbon composites were evaluated for the HCl sorption capacity for use in the dehalogenation process with PVC mixed plastics degradation. It is

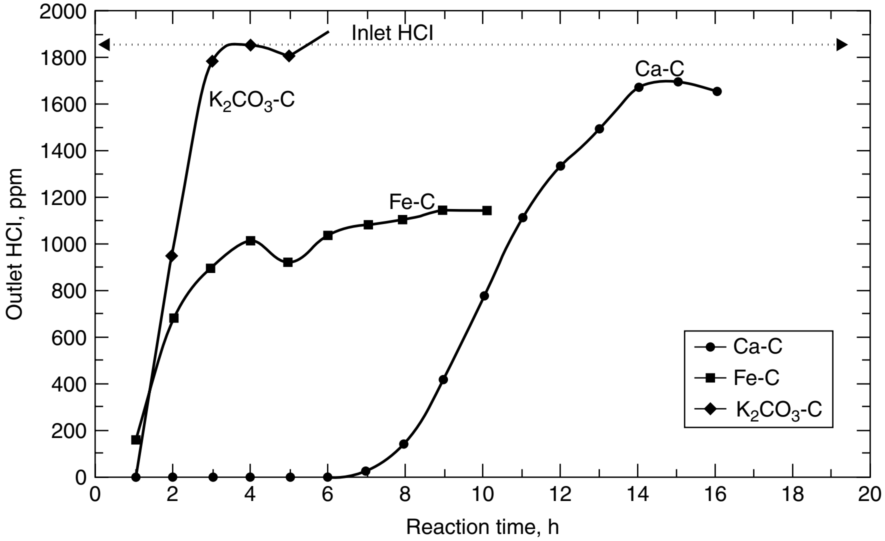


Figure 18.10 HCl reaction profiles with Ca-C, Fe-C and K_2CO_3-C sorbents at identical reaction conditions. (Reproduced with permission from the American Chemical Society)

well known that the presence of chlorine-containing plastics in the degradation process produces more than 95% of chlorine (depending on degradation conditions it may vary) in the form of hydrogen chloride and the remaining chlorine as some chlorinated hydrocarbons and some part in the residue. An effective sorbent should have high hydrogen chloride sorption capacity, be economical and should be recycled easily. A schematic experimental set-up for the reaction of hydrogen chloride with various sorbents, experimental and analysis conditions have been given in detail elsewhere [46].

The reaction of hydrogen chloride with calcium carbonate ($CaCO_3$)-, iron oxide (Fe_3O_4)-, and potassium carbonate (K_2CO_3)-based carbon composite sorbents and the results are presented in Figure 18.10. Figure 18.10 shows that the Ca-C sorbent completely captured the hydrogen chloride (1820 ppm) for a period of 7 h, Fe-C and K_2CO_3-C did not effectively adsorb the HCl gas. K_2CO_3-C reacted completely with the HCl gas for 1 h, but from the second hour onwards leakage from the reactor (sorbent) was observed and within a short reaction time of 3 h, the inlet and outlet HCl concentrations were same, indicating that there is no reaction with the sorbent after the third hour. The Fe-C sorbent released HCl from the first hour onwards. However, adsorbed HCl at a steady rate of 45% of inlet HCl concentration from third hour onwards. It indicates that the Fe-C reacts with HCl, but the reaction rate is slow compared with Ca-C.

The theoretical sorption capacities of three sorbents calculated based on stoichiometric equations and experimental sorption capacities calculated taking the HCl sorbed before breakthrough are presented in Table 18.5. Theoretical adsorption capacities of Ca-C, Fe-C, and K_2CO_3-C were 0.73 g/g, 0.95 g/g, 0.53 g HCl/g sorbent respectively. Observed sorption capacities of three sorbents (Table 18.5) until steady state level shows that the Ca-C (0.48) has higher sorption capacity per gram of sorbent than Fe-C (0.23) and K_2CO_3-C (0.17 g/g). Table 18.5 shows that the sorption capacity of Ca-C until the breakthrough

Table 18.5 Theoretical sorption capacities, consumed theoretical capacities during HCl reaction, and adsorption time consumed until steady state time for various sorbents[a]. (Reproduced with permission from the American Chemical Society)

Sorbent	(A) theoretical adsorption capacity [HCl(g)]/[ads(g)]	(B) amount of HCl adsorbed before the breakthrough[b] [HCl(g)]/[ads(g)]	Theoretical consumed capacity (B)/(A)100 [%]	Observed adsorption capacity until steady state [HCl(g)]/[ads(g)]	Adsorption time continued until steady state, h
Ca–C	0.73	0.31 (7 h)	43	0.48	16
Fe–C	0.95	0.00		0.23	10
K_2CO_3–C	0.53	0.04 (1 h)	8	0.17	6

[a] Parameters: temperature 350°C; weight of sorbent 2 g; total gas flow 535 mL/min; linear gas velocity 0.18 m/s; particle size (average diameter): 1 mm;

[b] breakthrough point was taken when the HCl leakage observed at the outlet of the reactor

point (43% of theoretical adsorption capacity) was much higher than K_2CO_3-C (8%) and Fe-C. Experimental (observed) sorption capacities were calculated based on the quantity of reacted HCl before breakthrough (leakage of HCl from reactor). The sorption of HCl with different sorbents carried out for different times, as the steady state level of sorbent with the HCl was reached at different time for various sorbents.

The reaction of various metal oxides with hydrogen chloride and the reverse reactions have been extensively studied [47] the reaction behavior of hydrogen chloride with various bivalent and trivalent metal oxides has been reported. Sakata *et al.* reported the spontaneous degradation of municipal waste plastics at low temperature [48] and also the dechlorination of chlorine compounds from PVC mixed plastics-derived oil using solid sorbents [22]. Courtemanche and Levendis [49] reported the control of HCl emission from the combustion of PVC by in-furnace injection of calcium–magnesium-based sorbents at gas temperatures of 850 and 1050°C. In the present study, the adsorption temperature 350°C was found to be optimum for the complete removal of hydrogen chloride at moderate concentrations (1820 ppm).

Some important parameters affecting the chlorinating process are sorbent size, HCl concentration, adsorption temperature, porosity, total surface area, and residence time. For effective heterogeneous reactions, the sorbent should be small in size, porous, and well dispersed in the combustion effluent gases. Superior intraparticle transport enhanced the reactivity of sorbent cenospheres, and increased calcium utilization were reported by Steciak *et al.* [22]. Small pores are prone to plugging by chlorination or sulfation products. These results suggest that calcium-based sorbents can be used for the complete removal of hydrogen chloride. The following paragraphs provide the optimized physical parameters for the HCl adsorption reaction parameters for a calcium-based sorbent.

The effect of temperature on HCl sorption capacity of Ca-C was studied using sorbent weight (2 g), average particle diameter (1 mm), total gas flow (530 mL/min), inlet HCl concentration (1820 ppm) and varied temperatures 100 200, 270, 350, and 400°C and the reaction profiles are presented in Figure 18.11. It can be clearly seen from the sorption profile at 100 and 200°C that the amount of reacted HCl is very small and that leakage from the reactor was observed from the first hour. The sorption profile obtained for 270°C showed that until 4 h (breakthrough point) the HCl is completely captured by Ca-C; leakage is observed from 4 h onwards and it reaches a steady state level after 13 h. Sorption profile obtained for 400°C shows that HCl leakage started from 5 h and

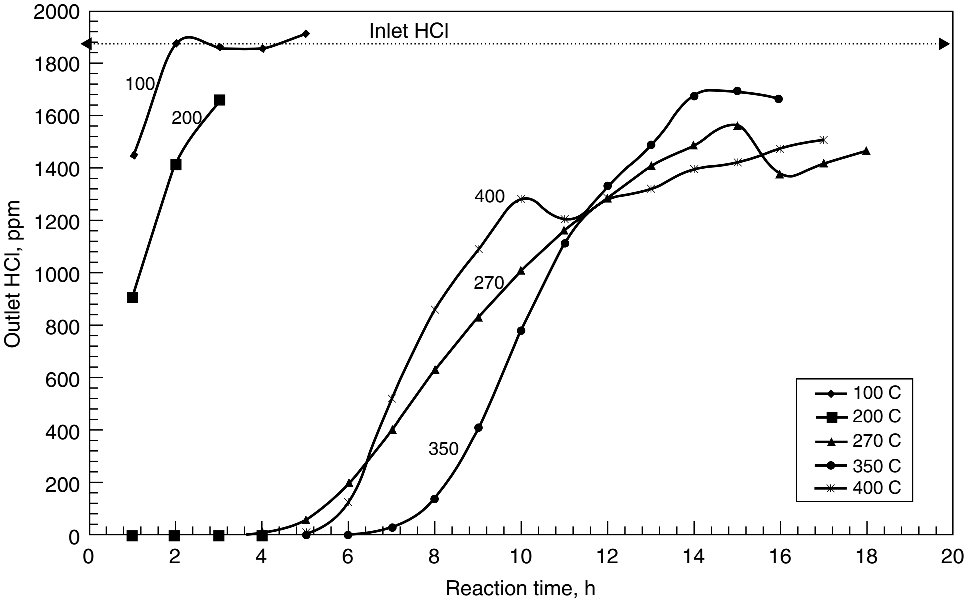


Figure 18.11 Effect of temperature on reaction profiles of HCl for Ca-C sorbent. (Reproduced with permission from the American Chemical Society)

after 10 h, it reached a steady state. It can be concluded that low temperatures and high temperatures are not favorable for the adsorption HCl gas without leakage and high breakthrough time. The sorption profile obtained at 350°C shows the complete capture of HCl up to 7 h (breakthrough point), reaching a steady state level around 14 h. From these results, the 350°C were found to be optimum temperature for the adsorption of HCl gas on Ca-C with higher breakthrough point. In a similar way Levendis *et al.* [50] reported the relative utilization of calcium-based sorbents for the capture of HCl gas using HCl gas diluted with nitrogen, and found that the chlorination of the sorbents occurred in the hot zone of the furnace at gas residence times ~1 s. They observed that the calcium carbonate reached a relative utilization of 54% in the mid-temperature range, while the calcium oxide reached an 80% relative utilization at the lowest temperature examined (600°C) [50]. The contact times during the present study were also less than 1 s and detailed studies on effect of gas flow rates were presented in the following sections. Weinell *et al.* [51] found that the reaction of calcium-based compounds with HCl ceases at a certain extent without complete conversion of the sorbent. This was defined as the maximum conversion, and was found to increase with the temperature. They also found that increasing particle diameter in the range of 0.2–2 mm and HCl concentration in the range 1.3–4 vol% led to a smaller conversion of $CaCO_3$ to $CaCl_2$. The progress of the reaction was reported to be influenced by pore blocking and at higher temperatures by a molten phase of $CaCO_3$ to $CaCl_2$. They reported that the conversion from $CaCO_3$ to $CaCl_2$ depends not only on particle size and HCl concentration, but also on the relative humidity of the gas.

The effect of inlet HCl concentration was studied with 1090, 1800, and 3900 ppm as inlet HCl concentration. The other reaction parameters such as sorbent weight (2 g), average sorbent particle diameter (1 mm), total gas flow (535 mL/min), linear gas velocity (0.18 m/s), and temperature of adsorption (350°C) was kept constant. The results showed that the sorption capacity with 1090 ppm was 37% and the sorption capacity value increased to 43% for 1820 ppm. At higher HCl concentration (3900) the adsorption capacity was decreased to 35%. The HCl adsorption capacity (43%) with 1820 ppm was more than 1090 and 3900 ppm, even though the observed HCl adsorption until saturation was less (1820 rather than 1090 on 3900 ppm). The adsorption capacity of Ca-C sorbent was more (43%) with 1820 ppm inlet HCl with 7 h breakthrough time. In similar conditions, the effect of total gas flow rate was studied using 250, 535 and 900 mL/min. The total gas flow was varied keeping the inlet HCl concentration as 1820 ppm. The results showed that the increase of flow rates decreased the breakthrough point and the sorption capacity of sorbent due to less contact time. The breakthrough of HCl for 250, 535 and 900 mL/min was 16, 7 and 3 h respectively. It is clear from these studies that the sorption capacities of Ca-C were found to decrease from 45 to 31% with the increase of flow rate from 250 mL to 900 mL/min.

The effect of particle size on the HCl sorption capacity of Ca-C was studied varying the particle sizes i.e. 0.25, 1.0, and 2.0 mm. The other reaction parameters such as sorbent weight (2 g), total gas flow (535 mL/min), linear gas velocity (0.18 m/s), inlet HCl concentration (1820 ppm), and temperature of adsorption (350°C) were kept constant. Figure 18.12 shows that with increase of sorbent particle size the breakthrough of HCl was found to increase from 11 h (0.25 mm) to 2 h (2 mm). The results calculated from the adsorption isotherms, such as amount of HCl adsorbed before breakthrough, observed HCl adsorption until steady state level and adsorption time until steady state are presented in Table 18.6. The adsorption capacity of Ca-C was 63% with particle size 0.25 mm. The increase of particle size from 0.25 to 2 mm decreased the theoretical consumed capacity from 63 to 11%. These studies clearly indicated that calcium-based sorbents are effective for the dechlorination of PVC mixed waste plastics pyrolysis process.

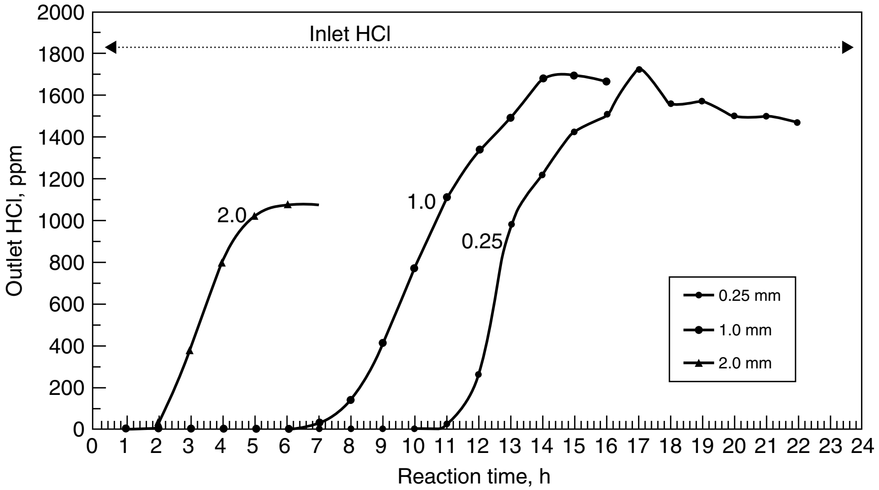


Figure 18.12 Effect of particle size on HCl reaction profiles for Ca-C sorbent. (Reproduced with permission from the American Chemical Society)

Table 18.6 Effect of particle size on consumption of theoretical capacity of Ca-C. (Reproduced with permission from the American Chemical Society)

Particle size of sorbent (mm) average diameter	(B) amount of HCl adsorbed before the breakthrough[b] [HCl(g)]/[ads(g)]	Theoretical consumed capacity (B)/(A^c)100 [%]	Observed adsorption amount until steady state [HCl(g)]/[ads(g)]
0.25	0.46 (11 h)	63	0.58 (22 h)
1.0	0.31 (7 h)	43	0.48 (16 h)
2.0	0.09 (2 h)	11	0.21 (7 h)

[a] Parameters: temperature 350°C; weight of sorbent 2 g total gas flow 535 mL/min;
[b] breakthrough point was taken when the HCl leakage observed at the outlet of the reaction;
[c] (A) theoretical adsorption capacity [HCl(g)]/[ads(g)] = 0.73

Table 18.7 Product yields and properties of liquid product from PVC mixed PP/PE/PS plastic degradation using Ca-C (6 consecutive runs) and thermal degradation. (Reproduced with permission from the American Chemical Society)

Degradation and run number using Ca–C	Yield of degradation products (wt %)			Liquid products	
	Liquid (L)	Gas (G)[b]	Residue (R)	Cnp[c]	Density (g/cm^3)
Thermal	63	24	13	10.4	0.79
1	67	23	10	10.8	0.80
2	65	22	13	10.7	0.79
3	67	21	12	10.7	0.79
4	69	21	10	10.9	0.80
5	75	15	10	10.8	0.81
6	70	20	10	10.6	0.80

[a] Weight ratio: PVC:PP:PE:PS = 1:3:3:3; weight of Ca–C: 4 g; degradation temperature 430°C; dechlorination temperature 350°C;
[b] $G = 100 - (L + R)$;
[c] Cnp = average carbon number of liquid products based on C−NP gram

4.5 LIQUEFACTION OF PVC MIXED PLASTICS AND DECHLORINATION WITH Ca-C

The pyrolysis of mixed plastics containing PVC (PVC/PP/PE/PS) was performed under atmospheric pressure in a batch process using Ca-C sorbent and thermal degradation (no sorbent). Table 18.7 shows the yield of products (gas, liquid, and residues) and average carbon number (Cnp), density of liquid products obtained during thermal degradation and using Ca-C sorbent. The thermal degradation (PVC/PP/PE/PS at 430°C) produced liquid products (63 wt%), with average carbon number of 10.4 and density 0.79 g mL^{-1}. The liquid product obtained during the degradation with Ca-C sorbent was about 67 (run 1) and 75 wt% (run 5). There is no appreciable change in the Cnp, and density of liquid products obtained during both in thermal degradation and degradation using Ca-C sorbent (Table 18.7). The gaseous products obtained during the thermal degradation were approximately the same as for degradation using sorbent. There is no appreciable change

Table 18.8 Chlorine content in PVC mixed PP/PE/PS plastic degradation liquid products using Ca-C and theoretical consumed sorbent capacity for each run[a]. (Reproduced with permission from the American Chemical Society)

Degradation and run number using Ca–C	Chlorine content in liquid products (ppm)	Consumed theoretical capacity of $CaCO_3$ (%)
Thermal	360	
1	0	18
2	0	35
3	0	53
4	0	71
5	150	89
6	3000	106

[a] Weight ratio PVC:PP:PE:PS = 1:3:3:3; weight of Ca–C 4 g; degradation temperature 430°C; dechlorination temperature 350°C

in amount of residue for the thermal degradation and degradation using sorbent from run 1 to run 4. Roy *et al.* [52] reported on the vacuum pyrolysis of commingled plastics (HDPE/LDPE/PP/PS) containing PVC at a final temperature of 500°C and under a total pressure of 2 kPa. During their vacuum pyrolysis studies, the pyrolysis oil contained 12 ppm Cl on a pyrolysis oil basis. Pyrolysis under vacuum reduces the incidence of secondary reactions in comparison with slow pyrolysis at atmospheric pressure [52].

The total chlorine content in liquid products obtained during thermal degradation, using Ca-C sorbent and theoretical consumed capacity of Ca-C sorbent during each run of mixed plastic degradation is presented in Table 18.8. As can be seen from the table, 360 ppm of chlorine content is found in liquid products obtained during thermal degradation. However, the chlorine content is zero (not detected) from run 1 to run 4 when using Ca-C sorbent (4 g), indicating that the chlorine compounds (inorganic and organic) were completely removed from the liquid products. The theoretical consumed capacity of $CaCO_3$ was calculated as follows. In the present study 1 g of PVC (for each batch 1 g of PVC) and 4 g of $CaCO_3$ (the same sorbent repeatedly used for run 1 to run 6) sorbent used for the experimental investigation. 1 g of PVC contains 0.524 g of Cl and 4 g of $CaCO_3$ can consume 2.92 g of Cl (1 g $CaCO_3$ can react with 0.73 g Cl). Table 18.8 shows that Ca-C sorbent consumed all the chlorine for run 1, indicating that about 18% ($0.524/2.92 \times 100$) of theoretical sorbent capacity was utilized. In a similar way, the theoretical consumed sorbent capacity was calculated for run 2 to run 6.

The chlorine content in aqueous NaOH trap was analyzed by an ion chromatograph. During thermal degradation about 92 wt% of HCl (gaseous) was found in NaOH trap, about 3 wt% chlorine was observed in residue. The degradation using Ca-C sorbent showed that there is no chlorine in oil from run 1 to run 4. However, there is a small amount of chlorine in the NaOH trap during run 3 (0.33 wt%) and run 4 (1.21 wt%). The degradation for run 5 and run 6 showed the presence of chlorine in the oil (Table 18.8) and in the NaOH trap (run 5 = 1.68 and run 6 = 55.3 wt%).

Meszaros [53] reported the pyrolysis of municipal plastic waste (MPW) containing 3% of PVC in an auger kiln reactor (Conrad recycling process). Lime was used in order to trap the HCl evolved, which resulted in liquid products with 25 ppm of chlorine. In the present process, the inorganic chlorine (HCl) was captured by Ca-C sorbent and the chlorinated hydrocarbons produced during the PVC mixed plastic pyrolysis process were dehydrohalogenated by Ca-C. About 71% of theoretical HCl sorption capacity of Ca-C was utilized for the four batches of PVC mixed PP/PE/PS plastic pyrolysis process. The chlorine content 150 ppm was observed during run 5 of degradation and the chlorine content increased from 150 ppm to 3000 ppm (run 6), which is higher than the thermal degradation. This clearly indicates that the sorbent cannot be used in the process after 71% of theoretical capacity (Table 18.8). The presence of a higher content of chlorinated hydrocarbons during run 6 (3000 ppm) than for thermal degradation (360 ppm) might be due to the hydrocarbons produced during the pyrolysis process reacting with the calcium chloride ($CaCO_3$ converted to $CaCl_2$ during process) and forming the chlorinated hydrocarbons in the liquid products. This is an additional process than forming the chlorinated hydrocarbons by reaction of free hydrogen chloride with hydrocarbons produced during the thermal degradation [54]. In the preset study; we were able to utilize about 71% of its theoretical capacity (up to 4 batch processes) without chlorine compounds in the liquid products. Bockhorn *et al.* [7] studied the pyrolysis of a PVC/PS/PE (1:6:3 by weight) mixture in three circulated-sphere reactors arranged in a cascade and they detected 44 ppm of chlorine in oil from the third reactor, which mainly contained aliphatic compounds. However, the chlorine content in the oil from the second reactor was still high at 210 ppm.

The C-NP diagram of liquid products showed that the hydrocarbons (C_6–C_{11}) during the thermal degradation and degradation using Ca-C sorbent was 47 wt%. As with the C-NP diagram, the carbon number distribution of chlorinated hydrocarbons (wt% of chlorinated hydrocarbons = g(Cl)/g(Oil) × 100 wt%) in the liquid product was prepared from the gas chromatogram obtained using a gas chromatograph with an atomic emission detector (GC-AED). The wt% of chlorinated hydrocarbons is shown in a Cl-NP diagram in Figure 18.13. The hydrocarbons containing the chlorine were distributed in the range

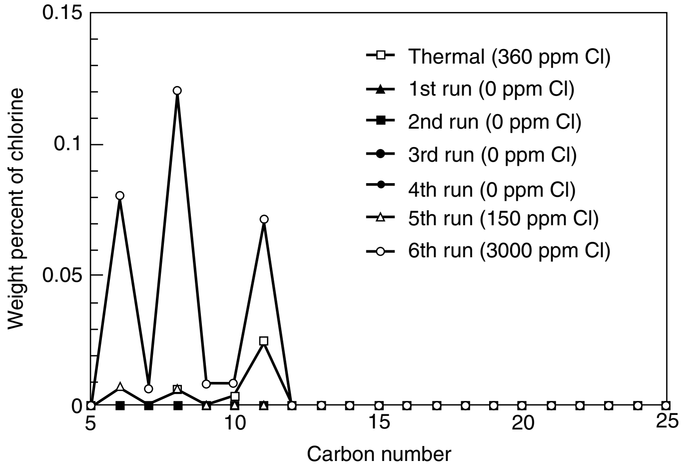


Figure 18.13 Cl-NP gram of liquid products obtained during PP/PE/PS mixed with PVC thermal degradation and degradation using Ca-C sorbent. (Reproduced with permission from the American Chemical Society)

of C_6–C_{11}. The liquid products were analyzed by GC-MS to identify the compounds. Both the chlorine content and concentration of chlorine-containing organic compounds in liquid products were determined by gas chromatography with an atomic emission detector (GC-AED), which provides selective detection of Cl in the liquid products.

The selective chlorine compounds analyzed by GC-AED chromatograms are presented in Figure 18.14. The presence of chlorinated compounds during the thermal degradation and degradation with sorbent (run 5 to run 6) was observed. 2-Chloro-2-phenyl propane was the major chlorine compound observed during thermal degradation (Figure 18.14a) and also during run 6 (Figure 18.14d). 2-Chloro-2-methyl propane, 2-chloro-2-methyl pentane, and α-chloro ethyl benzene was also identified during runs 5 and 6 (Figure 18.14c and 18.14d). The formation of chlorinated hydrocarbons might be due to either of the following reactions: Cl radicals produced by the thermal degradation of PVC reacting with cracked hydrocarbon species, or free hydrogen chloride reacting with cracked hydrocarbon species. We suggest the latter, i.e. that organic compounds are produced by the reaction between hydrogen chloride originating from PVC and the hydrocarbons obtained from the degradation of PE, PP and PS [22]. The chlorinated hydrocarbons formed during the pyrolysis of commingled plastics were different from those obtained during the thermal

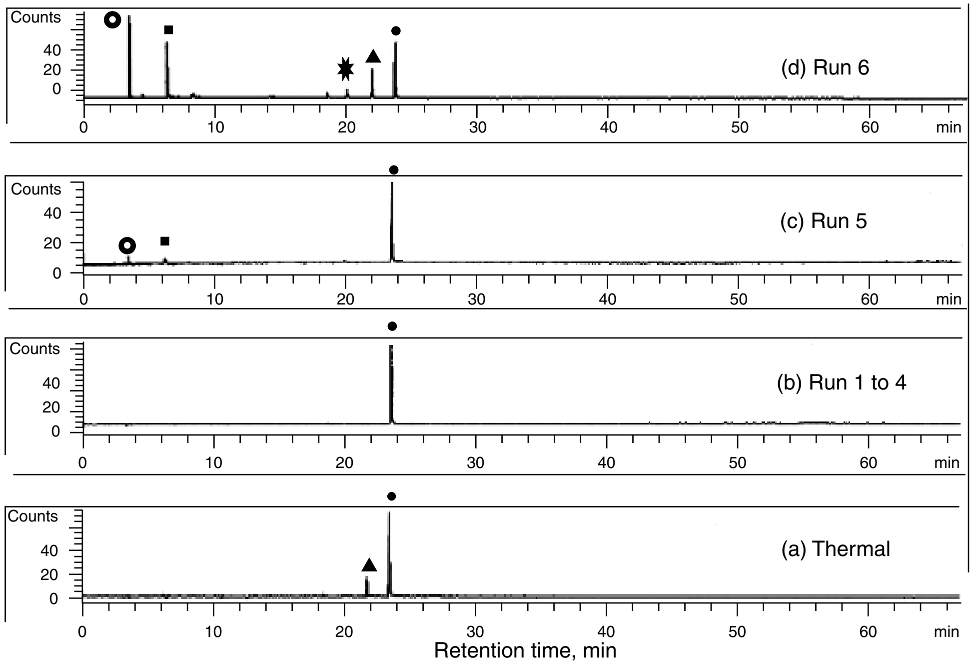


Figure 18.14 GC-AED chromatograms of chlorine compounds for PP/PE/PS mixed with PVC thermal degradation and degradation using Ca-C. (Reproduced with permission from the American Chemical Society)

● Internal standard for chlorine (1,2,4-trichloro benzene)
▲ 2-chloro-2-phenyl propane
✱ α-chloro ethyl benzene
■ 2-chloro-2-methyl pentane
○ 2-chloro-2-methyl propane

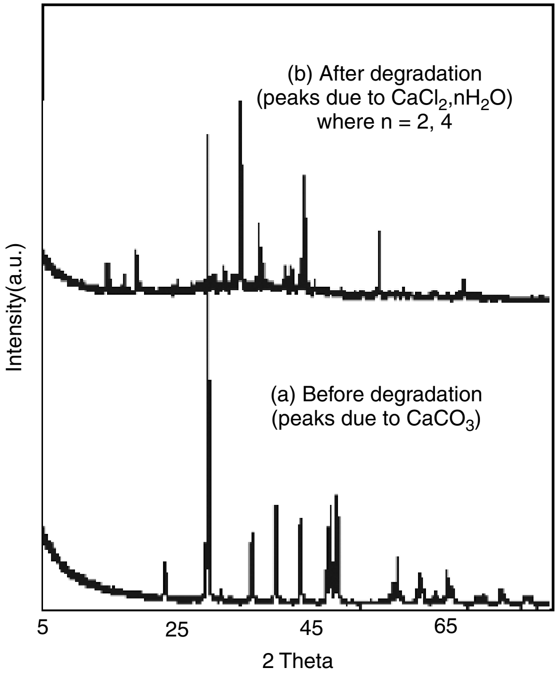


Figure 18.15 X-ray diffraction patterns of Ca-C sorbent before and after the pyrolysis: (a) before degradation (peaks due to $CaCO_3$); (b) after degradation (peaks due to $CaCl_2$ nH_2O), $n = 2, 4$. (Reproduced with permission from the American Chemical Society)

decomposition of pure PVC. However, the hydrocarbons produced in the oil fraction were similar to those identified during the pyrolysis of single plastics [52].

Representative X-ray diffraction patterns of the Ca-C before and after the degradation experiment are shown in Figure 18.15. The X-ray diffraction pattern before degradation indicates the presence of a $CaCO_3$ phase (Figure 18.15a) but after degradation peaks due to $CaCl_2.nH_2O$ (where $n = 2$, 4) phase (Figure 18.15b) were observed, indicating the sorption of chlorine by $CaCO_3$. It was demonstrated that the pyrolysis of PVC-containing PP/PE/PS mixed plastics (degradation at 430°C) using Ca-C sorbent gave halogen-free liquid products (dechlorination at 350°C). The Ca-C sorbent was used successfully for the consecutive 6 batch processes and obtained halogen-free liquid products up to 4 run by utilizing 71% of sorbent theoretical HCl sorption capacity. The use of the same sorbent beyond its experimental sorption capacity produced more chlorinated compounds than the thermal degradation. In order to see the debromination effect of Ca-C sorbent, the Ca-C has been used during the pyrolysis of brominated flame retardant containing high-impact polystyrene (HIPS-Br), PVC and PE, PP, PS mixed plastics.

4.6 LIQUEFACTION OF PP/PE/PS/PVC WITH HIPS-Br AND DEHALOGENATION WITH Ca-C

The thermal degradation of mixed plastics (weight ratio PP/PE/PS/PVC/HIPS-Br = 3:3:2:1:1) was carried out under atmospheric pressure in a batch process at 430°C and

Table 18.9 Product yields and properties of liquid products from PP/PE/PS/PVC/HIPS-Br degradation at 430°C in the absence and presence of Ca-C sorbent (weight ratio PP:PE:PS:PVC: HIPS-Br = 3:3:2:1:1). (Reproduced with permission from The Royal Society of Chemistry)

Degradation method	Yield of degradation products (wt%)			Liquid products	
	Liquid (L)	Gas (G)[a]	Residue (R)	C_{ap}[b]	Density (g cm^{-3})
Thermal	71	17	12	13.7	0.82
Ca–C (2 g)	62	26	12	11.9	0.81
Ca–C (4 g)	66	25	9	12.4	0.81

[a] $G = 100 - (L + R)$;

[b] C_{ap} = average carbon number of liquid products based on C-NP gram

degradation also carried out with Ca-C. Table 18.9 shows the yield of products such as gas, liquid, residue, average carbon number, and density of liquid products obtained during thermal degradation and also degradation using Ca-C. The thermal degradation yielded liquid products (71 wt%) with the average carbon number 13.7 and density 0.82 g cc^{-1}. The use of Ca-C sorbent in the degradation process decreased the liquid products from 71 to 62 wt% (Ca-C 2 g) and 66 wt% (Ca-C 4 g). The amount of residue observed with thermal degradation and Ca-C (2 g) was 12 wt%. However, the residue in the degradation process with Ca-C 4 g was about 9 wt% (Table 18.9). The density of liquid products did not change in the presence or in the absence of Ca-C sorbent. The gaseous products, which are not condensed as liquid products, were passed through a high-temperature furnace (900°C) with aspirator. During this, the gaseous halogenated organic compounds (if any) were converted into inorganic halogen compounds, which were then passed through a water trap to capture HBr or HCl.

It is noteworthy that the AED-GC can detect the chlorinated and brominated compounds selectively. The quantitative analysis of chlorine and bromine in the liquid products was carried out by GC-AED and the results are presented in Figure 18.16. As can be seen from Figure 18.16 that the thermal degradation of mixed plastics (weight ratio PP/PE/PS/PVC/HIPS-Br = 3:3:2:1:1) produced liquid products with 7300 ppm of bromine and 1120 ppm of chlorine. However, the use of 2 g Ca-C in the degradation process drastically decreased the halogen content, the bromine content to 320 ppm and chlorine to 115 ppm. With the increase of sorbent from 2 to 4 g in the degradation process, the halogen content was completely removed from the liquid products.

The liquid products were analyzed by GC-MS to identify the compounds. In our present study, the major hydrocarbons during (thermal and Ca-C) degradation were aromatic hydrocarbons such as benzene, toluene, ethylbenzene, propylbenzene, styrene, 1-methylethylbenzene, butylbenzene, α-methylstyrene, etc. In addition to these compounds, anthracene, naphthalene and substituted derivatives of anthracene, naphthalene were also observed during the thermal degradation. The presence of chlorinated and brominated compounds during both the thermal degradation and degradation using 2 g Ca-C was observed. The chlorinated hydrocarbons found during the thermal degradation were 2-chloro-2-phenyl propane, 2-chloro-2-methyl propane, 2-chloro-2-methyl pentane, and α-chloro ethyl benzene and brominated hydrocarbons

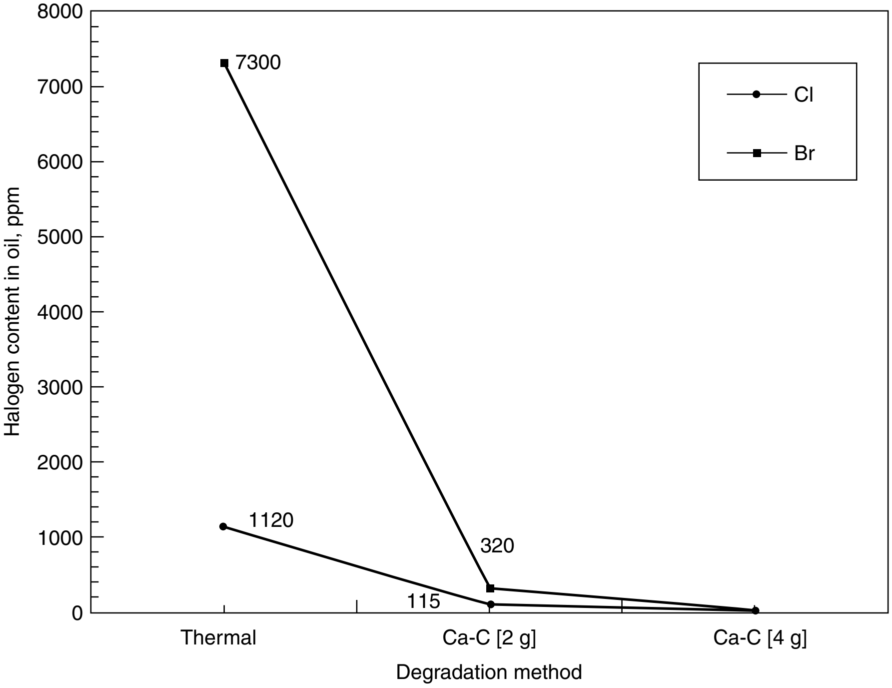


Figure 18.16 The effect of Ca-C sorbent for dehalogenation (Cl and Br) during PP/PE/PS/PVC + HPS-Br degradation at 430°C. (Reproduced with permission from The Royal Society of Chemistry)

were bromocyclohexane, and 1-(bromoethyl) benzene, etc. The formation of $SbBr_3$ is observed in earlier studies on thermal degradation of polyester flame-retarded with antimony oxide/brominated polycarbonate [55]. However, we have not observed any such compounds in the liquid products obtained during HIPS-Br mixed with PVC/PP/PE/PS at 430°C.

Striebich *et al.* [56] reported that the high-temperature degradation of polybrominated flame-retardant materials produced Br-benzenes, Br-phenols, polybrominated dibenzodioxins (PBDD) and polybrominated dibenzofurans (PBDFs). However, they were subsequently destroyed at high temperature (800°C). Dioxin formation (PHDD) and furan formation (PHDF) in the thermal treatment of plastics containing polybrominated diphenyl ether with several flame retardants and the diantimony trioxide and decabromodiphenylene ethers (heating of HIPS for 20 min) produced the dioxins at 275°. Former test campaigns by the Forschungszentrum Karlsruhe and the Association of Plastic Manufacturers in Europe, at the Karlsruhe TAMARA test facility for waste combustion, focused on the existence, partitioning, and destruction of bromine and its influence on the formation of bromine containing dibenzo-*p*-dioxins and dibenzofurans. In the present study, we have not found any such compounds, and the gases (which are not condensed) were passed through the furnace at 900°C for complete destruction of compounds [57].

The average carbon number (Cnp) of the liquid product decreased due to the cracking of higher-molecular-weight compounds in the presence of Ca-C sorbent (Table 18.9 and

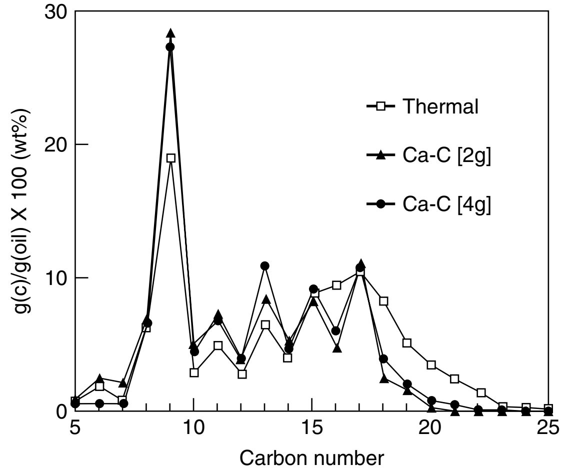


Figure 18.17 C-NP gram of liquid products obtained during PP/PE/PS/PVC + HIPS-Br thermal degradation and degradation using Ca-C sorbent. (Reproduced with permission from The Royal Society of Chemistry)

Figure 18.17). Figure 18.17 shows the C-NP diagram of the liquid products obtained by analyzing their gas chromatogram. The carbon numbers in the abscissa of the NP diagram are equivalent to retention values of the corresponding normal paraffin and the ordinate shows the weight percent of the corresponding hydrocarbons. The higher hydrocarbons decreased in the presence of Ca-C at 430°C. The hydrocarbons in the C_6-C_{10} range during the thermal degradation was 20 wt%, and in the presence of Ca-C [2 and 4 g] degradation produced approximately 30 wt%. However, the hydrocarbons in the range C_{16}–C_{20} were decreased in the presence of Ca-C sorbent (Figure 18.17). In contrast to the PVC, there has been various problems with the brominated flame-retardant plastics, as they contain synergists and also other additives. The effect of antimony trioxide (Sb_2O_3) on the degradation products and their composition were well discussed elsewhere [58]. The degradation of PVC and HIPS-Br and dehalogenation by iron oxide–carbon composites, effect of PET on the mixed plastics with HIPS-Br and HIPS-Br with PET have been extensively studied by Bhaskar *et al.* [59–62].

4.7 LIQUEFACTION OF REAL MUNICIPAL WASTE PLASTICS

The thermal degradation of MWP, 3P/PVC and 3P/PVC/PET was performed under atmospheric pressure at 430°C,where 3P = PP/PE/PS. Table 18.10 shows the yield of degradation products and average carbon number (Cnp), density of liquid products. The liquid products (59 wt%) produced with the MWP (20 g) were higher than 3P/PVC/PET and lower than 3P/PVC liquid products (Table 18.10). It is clear from Table 18.10 that the presence of PET has predominant effect on the formation of liquid products. The degradation residue during the MWP thermal degradation was higher than that of model plastics, due to the presence of various additives in the MWP. There is no appreciable change in the Cnp, and density of liquid products obtained from PET containing samples such as 3P/PVC/PET and MWP.

Table 18.10 Products yield and properties of liquid product from 3P/PVC, 3P/PVC/PET and MWP (20 g) thermal degradation at 430°C. (Reproduced with permission from Elsevier)

Plastic sample	Yield of degradation products (wt%)			Liquid products	
	Liquid (*L*)	Gas (*G*)[a]	Residue (*R*)	Cnp[b]	Density (g cc^{-1})
3P/PVC	70	25	5	12.1	0.80
3P/PVC/PET	53	34	13	11.6	0.82
MWP	59	25	16	11.9	0.84

Weight of plastic samples PE (6 g) + PP (6 g) + PS (6 g) + PVC (2 g); PE (6 g) + PP (6 g) + PS (6 g) + PVC (2 g) + PET (2 g); MWP (20 g)

[a] $G = 100 - (L + R)$

[b] Cnp, average carbon number of liquid products based on C–NP gram

Table 18.11 The distribution of chlorine content in various thermal degradation products of 3P/PVC, 3P/PVC/PET and MWP (20 g) at 430°C. (Reproduced with permission from Elsevier)

Plastic sample	Chlorine in degradation products (mg)				Total (mg)
	Liquid (*L*)	Gas (*G*)		Residue (*R*)	
		Organic	Inorganic		
3P/PVC	17	0.3	870	2.7	890
3P/PVC/PET	28	3.2	760	21	812
MWP	52		57	53	162

Weight of plastic samples PE (6 g) + PP (6 g) + PS (6 g) + PVC (2 g); PE (6 g) + PP (6 g) + PS (6 g) + PVC (2 g) + PET (2 g); MWP (20 g)

The liquid products were analyzed by a gas chromatograph equipped with an atomic emission detector for the quantitative estimation of chlorine content in liquid products. As can be seen from the Table 18.11, that the presence of chlorine content in liquid products is higher with 3P/PVC/PET (28 mg) than 3P/PVC (17 mg). Furthermore, the chlorine content in liquid products is almost doubled in the MWP (52 mg) pyrolysis. It is interesting to note that the presence of PET in model and MWP decreased the formation of inorganic chlorine content (Table 18.11). The inorganic chlorine content during 3P/PVC (870 mg) was higher than 3P/PVC/PET (760 mg) and MWP (57 mg). The presence of chlorine content in degradation residue is higher in MWP than the mixed model plastics 3P/PVC and 3P/PVC/PET. Meszaros [53] reported the pyrolysis of municipal plastic waste (MWP) containing 3% of PVC in an auger kiln reactor (Conrad recycling process). Lime was used in order to trap the HCl evolved, which resulted in liquid products with 25 ppm of chlorine.

Figure 18.18 illustrates the C-NP diagram of the liquid products obtained by analyzing their gas chromatogram. The carbon numbers in the abscissa of the NP diagram are equivalent to retention values of the corresponding normal paraffin and the ordinate shows the weight percent of the corresponding hydrocarbons (g(Cn)X100/g(Oil), wt%). The hydrocarbons in the range C_7–C_{10} were very high and about 10 wt% of liquid products are in the ranges C_{13}–C_{15} and C_{17}–C_{19}. The hydrocarbons containing chlorine were distributed in the range of C_5–C_9, C_{10}–C_{12}, C_{14} and C_{21} range in both the model mixed and

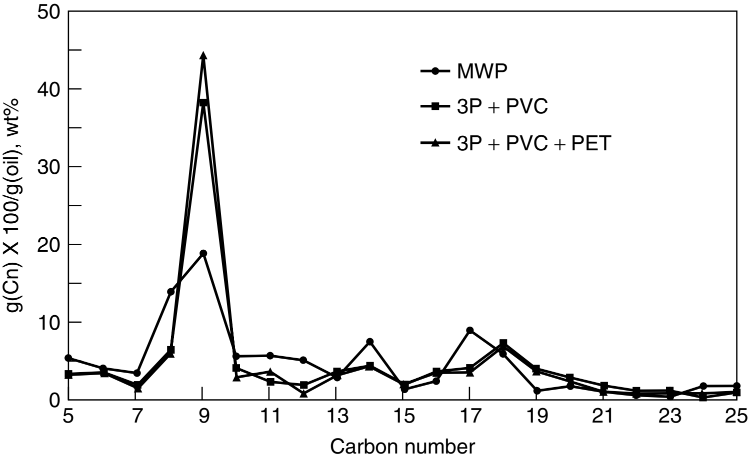


Figure 18.18 C-NP gram of liquid products obtained during real MWP and model mixed plastics (3P/PVC and 3P/PVC/PET) thermal degradation at 430°C. (Reproduced with permission from Elsevier)

MWP. However, the quantity of chlorinated hydrocarbons during MWP degradation was higher than 3P/PVC/PET and 3P/PVC degradation liquid products. Gas chromatography equipped with an atomic emission detector (GC-AED), was used for selective detection of Cl in the liquid products. As can be seen from Figure 18.19, the presence of PET produced the additional chlorinated hydrocarbons than 3P/PVC. The liquid products were analyzed by GC-MS to identify the compounds. The presence of chlorinated compounds with model and MWP were observed as 2-chloro-2-phenyl propane, 2-chloro-2-methyl propane, 2-chloro-2-methyl pentane, and α-chloro ethyl benzene.

In addition, the presence additional chlorinated compounds in the PET mixed plastics such as 3P/PVC/PET and MWP were found to be chlorine derivatives of benzoic acids. Kulesza and German [36] reported the influence of poly(vinyl chloride) on poly(ethylene terephthalate) pyrolysis. They reported that the chloroesters of terephthalic and benzoic acids were found with PVC and PET mixtures (1:1). In our present investigation, the PVC/PET ratio was 1:1 and contains the other plastics such as PE, PP and PS. The ratio of mixed plastics PP: PE: PS: PVC: PET was 3:3:3:1:1 and this composition was prepared are similar to the real municipal waste from Sapporo, Japan. 2-Methyl benzoylchloride was identified as one of the additional chlorinated hydrocarbons observed in 3P/PVC/PET and MWP degradation than 3P/PVC degradation chlorinated hydrocarbons. The other chlorinated hydrocarbons could not be identified in 3P/PVC/PET and MWP degradation. It is evident from the studies that the new chlorine compounds obtained due to the presence of PET in plastic samples in either model mixed on MWP.

5 PILOT PLANT SCALE STUDIES FOR THE LIQUEFACTION OF PVC MIXED PLASTICS

Based on the laboratory-scale study, the degradation of both model waste plastics (3P [150]/PVC [3], 153 kg) and MWP (50 kg) was carried out in a large-scale pilot plant

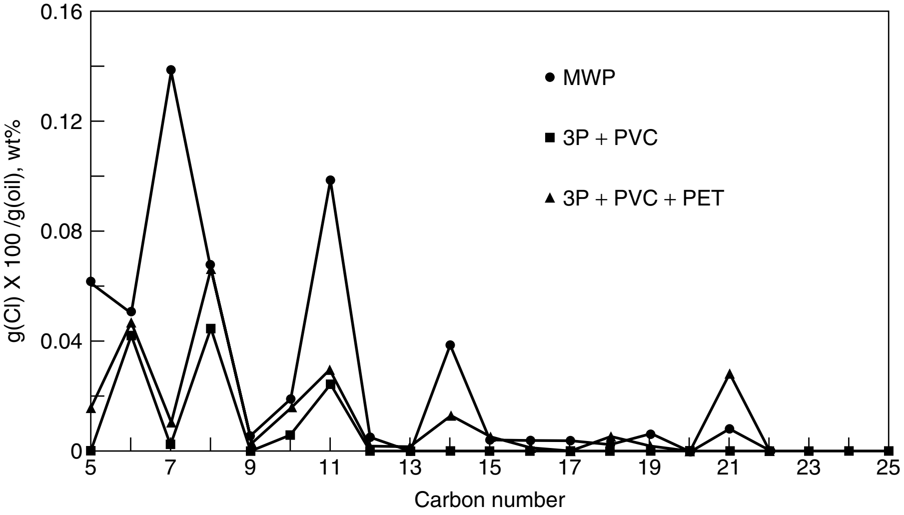


Figure 18.19 Cl-NP gram of liquid products obtained during real MWP and model mixed plastics (3P/PVC and 3P/PVC/PET) thermal degradation at 430°C. (Reproduced with permission from Elsevier)

Table 18.12 Raw materials plastics used by operation in pilot plant, and product yields and Cl concentration in products for thermal and catalytic degradation of 3P/PVC[a] mixture and municipal waste plastics[b]

No.	Raw materials plastics (kg)						Sorbent (kg)	Product yield (wt%)			Cl content (ppm)	
	PP	PS	PE	PVC	MWP	Total	Ca–C: 8 mm ϕ	Liquid (*L*)	Gas (*G*)[c]	Residue (*R*)	Oil	Water trap
1	50	50	50	3		150		69	28	3	530	2940
2	50	50	50	3		153	20	82	16	2	ND[d]	6
3					50	50	20	53	39	6	100	7

[a] Cl content of PVC polymer 52.4 wt%;
[b] MWP = municipal waste plastics were supplied by Sapporo city, Japan
[c] $G = 100 - (L + R)$;
[d] ND = not detected (less than the detection limit of instruments)

set-up (250 kg/batch) using calcium-based carbon composite and thermal degradation. Mixed model plastics and MWP used in pilot plant operation and the distribution of products, chlorine content are shown in Table 18.12. Municipal waste plastics were supplied by Sapporo City, Japan, and may contain 5–7% of PVC. Table 18.12 shows the yield of products such as liquid, gas and residue and chlorine content. The thermal degradation of 3P/PVC mixture was carried out and the liquid products contained 530 ppm of chlorine (organic) and the water trap contained 2940 ppm of HCl. However, degradation with Ca-C removed all organic chlorine compounds and the concentration of HCl decreased to 6 ppm (water contained 5–7 ppm HCl). In the case of the degradation of MWP, the derived oil contains 100 ppm of organic and the water trap contains 7 ppm.

The halogen-free plastic-derived oil obtained during the pilot plant studies was tested in diesel power generation engines in a 1:3 mixture with commercial fuel oils (kerosene) and the test was successful.

6 CONCLUSIONS

Studies on the liquefaction of mixed plastics containing PVC at laboratory scale and pilot plant scale suggest that it can successfully produce chlorine-free plastic-derived oil. Removal of a major portion of chlorine in PVC as HCl is an important step to avoid the formation of high-chlorine-content organic compounds in the liquid products. Optimization of liquefaction conditions and selection of dehalogenation catalyst/sorbent are essential for the successful production of halogen-free liquid products. Iron oxide carbon composites worked as dechlorination catalysts and calcium carbonate carbon composites worked as chlorine sorbents. However, the waste plastic stream should not mix with other condensation polymers such as poly(ethylene terephthalate) etc. The presence of PET produces high amounts of organic chlorine that is difficult to remove by low-cost, iron and calcium-based catalyst/sorbents. In a similar way, the brominated plastics were also used for the liquefaction and completely removed the bromine content from the liquid products using the iron- and calcium-based composites. Protection of the environment and recovery of valuable organic content from halogenated waste plastics (PVC and HIPS-Br) by liquefaction are important aspects.

The Japan Energy Corporation(JEC) has agreed and accepting the Waste Plastics Derived Oil(PDO) into the existing refinery plant as a feedstock from 2002.The PDO was produced by waste plastics liquefaction plants in Japan with advanced dechlorination technology, which is a key technology for the feedstock recycling of halogenated mixed waste plastics.

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19

Liquid Fuel from Plastic Wastes Using Extrusion–Rotary Kiln Reactors

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1 INTRODUCTION

This chapter examines the production of liquid fuels from waste plastics by pyrolysis using rotary kiln reactors. Due to increased environmental awareness and depletion of natural oil deposits, many industries are looking for alternative fuel sources to drive their processes. One area that has gained notable attention and popularity in recent years is the production of fuels from waste organic materials. These materials range from waste plastics to waste biomaterials (e.g. used cooking grease, beef fat and vegetable oils). Pyrolysis can be one solution [1–6].

There is strong evidence that we have limited time before our natural resources of crude oil and gas run out. Currently, many of the large oil companies such as BP and Mobil are investing in alternative energy sources such as wind and solar energies.

The industrial revolution provided us with the phenomenal power to create energy, advanced materials and processes, which improved our everyday lives. In a sense, we attribute most of our daily comforts to the industrial revolution. However, we have learned that nothing in this world is free and every thing comes with a cost. Until present day crude oil has been the major source of energy. This is because crude oil has always been cheap and plentiful, but this is no longer the case. As indicated by many monitoring organizations, we have limited supply of oil, coal and gas. Thus, there is a need to use our most valuable asset wisely or other wise we could be faced with serious repercussions.

In modern day engineering, plastics and plastic-derived materials are the most commonly used products. In most cases these materials are obtained from chemical alteration of crude oil. Compared with steel and other metallic products, most of these plastics have

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much greater life expectancy. At present plastics provide a fundamental contribution to all activities such as agriculture, the automobile industry, electricity and electronics, building materials, packaging and so on.

Not only do we have a shortage of energy resources, but also an increasing amount of nondegradable waste materials. These waste materials are generated as a result of many industries and domestic processes. At present most of these waste materials are landfilled. In the United States alone, up to 20 million tonnes of waste plastics and 45 million tonnes of hydrocarbon waste were generated in 2001 [1]. At the present time, we have very few remedial processes that can reduce these wastes and harness their energy. Thus, processes that can reuse these wastes and generate energy are highly beneficial.

One option is to reuse or incorporate the waste in new products. This can occur only if the waste plastic has the correct specification required by product design. Incineration of plastic waste to produce heat may also be a possibility, but its organic content would be destroyed and converted into CO_2 and H_2O. In addition, depending on its nature, combustion may produce pollutants such as light hydrocarbons, nitrous and sulphur oxides, dusts, dioxins and other toxins that have a highly negative impact on the environment. Pyrolysis is one of the best methods for preserving valuable petroleum resources, in addition to protecting the environment, by limiting the volume of nondegradable waste [2].

More importantly, due to global instability, the price and availability of crude oil can vary considerably from day to day. Waste fuels can help to solve some of the problems relating to environmental and economic issues which may lead to the shortage of safe fuel. Renewable or recycled fuels can help with:

- decreasing toxic air emissions;
- diminishing imports of crude oil and also increasing energy security;
- increasing local employment and income and stimulating economic development.

In summary, pyrolysis is a tertiary recycling process that is used to break down large polymer molecules. In this process, the polymer samples are heated in an inert atmosphere, which causes the carbon–carbon bonds to break along the polymer backbone. This depolymerization step results in monomers (short-chained compounds) being formed. Generally, three types of products are formed from pyrolysis reactions: gas, oil and char. All three have the potential to be used as a fuel or chemical feedstock. Depending on the feed polymer and the reaction conditions, different products can be obtained. The pyrolysis oil can either be used directly or can be used as a raw material for the petroleum industry [1–5].

At present several pyrolysis plants have been built based on different processes such as: the BASF pyrolysis process, the BP University of Hamburg fluidized-bed pyrolysis process, the VEBA hydrogenation process, and several more are under way [4, 5].

2 PYROLYSIS

As discussed in the previous sections, plastic waste is a major issue. Pyrolysis is one method of reducing waste plastics and other hydrocarbon waste. If applied correctly, it should allow the recycling of some of the stored energy within the waste plastics (Figure 19.1).

General advantages of pyrolysis include [5]:

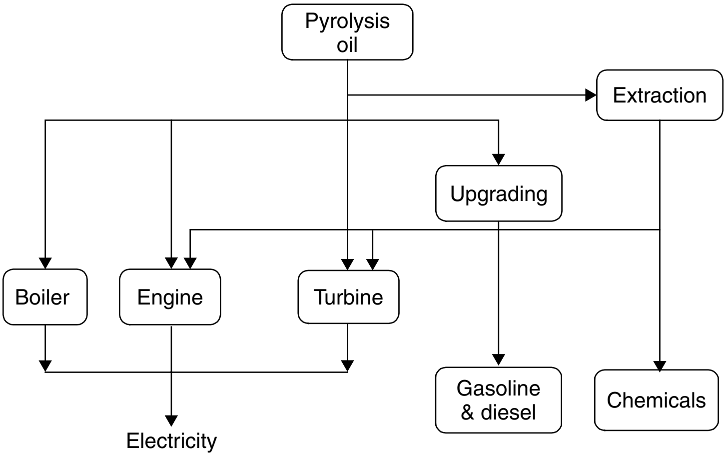


Figure 19.1 Application of pyrolysis oil [6]. (Reproduced with permission from Elsevier)

- very low energy consumption;
- it can handle plastic wastes, which cannot be efficiently recycled by other recycling process;
- it operates without the need of air and at low pressures;
- the HCl produced from pyrolysis of PVC plastics can be recovered and utilized as a raw material;
- since pyrolysis is conducted in a closed system, there are no pollutants.

Table 19.1 lists the calorific values of some common polymers and compares them with some conventional fuels. As illustrated in the table, the calorific values of these plastics are very similar to those of liquid fuels. Thus, there is a potential for recycling of these waste plastics as liquid fuels.

2.1 INDUSTRIAL-SCALE PYROLYSIS PROCESSES

This section examines some of the established extrusion–rotary kiln pyrolysis processes currently operating. As illustrated in the previous sections of this book, pyrolysis is a

Table 19.1 The calorific value of some major plastics and common fuels [7]. (Reproduced by permission of John Wiley & Sons, Ltd)

Sample	Calorific value (MJ kg^{-1})
Polyethylene	46.50
Polypropylene	46.50
Polystyrene	41.90
Kerosene	46.50
Gas oil	45.20
Heavy oil	42.50

process that uses high temperatures to break polymer structures into smaller hydrocarbon molecules. These molecules can be reused either directly, or as a feedstock material for the petroleum process. Thus, pyrolysis can be considered as a multi-step plastic recycling process [5]. The industrial rotary kiln processes that are examined in this section are: the VEBA hydrogenation process and Conrad recycling process.

Rotary kiln processes are continuous processes that use a rotary kiln reactor to depolymerize plastic [4, 5]. They have a lower capital cost compared with fluidized-bed processes and their liquid product resembles crude oil. The following are some general characteristics of kiln processes:

- the liquid yield depends on feed, reaction temperature and reaction time (i.e. residence time);
- heteroatom capture is a problem. Heteroatoms such as chlorine and oxygen generated from PVC and PET are not trapped and pass through the process, thus, requiring further cleaning steps to purify the oil products;
- fouling on the reactor wall occurs due to carbon deposits.
- lower capital cost;
- lower processing rate;
- feedstock feeding can be a problem (air lock).

2.1.1 Veba Pyrolysis Process

The Veba Oel pyrolysis processes was originally designed for the upgrading of heavy oil hydrogenation residues (such as coal and petroleum residues). The pyrolysis process uses a rotary kiln reactor with spheres and crossform bodies to prevent coke deposition. The kilns used in this process were operational until 1964. However, it was found that these kilns had three disadvantages [8]:

- spheres were abrasive;
- the rotary kilns had poor sealing;
- low specific throughput of the kiln.

Based on these disadvantages Veba Oel Technologies constructed a new pilot plant for the pyrolysis of refinery and hydrogenation residues using indirectly heated rotary kilns (Figure 19.2 shows the process flow diagram).

As described by Wenning [8] the solid waste is fed into the rotary kiln by a screw conveyor. The kiln used in this process has an inner diameter of 0.8 m and a length of 7 m. Gas burners at a slight over pressure (∼10 mbar) are used to generate the heat required for pyrolysis. The process is carried out in an oxygen-free atmosphere and operated at above 650°C. The reactor used in this process is built from high-temperature-resistant steel, which allows the reactor to be operated at temperatures of 850°C. The residence time of the materials is varied by changing the inclination and the rotating speed of the kiln.

As a result of the thermal cracking, solid coke and pyrolytic vapours are produced. The coke is removed from the reactor and utilized further, while the vapour products are passed into a two-step condensation system. Wenning [8] states that, in order to prevent

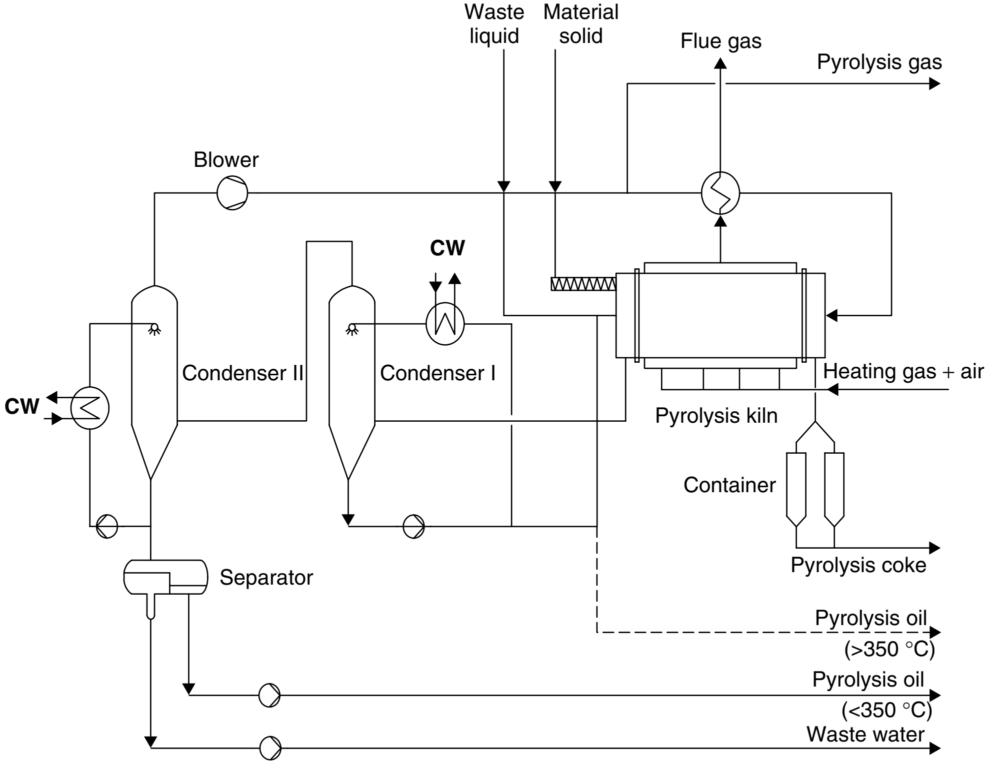


Figure 19.2 Veba Oel pilot plant flow diagram [8]. (Reproduced with permission from Elsevier)

partial condensation of high-boiling pyrolysis oils in the coke discharge outlet of the kiln, part of the pyrolysis gas is reheated using the flue gas and is recycled back into the coke discharge area. In the first stage of condensation the vapours are cooled to 300°C, allowing the high-boiling-point oils to be separated out. This is carried out by direct quenching using the condensed pyrolysis oil. The second condenser cools the remaining vapours down to 35°C to condense out the light hydrocarbons. The noncondensable gases are separated and purified to remove harmful substances. These gases are also used as fuel to heat the pyrolysis reactor [5, 8].

According to Wenning [8] the pilot plant processed a total of 1600 tonnes of residues by mid-1989. The pilot was operated for a total time of 7800 h. At the conclusion of these experiments Veba Oel Technologies examined the use of different feed material such as plastic waste. Wenning [8] described a proposed design of a mixed plastic waste pyrolysis plant (Figure 19.3) that has a throughput of 12.5 t/h (100 000 t/a) (Table 19.2 shows the feed composition of mixed plastic waste). Since the mixed plastic waste contains PVC they suggested that the feed be initially treated in a PVC decomposition process and then pyrolysed to produce liquid oil, coke and gas free of chlorine contaminate. They suggested that the dechlorination process should be carried out by melting the plastic waste in an extruder at a temperature of about 350°C. At this temperature HCl

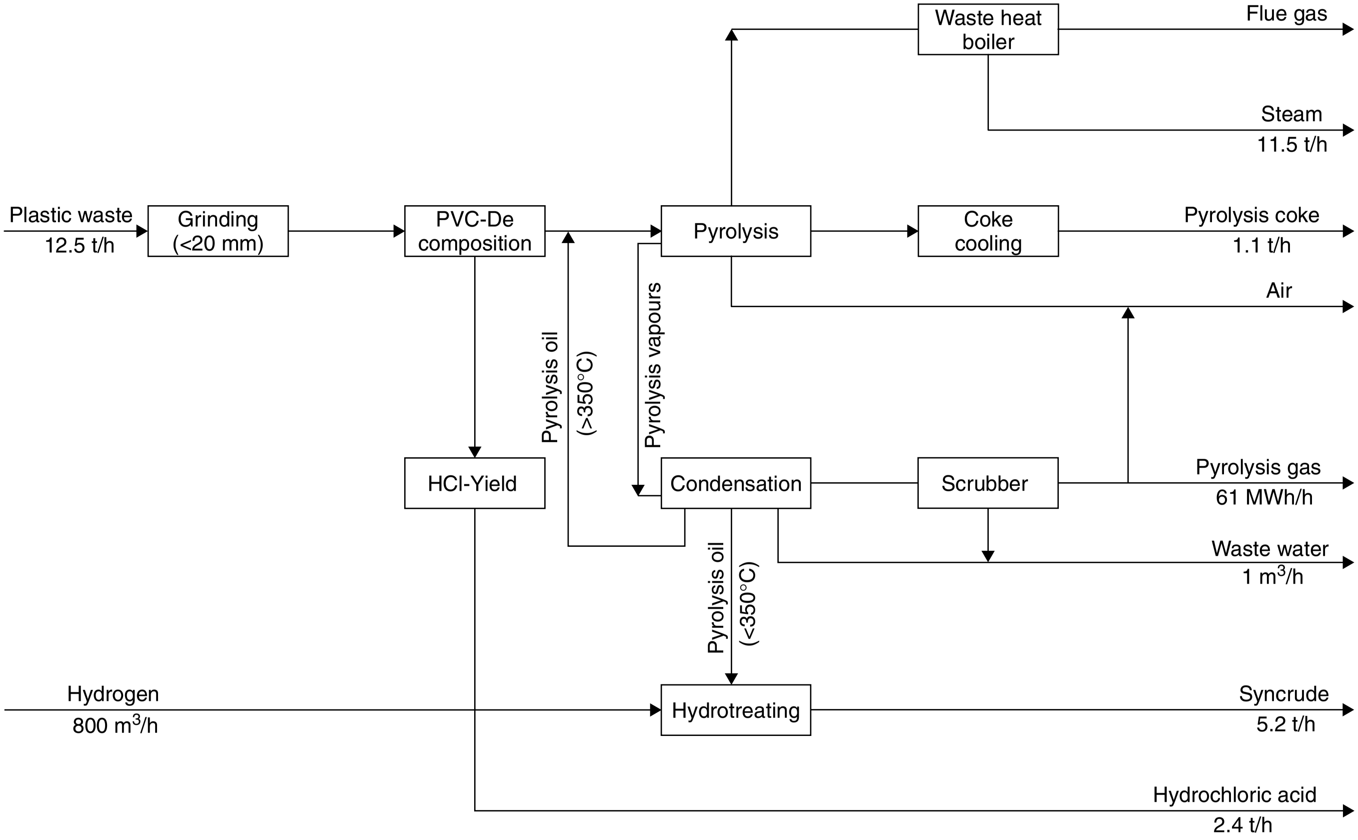


Figure 19.3 Flow diagram of a mixed waste plastic pyrolysis plant [8]. (Reproduced with permission from Elsevier)

Table 19.2 Feed composition of mixed plastic waste [8]. (Reproduced with permission from Elsevier)

Feed material	Composition (wt%)
Polyethylene (PE)	60
Polypropylene (PP)	5
Polyvinyl chloride (PVC)	10
Polystyrene (PS)	15
Polyamide (PA)	5
Polyethylene terephathalate (PET)	5

gas is produced which then can be removed from the process. The chlorine-free feedstock is then passed through a rotary kiln reactor where the pyrolysis reaction would take place. The pyrolysis gases are condensed into light and heavy fractions and the noncondensable gases are recycled back into the system for process heating. These oils can then be reprocessed using the hydrogenation process to produces synthetic crude oil.

2.1.2 Conrad Recycling Process

The other industrial kiln reactor that is examined in this chapter is the Conrad recycling process. This process uses an auger kiln reactor to transform plastic and/or tyres in the absence of oxygen into liquid petroleum, solid carbonaceous material and noncondensable gases at high temperatures. Conrad currently has two facilities in operation. They have a 200 lb/h pilot unit and a 2000 lb/h commercial scale unit at Chehalis research facility (Figure 19.4 shows the process diagram) [9].

The Conrad reaction process is well described by US Patent 4412889 [10]. Initially the feed material (14) from storage tank (16) is fed through a rotary feed valve air lock (18) down into an infeed screw conveyor. The conveyor (20) conveys the feed material up into the top end of the vertical inlet conduit (22) of the reactor. The feed material is then fed into the reactor (10) were it is depolymerized into gases, liquids and solids. Note that the feed material initially travels through an inlet region (24) slightly cooler than the reactor to stop feed material from vaporizing before entering the reactor. This area is cooled by a stainless steel cooling jacket (56) around the inlet conduit (22) using cold water. Typically the reaction chamber is heated to 1400°F (760°C). The reaction chamber in this process uses an impeller shaft (36) and impeller blades (38) to convey the feed material through the reactor (Figure 19.5 shows the reactor design). The Conrad pilot plant uses a single-pass auger kiln reactor 6 ft in length. The relatively short length of the reactor makes the determination of the optimum reaction temperature and feed rate very difficult. However, commercial-scale Conrad units consist usually of two larger reactors in series that allow for a longer residence time [9].

The solid products are removed from the reaction chamber through an outlet conduit (40) into an outfeed screw conveyor (42) and into a storage container (44).The gas and liquid product are removed from the reaction chamber through an outlet conduit (32) into a recovery system (70). The recovery system includes a water spray system to separate

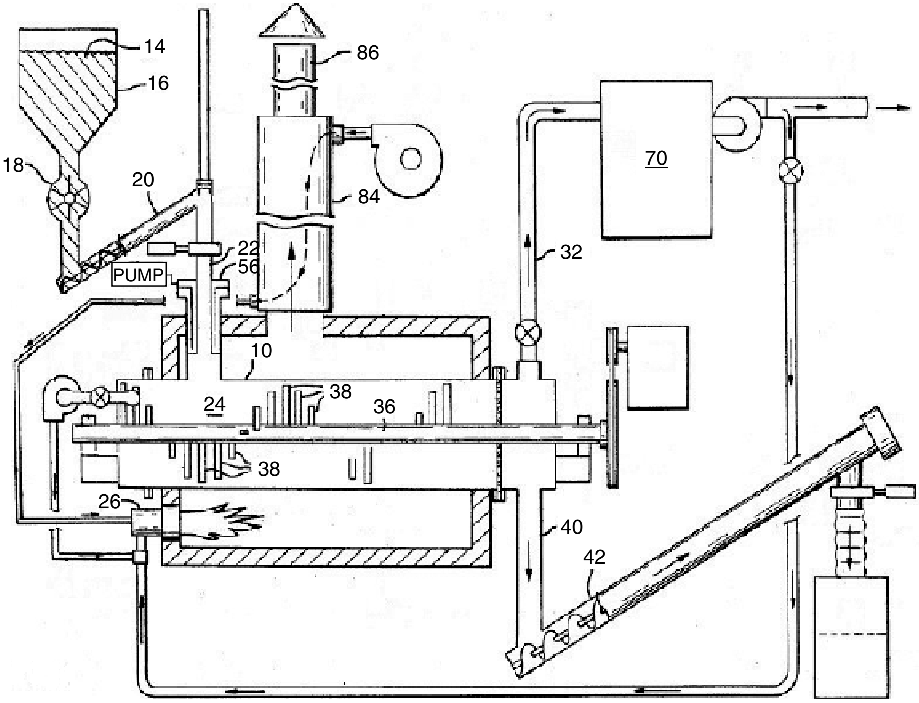


Figure 19.4 Process diagram of a Conrad pyrolysis plant [10]. (Reproduced by permission of the US Copyright Office)

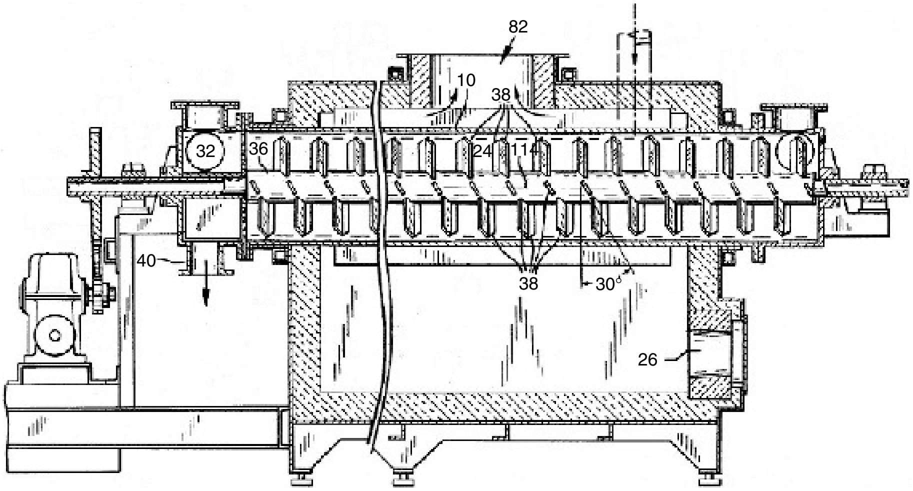


Figure 19.5 Reactor design of Conrad pyrolysis plant [10]. (Reproduced by permission of the US Copyright Office)

out liquid vapour from noncondensable gas. The recovery system could also contain a gas-filter and a cyclone separator to separate out solid particles from the pyrolysis gas. The system uses a portion of the noncondensable pyrolysis gas to heat the reactor up. Heat is supplied by combustion of pyrolysis gas and natural gas is used only during start-up (26). The combustion gases produced by the burner flow co-current with the flow of feed materials through the reaction chamber and escape out from the reactor through an exhaust (86). However, before the gases are released into the atmosphere they go through a heat exchanger (84) cooled using air. The heated air from the heat exchanger is then recycled into the burner for combustion.

According to Meszaros [9], the feed preparation is simplified in comparison to other processes, which require size reduction, washing and removal of nonplastic contaminants. Furthermore the inorganic contaminants in the plastic feed do not disrupt the process and exit the unit with unreacted material and carbonaceous products.

Researchers at the Chehalis facility carried out 18-months of parametric study to assess the Conrad recycling process [9]. Their objective was to identify process bottlenecks, develop operating parameters and begin to assess product value and markets. For the initial experiments a base feed mixture of 60:20:20 high-density polyethylene, polypropylene and polystyrene (HDPE: PP: PS) was used as representative of the major constituents found in post-consumer plastic streams.

The initial results obtained by the pilot plant illustrate that the final yield depends on feed rate, auger rotation speed and reaction temperatures (Tables 19.3–19.5). It was found that by reducing the feed rate and the auger rotation the formation of liquid product was increased and the wax formation was reduced.

In order to improve the understanding of the process capabilities and product yields, further studies were carried out by Meszaros [9], using base feed enriched with LDPE, PS and PET. The results obtained showed that the LDPE-rich feed containing 20:48:16:16 LDPE: HDPE: PP: PS behaved similar to that of the base feed. However, slightly higher yields of C_{12}–C_{15} aliphatics were produced. A PS-rich feed containing 48:16:36 HDPE: PP: PS also produced similar yield to that of base feed mixture. However, in the liquid product higher yields of styrene were observed. Also slightly lower yields of higher molecular weight ($>C_{12}$) were obtained. The PET-rich feed mixture containing 20:48:16:16 PET:

Table 19.3 Product yield from base feed at different reaction temperatures [9]. (Reproduced by permission of the American Chemical Society)

Oven temperature (°F)[a]	Liquid yield (wt%)[b]	Gas yield (wt%)	Solid yield (wt%)
1450 (788°C)	28	64	8
1300 (704°C)	48	51	1
1200 (649°C)	73	27	
1100 (593°C)	79	21	

[a] Retort temperatures are about 200° less than oven

[b] Combination of liquids and paraffin waxes from solids collection drum

Table 19.4 GC analysis of products from pyrolysis of base mixture [9]. (Reproduced by permission of the American Chemical Society)

Oven temperature (°F)	1300	1200	1100
Auger temperature (°F)	1095	980	895
Partial oil analysis (wt%)			
Benzene	7.0	2.3	1.1
Toulene	20.0	11.0	9.1
Ethylbenzene	9.0	5.7	4.8
Styrene	20.0	17.0	14.7
C_{10}	10.0	9.4	6.8
C_{11}–C_{15}	14.5	16.6	13.1
C_{16}–C_{20}	8.6	9.9	14.5
C_{21}–C_{25}	3.0	3.5	6.4
C_{26}–C_{30}	1.7	1.7	4.5
C_{31}–C_{40}	1.1	1.5	4.2
Partial Gas Analysis (vol%)			
H_2	4.0	2.6	2.2
Methane	18.0	13.6	10.5
Ethylene	19.4	18.1	13.8
Propylene	21.4	21.8	21.0
Isobutylene	5.0	6.1	6.8

Table 19.5 Physical analysis of oil product [9]. (Reproduced by permission of the American Chemical Society)

Specific gravity	0.8860
RVP (psi)	4.1
Pour Point (°F)	20
Viscosity@75 °F (cst)	3.5
Viscosity@122 °F (cst)	1.5

HDPE: PP: PS behaved differently from the base mixture and produced more solids at lower temperatures (Table 19.6). The products from these runs were analysed using gas chromatography.

In the second phase of the parametric study the removal of halogens from the reaction products was examined. Two different halogen removal methods were studied. The first method used a calcium oxide fixed bed placed between the reactor and condenser to remove organochloride vapours. However, it was found that the calcium oxide bed would plug up very rapidly if PET was present in the feed mixture and would become ineffective. This is because the PET would depolymerize into terephthalic acid and CO_2 and would react with calcium oxide and cause it to plug up. The second method that was used for removal of chlorine was to add calcium oxide or hydroxide directly into the reactor with the plastic feed. It was found that this approach is far more effective than the previous method. Through trial and error it was found that calcium hydroxide feed of 10 wt% would remove the highest amount of chlorine (Table 19.7) [9].

Table 19.6 GC analysis of products from pyrolysis of base mixture [9]. (Reproduced by permission of the American Chemical Society)

Feed	Base + LDPE			Base + PS			Base + PET		
Oven temperature (°F)	1300	1200	1100	1300	1200	1100	1450	1300	1200
Auger temperature (°F)	1100	1010	925	1100	1000	910	1180	980	870
Yields (wt%)									
Liquids	41	45	50	36	45	50	32	55	59
Solids	3	8	32	3	8	28	1	7	21
Gas	56	47	18	60	47	22	67	38	20
Aliphatics	30.5	43.1	50.8	23.5	30.9	46.5	16.7	46.3	8.5
$<C_{25}$ saturated	6.2	7.7	10.8	5.5	5.5	5.57	3.8	6.8	10.9
$<C_{25}$ unsaturated									
1 unsaturation	13.9	23.9	27.5	9.7	16.8	25.8	5.9	25.7	32.9
2 unsaturations	6.8	7.7	6.1	6.1	4.7	7.1	4.5	8.1	8.7
C_{25}+aliphatics	1.7	1.7	5.4	0.8	2.7	4.9	1.7	3.4	5.0
Aliphatics by carbon number									
$<C_{10}$	20.1	27.5	21.2	14.4	16.6	23.2	5.0	28.2	21.3
$C_{11}-C_{15}$	4.6	8.5	12.6	4.1	7.7	9.4	3.0	9.2	17.6
$C_{16}-C_{20}$	2.8	3.8	7.2	3.1	2.3	5.9	5.0	2.9	9.9
$C_{21}-C_{25}$	1.4	1.6	4.1	1.1	1.5	2.9	2.0	2.5	4.7
$C_{26}-C_{30}$	0.6	0.7	1.8	0.4	0.9	1.9	0.7	1.7	2.2
$C_{31}-C_{35}$	0.4	0.4	1.2	0.2	0.7	1.2	0.4	0.7	1.2
$C_{36}-C_{40}$	0.2	0.2	0.8	0.0	0.5	0.7	0.2	0.3	0.6
C_{40}+	0.2	0.2	0.8	0.0	0.4	0.8	0.1	0.2	0.4
Aromatics	63.5	49.3	39.8	71.5	62.4	42.4	76.1	40.4	29.2
Benzene	7.0	3.2	1.0	6.3	1.9	1.4	19.6	3.0	1.4
Toulene	15.7	10.8	8.0	16.2	10.5	7.3	16.5	7.2	3.8
Ethylbenzene	7.6	5.5	4.6	8.6	7.9	5.5	3.14	3.7	2.6
Xylenes	2.1	1.3	0.5	2.2	1.1	0.7	2.0	1.4	1.1
Styrene	16.7	16.6	14.6	20.6	27.1	17.0	12.0	8.9	8.2
C3−benzenes	6.8	5.4	4.9	7.4	7.4	4.7	5.7	3.8	3.9
C4+benzenes	2.8	3.4	4.2	3.0	3.7	3.9	4.1	5.8	4.5
Napthalenes	4.7	3.2	2.0	7.0	2.8	2.1	13.1	6.8	3.7
Unidentified compounds	6.8	7.5	9.4	5.0	6.7	11.1	7.3	13.3	12.3

Table 19.7 Chlorine removal step [9]. (Reproduced by permission of the American Chemical Society)

Run	PVC (%)	PET (%)[a]	Feed rate (lb/h)		Temperature (°F)	Cl (ppm)
			Feed	$Ca(OH)_2$		
25	3.0	0.0	80	0	1215	2500–3500
34	0.5	0.0	134	10	925	4–19
35	1.0	0.5	120	12	950	4–12
36	1.0	10.0	120	12	975	6–13
41a	3.0	0.0	120	9	900	90–140[b]
41b	3.0	0.0	20	9	900	120[c]
41b′	3.0	0.0	120	9	900	80[d]
41c	3.0	0.0	120	12	900	60–70

[a] Percent PVC/PET in base mixture

[b] Average from run

[c] Individual sample from run, analysed unwashed

[d] Same sample as 41b, but washed with water to remove inorganic chlorides

Note, these experiments were carried out using a laboratory-scale process

2.1.3 Screw Kiln Reactor

Serrano *et al.* [11] studied the use of a laboratory-scale screw kiln reactor to transform low-density polyethylene (LDPE) into petrochemical feedstock. In this process, pyrolysis was carried out at reaction temperatures of 400–550°C and screw speeds of 3–20 rpm (Figure 19.6). In this process the plastic feed is initially heated in a feed hopper until the feed is melted. The melted plastic is then fed into the screw conveyor where it is depolymerized into gas, liquid and solid. The hopper is equipped with a stirrer to mix the feed plastic. Nitrogen is also used to provide an inert medium for pyrolysis.

The hopper and the reactor are heated using five separate electric furnaces (F_A, F_B, F_C, F_D and F_E). The hopper is heated to 300°C using F_A and F_B while the reactor can be heated up to 550°C using furnace F_D and F_E. Furnace F_C is used to keep the feed material in the molten state while F_D and F_E are adjustable and used to vary the reaction temperature (T_1 and T_2). The reaction zone consists of a screw conveyor inside a 52-cm-long stainless steel tube. The screw speed can be adjusted in the range of 0.5–25 rpm.

In order to determine the performance of the screw kiln reactor Serrano *et al.* [11] carried out several experiments looking at the effect of screw speed and reaction temperature. The output was calculated as the sum of the gaseous, liquid and solid products exiting from the reactor (Table 19.8).

The results obtained by Serrano *et al.* [11] illustrated that at higher reaction temperatures a higher product yield can be obtained (i.e. higher conversion of larger carbon molecules to smaller hydrocarbon molecules). This was achieved at reaction temperatures of 450–550°C. Table 19.9 gives details of product distribution.

The main products derived from the thermal degradation of LDPE in the screw reactor at the set operating conditions were gasoline and middle distillates. Serrano *et al.* [11] showed that the flow in the screw kiln is sufficient to avoid overcracking of heavy fractions into smaller hydrocarbons such as gas which commonly occurs in batch processes.

Product variation was observed when the screw speed was increased from 0.7 to 11 rpm (i.e. decreasing the residence time). The results illustrated that at longer residence times higher amount of gas is produced since a greater amount of thermal cracking takes place (Figure 19.7 and Table 19.10). However, the exception to this rule is at screw speeds of

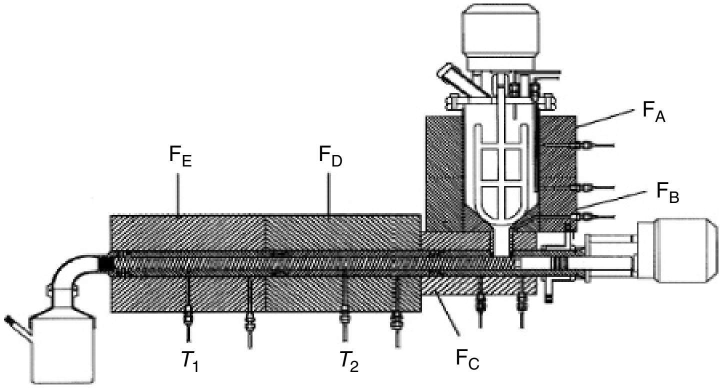


Figure 19.6 Screw kiln reactor [11]. (Reproduced with permission from Elsevier)

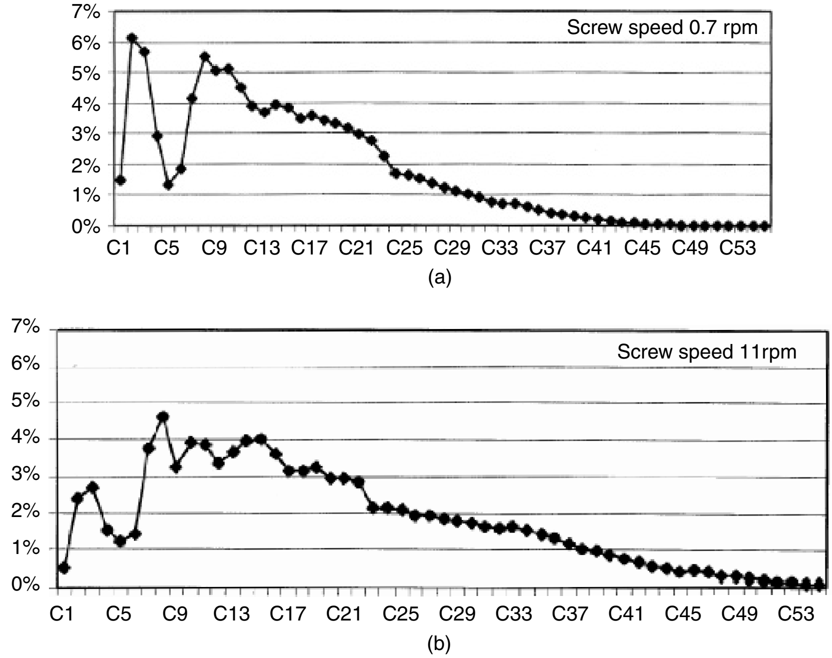
Table 19.8 Effect of temperature and screw speed on product [11]. (Reproduced with permission from Elsevier)

Experiment	Reaction temperature (°C)		Screw speed (rpm)	Output* (g/h)
	T_1, F_D	T_2(°C), F_E		
1	400	400	11	85.2
2	400	450	11	84.5
3	400	500	11	99.4
4	450	500	11	92.0
5	450	550	11	90.2
6	450	550	0.7	13.2
7	450	550	3.0	38.0
8	450	550	8.5	76.6
9	450	550	15.0	35.8
10	450	550	20.0	35.9

Output*: Total sum of the products exiting the reactor

Table 19.9 Effect of temperature on LDPE degradation (screw speed of 11 rpm) [11]. (Reproduced with permission from Elsevier)

Reaction temperatures (°C)		Product selectivity (wt%)				Olefin/paraffin
T_1	T_2	C_1–C_4	C_5–C_{12}	C_{13}–C_{33}	C_{34}–C_{55}	C_2–C_{20}
400	500	1.0	25.4	59.2	14.4	1.06
450	500	4.3	26.2	55.6	13.9	1.22
450	550	7.1	25.4	53.9	13.6	1.61



(a)

(b)

Figure 19.7 Effect of screw speed (450/550°C) on product yield (wt%): (a) screw speed 0.7 rpm; (b) screw speed 11 rpm [11]. (Reproduced with permission from Elsevier)

Table 19.10 Effect of screw speed on LDPE degradation (reaction temperature 450/550°C) [11]. (Reproduced with permission from Elsevier)

Screw speed (r.p.m.)	Product selectivity (wt%)				Olefin/paraffin
	C_1-C_4	C_5-C_{12}	$C_{13}-C_{33}$	$C_{34}-C_{55}$	C_2-C_{20}
0.7	16.4	31.3	48.4	3.9	1.45
3	9.6	28.9	51.2	10.3	1.30
8.5	6.8	27.6	53.2	12.4	1.48
11	7.1	25.4	53.9	13.6	1.61
15	10.1	29.2	51.1	9.6	1.68
20	10.2	29.8	51.4	8.6	1.71

15 and 20 rpm. The results obtained at these speed were very similar to that of 3 rpm. This is because at higher screw speeds less plastic is fed through the reactor.

2.2 EFFECT OF CATALYST ON THE PYROLYSIS REACTION

To improve the reaction yield or to change the properties of the liquid products some processes have examined the use of catalysts. These catalysts range from acid to nonacidic solid catalysts. However, the common catalysts that are used are zeolite (ZSM-5) and silca–alumina [5, 11–14].

Aguado *et al.* [12] studied the effect of catalyst on the conversion of low-density polyethylene using a continuous screw kiln reactor (see Figure 19.6). In this study, mesoporous Al-MCM-41 was used as the catalyst. Initially the plastic feed and the catalyst were mixed together in the hopper at 300°C before being fed into the screw kiln reactor for pyrolysis. The feed mixture consisted of 250 g LDPE and 5 g of catalyst (50:1 w/w plastic: catalyst ratio). The results obtained showed that the catalytic cracking over AL-MCM-41 generates more hydrocarbon products within the gasoline range with up to 80% selectivity (Table 19.11). This is highly favourable since thermal cracking generates a broad range of products and in most cases the products need further refining before they can have any industrial value.

Serrano *et al.* [11] also studied the effect of catalyst on the conversion of LDPE using a continuous screw kiln reactor. The same experimental method was used as Aguado *et al.* [12]. They also noticed that when using mesoporous MCM-41 aluminosilicate catalyst a higher yield of gasoline fraction can be obtained (Table 19.12). They believe that the cause of this is secondary reactions that take place inside the reactor between the smaller volatile groups as they travel through the kiln. This occurrence is greatly improved in the catalytic cracking since the catalyst strongly promotes secondary reactions (i.e. oligomerization) between volatiles.

2.3 EFFECT OF TEMPERATURE

Temperature is one of the most important parameters in pyrolysis reactions. Reaction temperature has direct correlation with product yield. For example, from an economic prospective solid product produced by pyrolysis is the least desired product. This is

Table 19.11 Catalytic and thermal cracking of LDPE [12]. (Reproduced with permission from Elsevier)

Experiment	Screw speed (rpm)	T_1/T_2 (°C)	Output (g/h)	Conversion (wt.%)	TOF (s^{-1})	Selectivity (wt%)			
						C_1–C_4	C_5–C_{12}	C_{13}–C_{23}	C_{24}–C_{55}
ST	3.0	450/550	38.0	100	–	9.4	28.9	35.7	26.0
SC1	3.0	400/450	19.6	69.1	0.291	21.4	66.4	4.6	7.6
SC2	6.0	400/450	26.9	64.9	0.374	18.1	69.3	9.7	2.9
SC3	15.0	400/450	41.2	51.4	0.454	18.3	77.7	2.0	2.0

ST, SC: thermal and catalytic cracking

TOF: turnover frequency. Values calculated as mass of converted LDPE/mass of Al in the catalysts, but this will not give S^{-1} unit

Note, the catalytic cracking of LDPE was performed at T_1/T_2 400/450 at screw speeds of 3–15 rpm. The results were compared with a previous thermal cracking experiment carried out by Serrano *et al.* [11] using screw speed of 3 rpm and reaction temperature of 450/550°C.

Table 19.12 Catalytic cracking of LDPE at screw speed of 8.5 rpm [11]. (Reproduced with permission from Elsevier)

T_1/T_2 (°C)	Conversion (wt.%)	Productivity (wt%)			
		C_1–C_4	C_5–C_{12}	C_{13}–C_{33}	C_{34}–C_{55}
400/400	24.8	16.1	76.5	7.1	0.3
400/450	60.8	9.0	81.0	10.0	0.0
450/450	87.9	5.1	80.3	13.1	1.5
450/500	100	12.6	74.2	11.9	1.3

because the solid product has very little use. However, Williams and Besler [15] showed that the solid product could be reduced if higher reaction temperatures were used. They found that at 720°C the final product contained less solid. This is because at the higher temperatures more of the solid is converted into liquid and gas. This has also been the case for most processes described in this chapter. For example, Meszaros [9] illustrated that as the reaction temperature in the Conrad process was increased less solid product was produced.

Li *et al.* [16] also studied the influence of pyrolysis temperature on the pyrolysis products derived from solid waste in a rotary kiln reactor. They used an externally heated laboratory-scale rotary kiln pyrolyser (Figure 19.8). The length of the rotary kiln was 0.45 m with an internal diameter of 0.205 m. Kiln rotation speed can be adjusted from 0.5 to 10 rpm. The raw materials used in this study were polyethylene (PE), wood and waste tyres. The results obtained by Li *et al.* [16] reiterated that as the reaction temperature profile changes so does the product yield (Figure 19.9).

In summary the operating temperature determines the amount of solid, liquid and gas products that are produced from a given pyrolysis process. At higher reaction temperatures more gaseous and liquid products are produced. However, at lower temperatures more coke-like solid is produced. Depending on the process and feedstock composition the optimal reaction temperature can be different. From an economic perspective higher amounts of gas and liquid products are more beneficial.

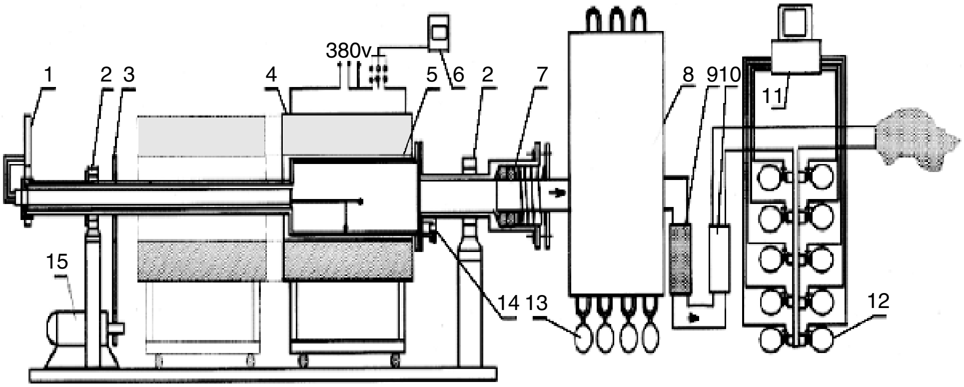


Figure 19.8 Rotary kiln reactor. 1 thermometer; 2 bearing; 3 gear transmission; 4 electric furnace; 5 rotary kiln; 6 temperature controller; 7 seal; 8 tube condenser; 9 filter; 10 total flow meter; 11 computer; 12 gas sampling device; 13 tar reservoir; 14 feed and discharge opening; 15 electric motor [16]. (Reproduced with permission from Elsevier)

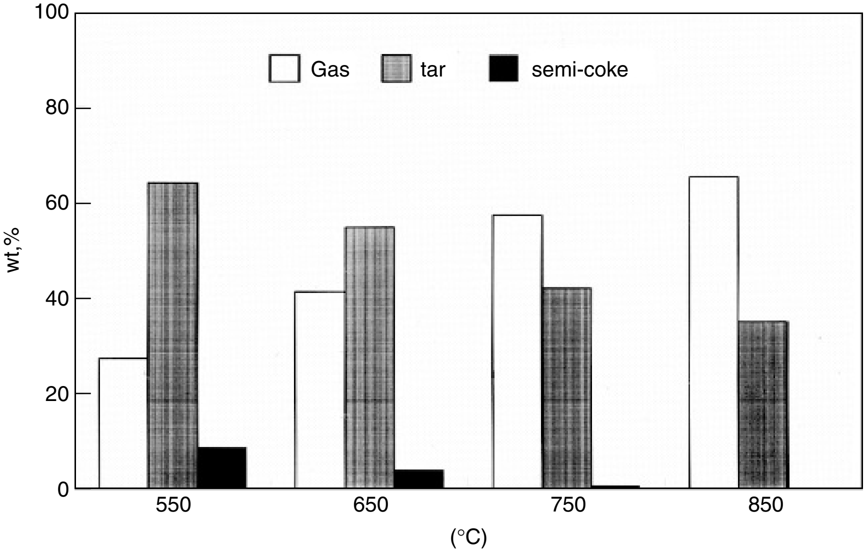


Figure 19.9 Effect reaction temperature on product yield [16]. (Reproduced with permission from Elsevier)

2.4 ROTARY KILN REACTOR VS FLUIDIZED BED

As described previously pyrolysis is a process that thermally degrades organic waste at high temperatures in absence of air and oxygen. This process can be carried out in a rotary kiln reactor or in a fluidized bed. In a rotary kiln process the feed material is conveyed through a rotating drum (i.e. reactor) and is then pyrolysed in the hot atmosphere into gas and solid residues. The residence time of the reaction is dependent on the rotating speed of the drum, i.e. the faster the drum rotates the shorter the residence time. The reactor is heated externally using some of the gases produced by the process and in some cases by natural gas. Rotary kiln processes are described to have lower capital cost which makes them an attractive option. However, they have a lower processing capability and tend to have longer residence times [5, 8, 9]. Furthermore, rotary kiln reactors have large temperature gradients across their diameter and tend to have poor temperature control. As a result they tend to have a wide number of products with varying composition.

In a fluidized-bed process the fed plastic is heated by exposing it to a hot medium (i.e. quartz sand). The advantage of this is that it allows for more uniform heating which in turn produce a more uniform product in a shorter residence time. A fluidized bed can have a residence time of seconds to a few minutes. This is due to the even heating of the fluidized bed. The fluidized bed is heated by indirect heating from heat pipes that carry flue gases through the bed [5, 17–19]. The following are some general characteristics of a fluidized-bed process:

- high liquid yields;
- good temperature control;
- difficulties with solid removal;
- low process durability;
- higher capital cost;
- higher processing rate;
- process costs 13–16 cents/lb;
- products may have higher value than those obtained from kiln reactor;
- better heteroatom capture.

However, it should be noted that both processes have the same economic disadvantage. Both processes are faced with high collection and sorting cost of waste plastic. The processes will not be attractive unless some form of subsidies are provided [5]. In summary both process are available on pilot plant and industrial scale [4, 5, 8, 9].

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20

Rotary Kiln Pyrolysis of Polymers Containing Heteroatoms

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1 INTRODUCTION

Pyrolysis of polymers means thermal decomposition of the material in the absence of oxygen. During the process pyrolysis gases or oils are evolved. Today pyrolysis units use polymers with a wide spread of constitution: mixtures, spilled mixtures as well as mono fractions. A heterogeneous feed yields a broad spectrum of pyrolysis products, thus dramatically reducing the economic attractiveness of the process. Present technologies are melting vessels, autoclaves, tube reactors, fluidized beds, stirred reactors, cascades of stirred reactors and rotary kilns. Technologies that convert plastic wastes back to their starting materials or to general decomposition products are a promising development in plastics recycling. An initial challenge for these new recycling technologies is to develop cost-effective and versatile process units which can handle a variety of mixed plastic resins and additives typically found in post-consumer waste streams. The Haloclean Process – a rotary kiln process – documented within this chapter has successfully met this challenge and demonstrated its applicability to brominated electronic scrap during extensive parametric studies.

Therefore, rotary kilns are the special application of this chapter and are compared with competing technologies. A closer look is given to the treatment of thermoplastic, thermosetting or elastomer-based polymers, containing heteroatoms such as nitrogen, chlorine or bromine.

2 TECHNICAL VARIATIONS

Typically two major types of rotary kilns are used for pyrolysis processes either internally or externally heated systems. For internally heated kilns a heat exchanger based on steam-

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or gas-powered tubes or electrical heaters are used. For externally heated systems we find steam, gas (direct or indirect) or electrical powered systems. The following three examples show engineering solutions for processing of highly volatile feeds and their relevance in processing.

2.1 CONRAD PROCESS

Any post-consumer plastic stream will contain some halogens in the form of polyvinyl chloride, polyvinylidene chloride, brominated flame retardants, halogenated additives, food waste, or salt. Therefore, two issues must be considered. First, the gas stream resulting from the depolymerization of plastics must be scrubbed to remove any halogenated gases to satisfy emissions controls. Second, halogens in the liquid product must be minimized to increase its value and marketability. Therefore the Conrad process has been developed. It is a robust process unit that can accommodate a variable feedstream and produce a consistent product, free of nonhydrocarbon impurities by low feed preparation costs.

The Conrad recycling process uses a horizontal auger kiln reactor that applies heat to plastics and/or tires in the absence of oxygen to produce liquid petroleum, solid carbonaceous material, and noncondensable gases [1–3]. The control of the pyrolysis process is decided by temperature and especially auger speed and temperature.

2.2 DOUBLE ROTARY KILN PYROLYSIS

The double rotary kiln pyrolysis is designed for mechanical coupling of a pyrolysis unit and a combustion unit. The coaxial system of two rotary kilns opens up the possibility to evaporate organics from the feed material in the inner kiln while the carbonaceous residues are transported through the external kiln to a combustion zone. The process heat of combustion is used to heat the inner kiln while the ashes leave the system [4]. Both kilns can be equipped with lifters or spiral lifters. A comparable system has been purchased by Kurimoto industries, Japan for drying and calcining processes.

2.3 PYROLYSIS OF TIRES: FAULKNER SYSTEM

The pyrolysis of tires based on rotary kiln technology started quite early in the 1970s. A field-scale rotary kiln at Rocky Flats is documented in [5]. Very new developments can be found in [6]. The rotary kiln developed by Faulkner has several distinct heating zones independent from each other. The system consists of a rotary feed cylinder that includes a screw-like flight extending from the inner wall of the feed cylinder. As the feed cylinder rotates, the flight directs the supply of vehicle tire pieces into the infeed end of the pyrolysis section. The temperature levels of the kiln zones decrease from a maximum of 800°C to 500°C at the end of the kiln. A separation of char and scrap steel is performed by a trajectory diverter at the end of kiln. The char passes through the slots, whereas the scrap steel is transported to the outlet.

2.4 VTA PYROLYSIS: A ROTARY KILN FOR THE TREATMENT OF PETROCHEMICAL RESIDUES AND HYDROCARBON RESIDUES

The low-temperature carburization LTA process developed by VTA meets the worldwide need for a process which economically reduces petrochemical and hydrocarbon residues into recyclable products, feedstocks or clean fuels. The indirectly fired rotary kiln system can be operated up to 850°C. The throughput varies in between 800 and 2000 kg/h.

LTC in a VTA rotary kiln is an economical process, because of process flexibility and simple design. VTA's kiln design can process, solids, slurrys, sludges, viscous liquids, volatile, and materials difficult to handle in other types of equipment. The LTC kiln sealing system allows operating the system under positive pressure, assuring no leakage of air which can produce an explosive mixture.

The kiln consists of four operating zones, a vaporization, cracking, polymerization and carburization zone. The remaining residues are transported out of the system by a screw flight.

For cleaning the kiln wall from carbonaceous materials and feed, VTA invented a cylindrical cleaning device lying on the bottom of the rotary kiln, equipped with high-temperature bearings effective over a temperature range up to 1100°C, running up to 8000 h/yr without lubrication. The cylindrical unit is mounted on the infeed side of the kiln and ends in the carburization zone of the kiln. A cone segment connects to the infeed zone. VTA is specifies the advantages of the rotary kiln as follows [7]:

- compliance with present-day stringent environmental requirements;
- less capital investment in comparison with incineration units;
- due to the unique sealing system on the inlet and outlet side and the supervisory monitoring system, the rotary kiln meets or exceeds the most stringent criteria for emissions;
- high-temperature efficiency and maximum capacity are assured by the patented kiln wall cleaning device, equipped with maintenance free high-temperature bushings (no lubrication);
- based on the improved design, the on-stream time of the rotary kiln is increased to 8,000 h/yr operating at 850°C continuously.

3 STATE OF THE ART OF ROTARY KILN TECHNOLOGY (TABLE 20.1)

Use of the rotary kiln technology on a technical scale depends strongly on the economics of the process. In the past several process types were tested and applied. Usually 'operative mode' or 'shut down' were not affected by technical problems, but by the profitability of the processes. One example is the Siemens-KWU process. It has been dismantled in Germany due to technical and economic reasons, but is running in Japan at nine sites.

In terms of tire recycling several approaches were started in the past and are either shut down today or competing strongly for fuel substitution in cement kilns or as regranulation for use in the building industry. A promising approach in 2002–2003 by Ligmbh Germany [22] for the treatment of 60 000 tonnes of used tires never reached technical scale. The rotary kiln technology was implemented for the activation reaction of pyrolysis coke to activated carbon.

3.1 HALOCLEAN GAS-TIGHT ROTARY KILN

The Haloclean rotary kiln is especially designed for the pyrolysis of high amount of inert and/or thermosetting containing materials, e.g. electronic scrap. The invention is based on experience with a vertical reactor system for the conversion of thermoplastics the so called cycled-spheres reactor [8]. Hornung *et al.* [9] invented a system improving the heat transfer to poorly heat-transferring materials such as plastics, ensuring that decomposition on a laboratory scale can also be described with microkinetic analysis [10]. As shown in [8] the usage of a sphere-filled reaction vessel improves the heat conductivity by an order of magnitude at least 1. The system used a screw cycling metal spheres to keep the polymer melt hot and to heat up entering melt to reaction temperature by ‘mixing’ with metal spheres. Obviously the system was not suitable in the case of nonmelting plastics. The idea of heat-transferring metal spheres and a screw which transports not only spheres, but also feed material was transferred to an industrial-type reaction system, a rotary kiln [11]. To maintain the performance at low rates of consecutive reactions of the pyrolysis gases as well as low residence times of the pyrolysis gases in the system, the hollow screw shaft has been equipped with 200 sintered metal plates. These plates are permanently cleaned by the material passing their surface, thus keeping the inner core of the screw free from pyrolysis products and introducing the purge gas directly where the pyrolysis products are evolved, (Figure 20.1).

Today, applications in the fields of pyrolysis of shredder light fractions and electronic goods seem to be the most promising for pyrolysis. For both the feeds strong support

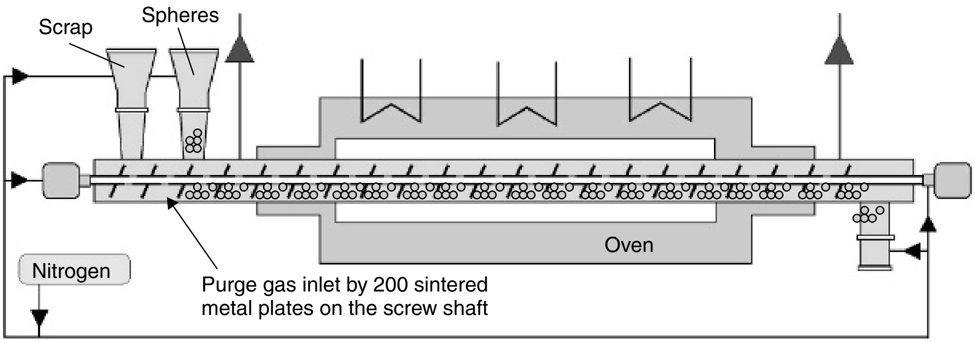

Figure 20.1 The Haloclean reactor

for recycling is given by European legislation. A detailed discussion of these applications can be found in the following sections.

A further promising field for application of pyrolysis (not a topic of this chapter) seems to be the coupling of the pyrolysis units with a thermal plant. The pyrolysis fractions can be used as precleaned feed support for the combined power plant as shown in Table 20.1 for ConTherm at Hamm-Uentrop with a capacity of 100 000 t/yr high caloric feed [15, 17].

4 ROTARY KILN PRINCIPLES

The effects of varying the parameters of standard rotary kiln pyrolysis processes on the pyrolysis product spectrum of shredder light fractions, tires, municipal solid waste as well as plastics has been investigated in detail by Wanzl, Lee and Co-workers [23–27]. They clearly showed the problems in transferring analytical data from micro- and laboratory-scale experiments to rotary kiln applications. Usually the residence time behaviour of the systems at micro and technical scale is different and therefore affects secondary reactions of the pyrolysis products. This is not a negative effect at all. In the case of longer residence times and higher temperatures in rotary kilns, especially in case of pyrolysis oils and gases from shredder light fractions the composition is shifted to more stable light aromatics. Furthermore, the use of catalyst can improve cracking and isomerization as well as chlorine removal [23, 24]. The chlorine removal in case of shredder light fractions is of high importance due to the fact that these feeds contain up to 10 wt% of chlorine. Chlorine scavenging strategies in general are described in the following section. Comparing the fluidized bed and rotary kiln technology the results of Wanzl *et al.* [23, 24] and Li *et al.* [26, 27] and Pasel [25] can be summarized as follows. A rotary kiln (although it provides lower heating rates) is flexible with regard to the residence time as well as time/temperature profile and can be adjusted to the process requirements as the length of the kiln can be varied. Moreover, an optimum temperature profile can be set via different heating zones being independently controlled. For example in comparison with a fluidized bed, a rotary kiln may be a suitable alternative for a conversion reactor in a recycling scheme for plastic wastes as it combines suitable reaction conditions with advantages in the mechanical treatment of the solid reactor feed. Li *et al.* [26, 27] checked for the heating rate influences in rotary kiln systems on gas production. Principally those studies can be transferred to technical application, taking into account the specific heat transfer conditions in the kiln, temperature levels to be adjusted, feed temperature and temperature conditions of the infeed zone and finally the feed/energy supply ratio. In terms of PVC, Li *et al.* have shown that the overall gas production per kg of feed can be increased by 80%, in continuous cracking, not only converting the gas species using temperatures up to 800°C, but also lowering the absolute amount of tar and semi-coke.

5 TREATMENT OF THERMOPLASTICS: PVC

New pathways in plastics recycling and the current status of plastics recycling has been recently highlighted by Kaminsky *et al.* [28]. The development of different viable recycling technologies for plastic waste materials is becoming increasingly important. The

Table 20.1 Rotary kiln processes

Company	Feed type	Site	Type	Reference	Start/feed/ remarks/ status [15]
Siemens-KWU-Schwelbrenn-Verfahren	Plastics/municipal waste	Fürth, Germany	Internal tube heat exchanger, low-temperature steam, high-temperature natural gas	[16]	1997/4 × 5 Mg/h/closed 1999/dismantled
KWU	Municipal waste Shredder light fractions	9 sites in Japan		[15]	1996–2003/6–20 Mg/h/ operating
PKA-Kiener	Municipal waste	Aalen, Germany	Low-temperature pyrolysis, internally tube heated	[17]	1982/3 Mg/h/dismantled in 2002
Kobe	Tires	Akoh, Japan	Externally heated drum	[18]	200 kg/h/1 Mg/h [18]
Noell	Plastic containing special wastes	Salzgitter, Germany	Indirectly heated drum	[16]	1996/7 Mg/h/shut down for economic reasons
Pleq	Soil decontamination	Herne, Germany	Externally heated	[15]	1989/7 Mg/h/operating
BKMI Burgau	municipal waste	Burgau, Germany	Externally heated, pyrolysis kiln under moderate pressure	[17]	1984/7 Mg/h/operating
BKMI	Shredder light fractions	Nassau, USA		[15]	1984/5 Mg/h/shut down 1996

MVU Rotopyr	Cables, rubber, municipal waste	Bochum, Germany	Externally heated drum	[17, 19]	
BC Pyrocom	Electronic scrap	Lübben, Germany	Electrically (externally) heated kiln	[20, 21]	Shut down
Conrad	Plastics/tires	Chehalis, USA	Auger kiln, externally heated	[2, 3]	Shut down
DAL	Municipal waste	Plaidt, Germany	Externally heated	[17]	2 Mg/h/shut down
VTA	Municipal waste, chemical residues	Gelsenkirchen, Germany/ Victoria, Texas, USA	Externally heated/indirectly gas fired	[15]	2001/2 Mg/h/in operation
Haloclean	Electronic scrap	Karlsruhe, Germany (Sea Marconi, Italy)	Internally and externally electrically heated/electrically heated screw with purge gas supply	[15]	Pilot scale, 40 kg/h/technical scale expected in 2005, (400 kg/h)
ConTherm	Municipal waste Plastic wastes	Hamm-Uentrop, Germany	Externally heated, gas fired	[15]	2000/2 × 6 Mg/h/ operating/secondary fuels for thermal plant

following overview of the literature offers the prospect of tailored pyrolysis to realize halogen-free or reduced feedstocks while modifying or optimizing the composition of pyrolysis products when pyrolysing polyolefines, polystyrene and/or polyvinylchloride.

Kaminsky [29] studied the thermal cracking of polyethylene (PE) in a fluidized-bed reactor over the temperature range 500–600°C. At temperatures below 550°C, high yields of useful products with low yields of gas and aromatics were obtained.

Ding *et al.* [30, 31] have studied hydrocracking of polyethylene (PE) using catalysts such as HZSM-5, shifting to more aromatic products. Agudo *et al.* [32] investigated the effect of β-zeolite on the degradation of polypropylene (PP), low-density polyethylene (LDPE) and high-density polyethylene (HDPE) at 400°C. In the case of LDPE and PP a shift to light products (C_1–C_4) was observed and in the case of HDPE a shift to C_5–C_{12} products was observed.

A series of studies dealing with the process integrated dehydrochlorination of plastic mixtures (polyvinylchloride, polystyrene and polyolefines) has been done by Hornung and Bockhorn [33–35]. By varying the temperature in distinct steps it was possible to evolve 99.6% of the HCl before the main pyrolysis of polystyrene and polyolefines appeared.

A detailed study on scavenging HCl by calcium-based sorbents (Ca-C sorbent, consisting of 90 wt% of $CaCO_3$ and 10 wt% of phenol resin) during or after pyrolysis has been completed recently by Bhaskar *et al.* [36] and is planned for technical application at a municipal plastic waste pyrolysis plant at Mizushima, Japan. Calcium-based scavenging is a strategy already followed in industry and studied deeply for fluidized-bed pyrolysis of thermoplastics by Sinn and Kaminsky [37–39].

For shredder light fractions, a mixture of polyolefins and polyurethanes containing as well as polyamides, PVC, polystyrene and blends, Wanzl *et al.* [23, 24] and Pasel [25] have shown for the treatment of the pyrolysis gases from rotary kiln pyrolysis that by using dolomite beds at 500°C and a residence time of 20 s, chlorine content can be reduced from 1000 ppm to below the detection limit of 1 ppm.

With the Conrad process [1–3] a set of experimental runs with a throughput of approximately 100–1000 kg/h with PVC contents of up to 3% in a 60:20:20 HDPE:PP:PS base mixture have been performed. Typically 70–80% of liquids and 1–3% of solids are obtained. In scavenging the chlorine from evolving gases by hot calcium oxide and before condensation of the liquid fraction with a content of about 25 ppm chlorine were possible. Similar results were obtained by treating the plastics in the kiln with calcium oxide during pyrolysis. A direct condensation without any calcium oxide treatment led to concentrations of up to 10 000 ppm chlorine.

6 PYROLYSIS OF MONO FRACTIONS: POLYMETHYLMETHACRYLATE PMMA

A special case in terms of application of rotary kiln technology is the pyrolysis of mono fractions such as styrene, PMMA, polycarbonate, or polyethylene terephthalate. Polymethylmethacrylate is an example illustrate the advantages in using fluidized beds or rotary kilns. The feed material does not have a heteroatom problem and the pyrolysis product can easily be handled as a monomer source instead of feedstock. Therefore the aim of the pyrolysis is a low amount of by-products and a high yield of monomer. For this example it has been shown by Sasse and Emig [40, 41] that the fluidized bed is advantageous. Even both techniques can be applied.

7 TREATMENT OF SHREDDER LIGHT FRACTIONS/SHREDDER RESIDUES

The treatment of shredder light fractions/shredder residues in rotary kilns is not as common as in the case of other fractions [42–45]. Due to the mixture of materials today, gasification, blast furnace, and fluidized-bed pyrolysis are preferred, transforming the feed into reducing agents, syngas or feedstock. Nevertheless several studies at laboratory and technical scale have shown the feasibility of rotary kiln application [23–25, 46–49]. Especially in terms of recovery of liquid products [23–25, 46, 47], instead of using them as reducing agent or to transform them to syngas [42, 43], in combination with the reuse of the solid fractions in different technological applications such as the ferrous and nonferrous metals industries and the building industry [49, 48] the rotary kiln technology seems to be promising. A technical-scale run at Siemens-KWU with 30 tonnes of shredder residue with a throughput of 143 kg/h and a total run time of 211 h has shown no problems in terms of the rotary kiln technology [48]. Recent studies have been performed by Harder [49] with a 500 L kiln at 600–700°C, showing a residence time of about 12 min and an amount of volatiles, excluding water, of 30–35 wt% of the feed.

A typical composition of shredder light fractions from the automotive industry and electronic goods is given in [43] with 32 wt% of plastics, 25 wt% of elastomers, 8 wt% of wood, cellulose and textiles, 4 wt% of colorants, 2 wt% metals, and 29 wt% of minerals, glass and stone. The composition of automotive shredder shifts slightly to more plastics with 35 wt%, 17 wt% of metals, and 18 wt% of minerals, glass and stone. Tecpol [43] is mentions an annual gasifier capacity for shredder light fractions in Germany in 2010 of about 210 000 tonnes for producing methanol.

The works cited on optimizing the pyrolysis gas composition show the principal disadvantage by pyrolysing shredder residues or shredder light fractions compared with packaging materials, even those containing PVC or mono fractions. The mixture of aliphatics and aromatics, containing acidic compounds and nitrogen-based pollutants need further post-treatment if pyrolysis oils are to be used. Presently, recycling quotas can be matched in terms of gasification with combined synthesis gas production and methanol synthesis and the processes are less sensible in terms of feed material compositions.

8 TREATMENT OF ELECTRONIC SCRAP

The treatment of electronic scrap is again more complicated and delicate than treating shredder residues or shredder light fractions. On one hand it is a mixture of thermoplastics and thermosettings, on the other hand it contains quite high amounts of bromine, precious metals, nonferrous metals, and useful inert materials. These two aspects are combined with the tendency of the material to react to high amounts of carbonaceous residue as well as forming brominated dibenzodioxins, and furans if treated not properly.

Today technologies offer different ways of proper treatment of these fractions such as co-combustion [50] or use in copper smelters [2, 51, 52]. Both technologies fail to reach the new European recycling quotas for electronic goods. The main reason is the energetic usage of the plastic instead of recycling it.

8.1 THE EUROPEAN DIMENSION

Plastics in electrical devices are composed of different additives such as phosphates, brominated compounds, chlorinated substances or antimony oxides in order to suppress the evolution of flames and the development of heat in case of fire.

However, especially brominated flame retardants are creating problems when electronic and electrical equipment reach end of life. If landfilled, toxic brominated flame retardants may slowly leach out into the groundwater, where they persist for several years or they can evolve into the air. If waste materials are burned toxic polybrominated dioxins and furans can be formed [53, 50].

Although phosphates are increasingly replacing brominated additives, there is still a wide range of manufacturers around the world using them. So waste will continue to contain these substances. Against the background of the European directive for waste electrical and electronic equipment introduced on 13 February 2003 and to be transferred into national law [54] an innovative technology to cope with bromine-containing electronic devices is required. The recommended quotas for the end of 2006 are given in Table 20.2.

8.2 THE PYROCOM ROTARY KILN

In the mid-1990s BASF, Ludwigshafen and APME, Brussels had run experiments with electronic scrap in cooperation with the BC-Berlin Consult plant in Lübben, Germany. The BC plant consisted of an indirectly heated rotary kiln with 300 mm inner diameter and 3 m heated length driven at 750–850°C [20, 21, 55]. Two types of material were investigated, a fine fraction and a typically shredded electronic scrap fraction. Up to

Table 20.2 Recycling quotas of the European Union

Category	Total quota, including thermal treatment (%)	Remarketing and recycling (%)
1 White goods	80	75
2 Brown goods	70	50
3 Lamps	70	50
4 Tools, electronic/electrical	70	50
5 Toys, electronic/electrical	70	50
6 System control and measurement	70	50
7 IT and telecommunication	75	65
8 Entertainment	75	65

Table 20.3 Pyrolysis products from BC-rotary kiln runs [20]

Trial	1	2	3	4	5
Type	Shredder	Fine	Fine	Shredder	Shredder
Temp/°C	850	750	850	750	750
Coke/wt.-%	72.8	43.1	43.5	74.5	77.1
Oil/wt.-%	11.8	18.9	17.7	9.9	5.2
Gas/wt.-%	11.5	27.4	26.9	13.5	16.1
Others/wt.-%	3.9	10.6	11.0	2.1	1.5
Duration/h	28	14	26	30	74
Feed/kg/h	35	22	16	30	24
Total/kg	1000	313	432	890	1751

1700 kg and feeds up to 35 kg/h were used. The experiments have shown that the metal-containing shredded fraction has been processed in the kiln without blockage. In terms of the fine fraction, and due to the high amount of plastics, carbonaceous residues were formed on the kiln wall and the processing had to be stopped. The pyrolysis products obtained in the runs are shown in Table 20.3.

8.3 THE HALOCLEAN ROTARY KILN PROCESS

Since 2002 a European consortium has dealt with the transfer of a pilot-scale Haloclean rotary kiln system to technical scale (Figure 20.2). By scaling up the pilot-scale unit with a throughput of about 40 kg/h, a technical scale with a feed of up to 3000 t/a will be realized. The Haloclean process, combined with its post-treatment facilities transforms electronic scrap into three typical fractions, residues containing metals, precious metals, carbon, glass and inerts, as well as phenolic-based oils and HBr [11, 51, 56–59].

By reaching the European recycling quotas the process is delivering a residue-based feed material for copper smelters, an oil low in bromine suitable for gasifiers with combined methanol synthesis, and HBr by post-treatment reactions.

On a pilot scale (Figure 20.2) several process parameters such as temperature, residence time and rotation speed and modes have been optimized. The temperature has been varied between 250 and 550°C. The residence time was between 1 and 4 h. The bromine content of all products was determined and especially the amount of brominated dibenzodioxins and furans in the residue fractions was determined and correlated with temperature.

Different fractions of electronic scrap were tested and pyrolysed. Figures 20.3–20.6 show feed materials and their related residues. In the case of populated and nonpopulated computer circuit boards as well as in the case of television boards a non-sticky residue results.

As worked out for several reaction temperatures and residence times, different materials such as populated and nonpopulated circuit boards from computers or television sets as well as housing fractions from computers or monitors can be processed at two distinct temperature levels of 350 and 450°C and residence times of 2 h for each stage. The residue amount under these conditions can be specified as 65 wt% for nonpopulated printed circuit boards up to 90 wt% for television printed circuit boards. In the case of housing fractions the entire feed fraction has been converted in oils and gases. This result is strongly dependent on the composition of the feed.

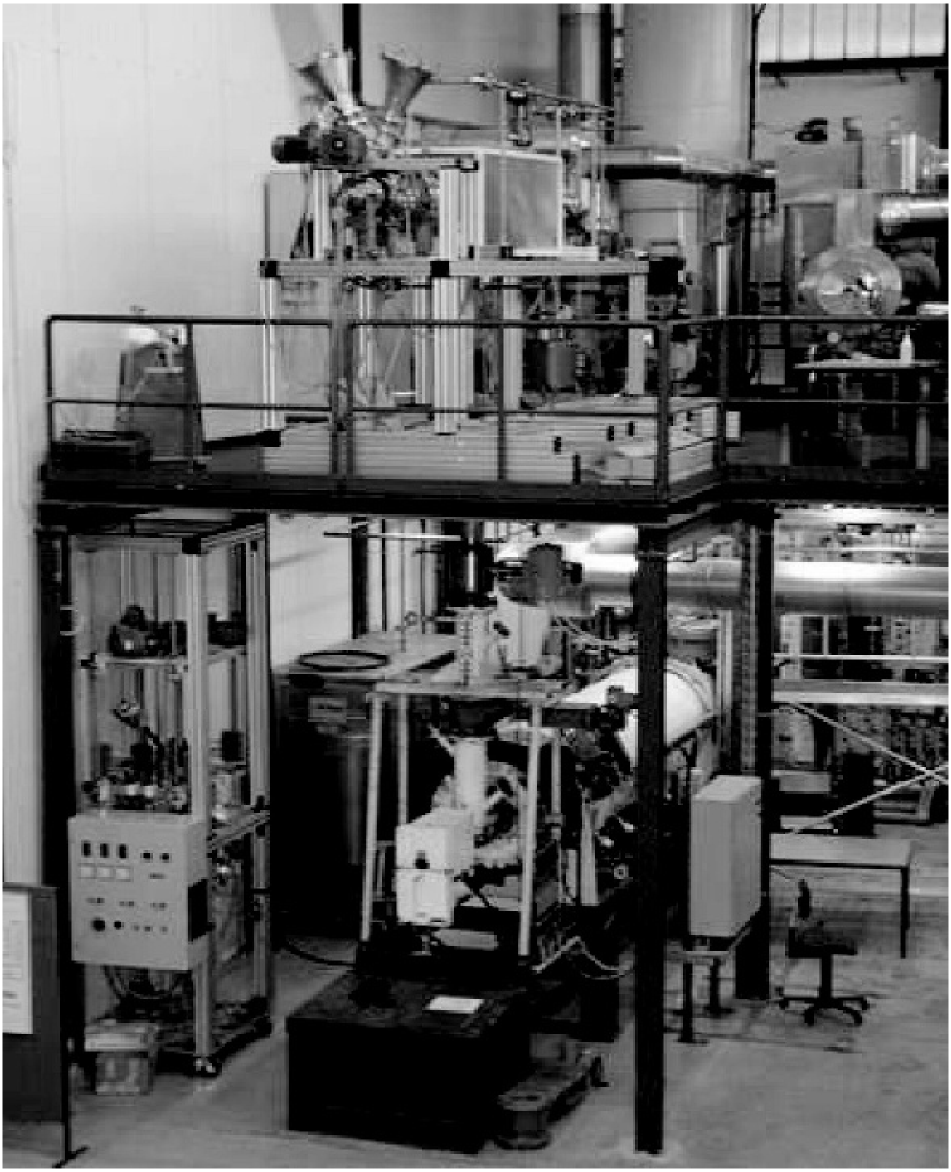

Figure 20.2 The Haloclean plant. The Haloclean kiln on top is combined with the Pydra rotary kiln as a second stage, and a standard rotary kiln, similar to the system used at Pyrocom

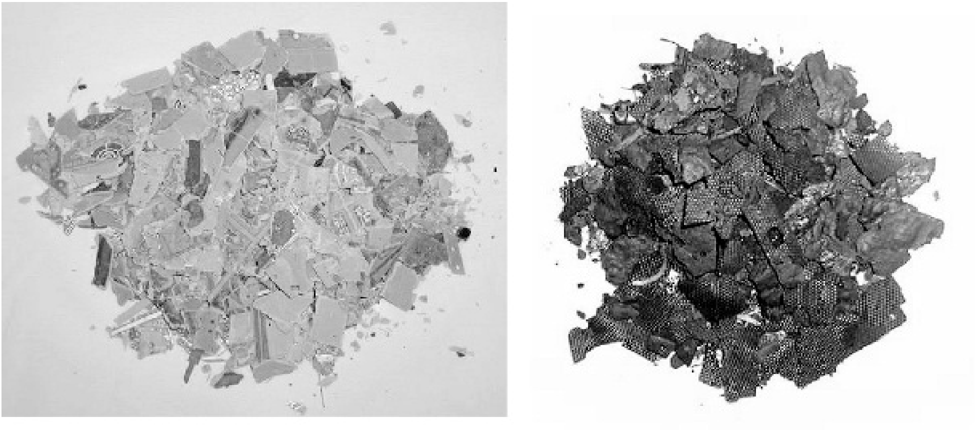

Figure 20.3 Nonpopulated computer circuit boards, pyrolysed at 350 and 450°C, 2 h at each stage and the corresponding residues. If necessary these residues can be sieved in fractions for accumulation of metals or used in total

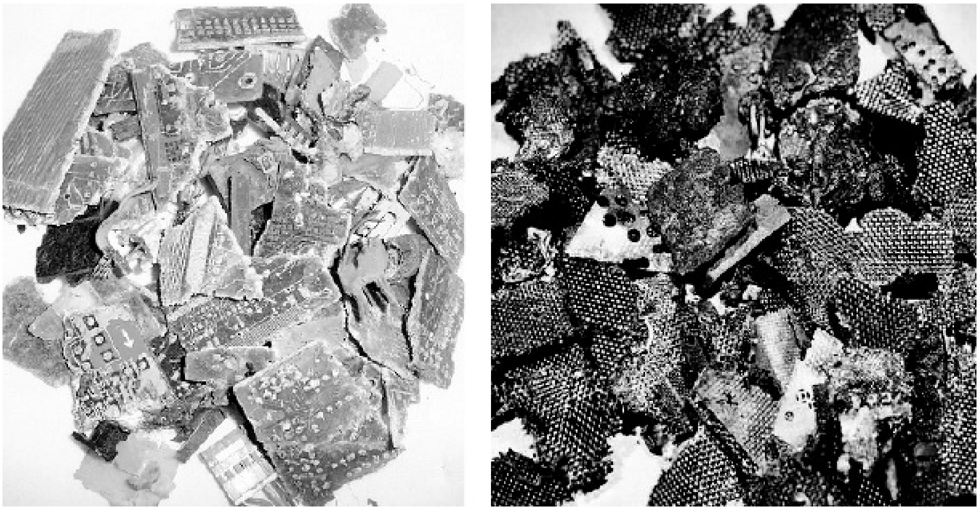

Figure 20.4 Populated computer circuit boards, pyrolysed at 350 and 450°C, 2 h at each stage and the related residues

The chosen reaction conditions ensure that all residue fractions consisting of brominated dibenzodioxins or furans below the given German limits of 1 μg/kg for 2,3,7,8-tetrabromodibenzo-*p*-dioxin, 1,2,3,7,8-pentrabromodibenzo-*p*-dioxin, 2,3,7,8-tetrabromodibenzofuran and 2,3,4,7,8-pentabromodibenzofuran and lower than 5 μg/kg for 1,2,3,6,7,8-hexabromodibenzo-*p*-dioxin, 1,2,3,7,8,9-hexabromodibenzo-*p*-dioxin and 1,2,3,7,8-pentabromodibenzofuran, as required by the Deutsche Chemikalien Verbotverordnung for free transportation of goods [60].

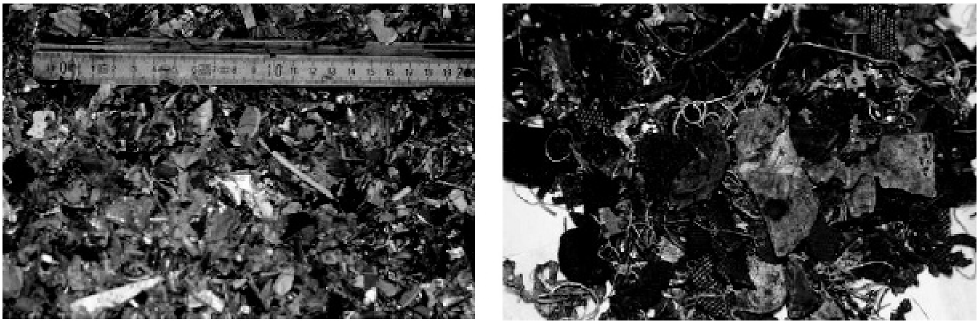

Figure 20.5 Television printed circuit boards, pyrolysed at 350 and 450°C, 2 h at each stage and the related residues

Figure 20.6 Housing fractions, pyrolysed at too low a temperature of about 350°C for 2 h, the residues becoming sticky

Finally, Figure 20.7 shows the constitution of the rotary kiln with its screw device after 1800 h operation with different materials. The screw blades and the screw shaft are free from carbonaceous residues due to permanent cleaning by metal spheres and shredded goods.

9 DEHALOGENATION OF PYROLYSIS OILS

This final section deals with the dehalogenation of pyrolysis oils from electronic scrap. In terms of using those materials for feedstock recycling, synthesis gas production or fossil fuel substitution, dehalogenation is strongly required. For feedstock recycling a 10 ppm

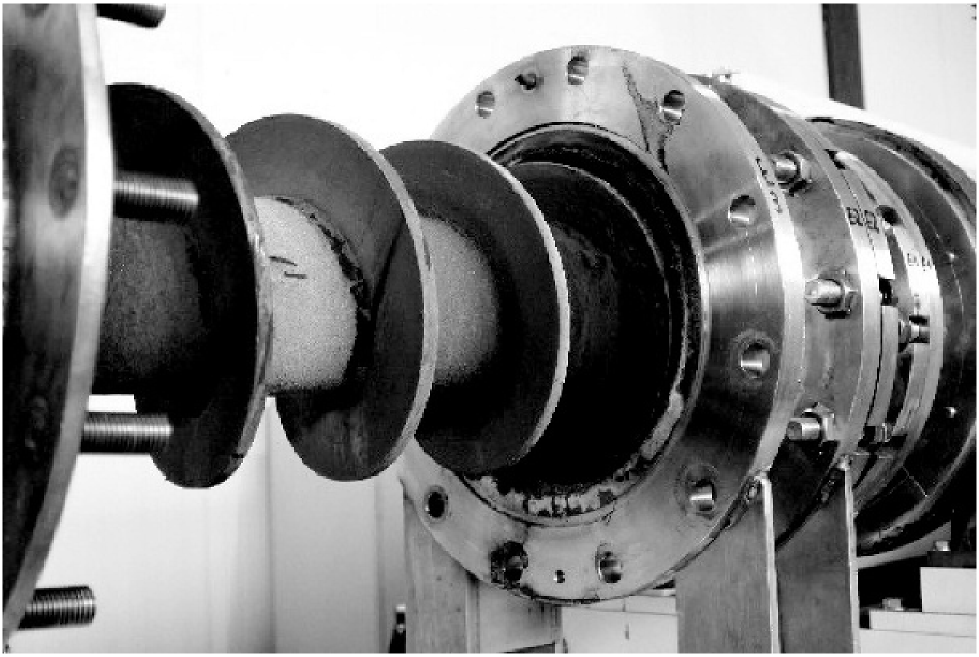

Figure 20.7 Opening of the unit after 18 months usage and approximately 1800 h operation

limit of halogens is specified [21]. Various methods for the dehalogenation of pyrolysis oils are given by Kühl [21]. He described physical, chemical and thermal methods which all failed in terms of dehalogenation of pyrolysis oils from Pyrocom runs due to too high a bromine content. Alternatives are given by Bhaskar *et al.* [36] for chlorine-containing feeds and Sakata *et al.* [61] for chlorine- and bromine-containing feeds from pyrolysis municipal waste or electronic scrap-related materials using calcium oxide and Ca-C (a mixture of calcium oxide and a phenolic resin). Blazsó *et al.* [62] described the debromination of flame-retarded polymers. Blazsó *et al.* showed several oxides and catalysts (Na-metasilicate, molecular sieve 5A (Ca), molecular sieve 13 X (Na, H)) suitable for the decontamination of pyrolysis products, treated directly after evolution during pyrolysis. This method seems to be promising, especially for fine treatment of low-contaminated oils. Experimental studies have been transferred to laboratory- and pilot-scale runs in the framework of the Haloclean activities.

A very different solution, and one suitable even for the selective production of HBr in the presence of chlorine, without any catalyst, is the treatment of the pyrolysis oils with molten polypropylene [13, 63, 56, 57, 59]. Polypropylene acts within a temperature range of 310–350°C as a hydrogen donor. HBr is evolving from the brominated phenols and substituted phenols are formed in the case of the decomposition of flame retardants such as tetrabromobisphenol A (Figure 20.8). Together with HBr small brominated aliphatics are formed. Those can be converted to HBr together with all noncondensable compounds in a final oxidative cleaning.

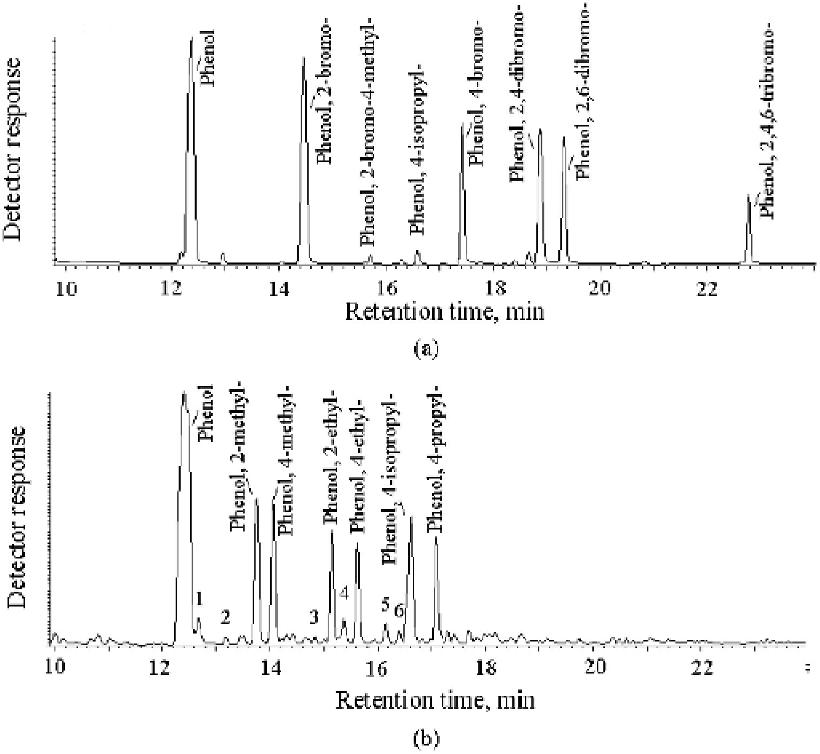

Figure 20.8 Dehalogenation of pyrolysis product from tetrabromobisphenol A (a) and by copyrolysis with PP in a closed ampoule (b), at 350°C for 15 min

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21

Microwave Pyrolysis of Plastic Wastes

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1 INTRODUCTION

Microwave pyrolysis of plastic (or plastic-containing) wastes is a relatively new area that has been studied only in the last decade or so. Because of this, there is considerably less information in the scientific literature compared with other approaches to the pyrolysis of plastics. Also, there is a substantial amount of information contained in patents, which suggests that the development of microwave pyrolytic processes has been more intuitive rather than strictly scientific. This chapter will summarize the developments in this area that are described both in scientific and commercial literature.

The chapter begins by introducing the concepts behind microwave heating and the properties that make plastics transparent to this kind of radiation. This is followed by a definition of microwave pyrolysis of plastics and the ways that microwave transparency of plastics can be overcome in order to use this microwave energy as a source of heat for pyrolysis. A number of microwave pyrolytic processes for materials other than plastics are also introduced.

The literature review of microwave-assisted or induced pyrolysis of plastics follows. In this section special attention is paid to the reactor configurations used, comparing them with the configurations found on more conventional pyrolysis equipment. The most important findings produced from this research are presented, including product yield, characteristics and composition. An analysis is presented to assess whether in any example there is evidence for nonthermal microwave effects promoting the pyrolytic reactions.

The last section will focus on a review of the 'commercial' literature, e.g. patents and companies' websites. The aim of this section is to analyse the claims made in these documents in the light of the information present in the scientific studies. Flow diagrams, equipment characteristics and process results are analysed in a new exercise that shows

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that there is a great deal of work needed to bridge the gap between the research and the commercial communities. Both communities can provide a substantial amount of experience and expertise in order to make microwave pyrolysis better understood and as a result more widely adopted.

2 BACKGROUND

2.1 MICROWAVE HEATING

2.1.1 Microwave Heating Fundamentals

The use of microwave radiation for practical purposes was investigated during the Second World War, in the course of intensive research on electromagnetic radiation in the frequency range from 500 MHz to 100 GHz in the development of high-definition radar. At that time the magnetron valve was invented; this is a very high-power source of microwaves with outstanding efficiency. After the war, further development led to the introduction of microwave radiation to processing equipment by using it for heating, especially in the food industry.

Microwave heating is categorized as an electric volumetric heating method. Other heating methods in this group are: conduction (DC to 6 Hz) and induction (50 Hz to 30 kHz) heating, where a current passes through the workload to cause I^2R heating; ohmic heating, which is essentially a variation of the former, but for liquids and slurries; radio frequency heating (1–100 MHz, often 27.12 MHz), used for workloads with high resistivity where the workload is placed between electrodes. Microwave heating is performed using frequencies close to 900 MHz ($\lambda = 33.3$ cm) and at 2.45 GHz ($\lambda = 12.2$ cm). These frequencies were chosen by international agreement to avoid interference with other bands allocated for other uses such as mobile telephony. Figure 21.1 shows the electromagnetic spectrum and some applications performed at various frequencies along with examples of electric volumetric heating.

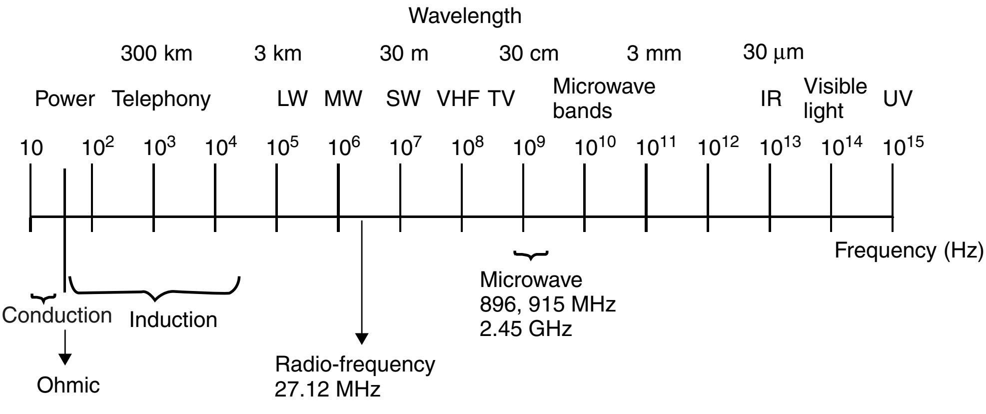

Figure 21.1 Electromagnetic spectrum with examples of applications and heating applications at various frequencies

Microwave heating is a process tool that has a number of advantages over other, more traditional, heating methods. Conventional heating is normally performed through a heated surface and is therefore governed by the temperature of that surface. Also, heating is limited by the physical properties of the material, such as density, heat capacity, and heat conductivity, i.e. the thermal diffusivity of the material. Microwave heating on the other hand is associated with a more even distribution of heat that leads to easier control over the temperature profile in the heated material.

The basic theory of microwave heating is well understood and described in several textbooks [1–4]. There are basically three mechanisms by which materials are heated in a microwave field. These mechanisms arise from the displacement of charged particles in the material when they are subjected to microwave radiation and are summarized as follows:

- The electrons around the nuclei (electronic polarization) or the atomic nuclei themselves (atomic polarization) are displaced from their equilibrium position, giving rise to induced dipoles, which respond to the applied field. In some materials (such as water) there are permanent dipoles due to the asymmetric charge distribution in each molecule. The dipoles, either induced or permanent, tend to reorient under the influence of a changing electric field.
- Another type of polarization arises from a charge build-up in the contact areas or interfaces between different components in heterogeneous systems. This phenomenon is also known as interfacial polarization and is due to the difference in the conductivities and dielectric constants (see below) of the materials at interfaces. The accumulation of space charge is responsible for field distortions and dielectric loss and is commonly termed 'Maxwell–Wagner polarisation'.
- Ionic conduction: some materials produce electric currents within themselves when subject to electromagnetic fields. When these electric currents flow within the structure of the materials, which in most cases have a relatively high resistivity, the material is heated.

Although most existing microwave heating processes are used to heat up materials, mainly water, that have permanent dipoles, some processes use the other two mechanisms.

The extent to which a material is heated when subjected to microwave radiation depends on two parameters: the dielectric constant ε' and the dielectric loss factor ε''. The dielectric constant describes the ease with which a material is polarized by an electric field, while the loss factor measures the efficiency with which the electromagnetic radiation is converted into heat. The ratio of these properties gives the dielectric loss tangent or dissipation factor:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{21.1}$$

which defines the ability to absorb and convert electromagnetic energy into thermal energy at a given temperature and frequency.

Since microwave heating depends mainly on the characteristics of the workload, when a material is suitable for this type of heating, the sources of microwave radiation enable high temperatures and high rates of heating and show excellent efficiencies of conversion of electrical energy into heat (80–85%). Modern equipment has very high reliability and is competitive with other heating methods.

As a result, there are an increasing number of industrial processes and applications that make use of microwaves for energy transfer. Modern microwave systems are used for, tempering and thawing, continuous baking, vacuum drying, pasteurization and sterilization [1]. Furthermore, there is a big potential for the use of this kind of technology in environmental engineering [5].

2.1.2 Microwaves and Plastics

Thermoplastics (with the exception of Nylon) normally have very low dielectric constants and low loss factors and therefore there is limited scope for the use of microwaves in their processing. This is further aggravated by the fact that when plastics start to heat and molecular mobility increases, the absorption of microwaves also increases and, at the gel transition or melting point, it can increase substantially. This can result in 'thermal runaway' where increasing amounts of microwave energy are absorbed as temperature rises. This effect could finally result in a poorly controlled pyrolytic reaction or combustion, depending on the conditions [6–9]. For some thermoplastics there is a 'critical temperature' for microwave heating which has been shown to correspond to molecular relaxations occurring at microwave frequencies. This means that some molecular segments can move on a timescale similar to the exciting microwave energy. Further information about the processability of polymers with microwaves has been described by Chen *et al.* [10–12]

2.2 MICROWAVE PYROLYSIS

2.2.1 Microwave Pyrolysis of Plastics

As mentioned in the previous section, plastics have very low dielectric constants and loss factors. This evidently means that they are not able to heat up efficiently or controllably to a temperature high enough for them to pyrolyse. So the obvious question arises: how are plastics, that are essentially transparent to microwaves, thermally degraded using microwave radiation? The most efficient solution involves, mixing plastics (microwave-transparent material) with a microwave-absorbent material. Microwave-heating of the latter material results in heat transfer by conduction to the plastic. This is what is know as microwave-induced (or microwave-assisted) pyrolysis, and will be referred to here simply as 'microwave pyrolysis'. In a sense this process utilizes a 'fourth' method for microwave heating since microwaves are used as indirect source of heat. Graphitic carbon and some inorganic oxides are materials that are used as microwave-absorbents, with carbon having a predominant role due to its low price and high abundance. When subjected to an electromagnetic field at microwave frequencies, some molecular structures of carbon absorb the energy, which is subsequently converted by ionic conduction and dipole rotation (the third and first mechanism explained in Section 2.1.1) into heat [13–15].

Microwaves are currently used to heat carbon for sintering in the ceramics industry, achieving good heating rates and high temperatures. Ceramics have very low loss factors for microwave processing at low temperatures, however, when the temperature reaches a certain value, the electrical conductivity of the ceramic drastically increases and the sample rapidly heats. Carbon has been used to accelerate the first stage of the heating process by applying a very thin coat (0.01 mm) to the ceramic surface [16–18].

Another area where microwave heating is used to heat carbon is in the regeneration of activated carbons. When spent activated carbon is subject to a microwave field, the heat generated within the particles produces rapid temperature rises and the release of other compounds adsorbed on the carbon [19–23]. In a similar process, carbon used as adsorbent to remove NO_x and SO_x from gas streams can be regenerated with microwaves producing CO_2 and N_2 as gases and elemental sulphur [24].

In microwave pyrolysis of plastics, when carbon (or other microwave-absorbent) is exposed to a microwave field, it can reach temperatures up to 1000°C in a few minutes (Evidently this depends on the amount of carbon and the power of microwave field. The given example can be achieved easily with 1 kg of carbon in a 5 kW (normal catering) microwave oven.) If shredded plastics are mixed with the carbon, prior to or during heating, the energy absorbed from the microwaves is transferred to the plastics by conduction, providing a very efficient energy transfer, and if carbon is used as microwave-absorbent, a highly reducing chemical environment. The latter avoids formation of undesired oxygenated organic compounds, in case oxygen is present in the system within molecules of plastifiers, additives, paints, inks or other materials such as paper or biowaste. The basic aim of this novel pyrolytic method is to provide a process for the disposal of plastic wastes, making use of the high temperatures that the carbon achieves when subject to a microwave field, and has advantages over other more conventional pyrolytic processes [25]. In summary, microwave pyrolysis combines the advantages of microwave heating with the environmental benefits and commercial opportunities arising from the pyrolysis of wastes.

Microwave pyrolysis has been proven to be a useful process to treat some real plastic wastes. Tests have shown the potential of microwave-induced pyrolysis for the treatment of plastic/aluminium laminates [26]. These materials, which are a common example of a waste made of plastic attached to other components, are used mainly as packaging for food, beverages and other products like toothpaste. A common name used to refer to these 'drink cartons', particularly when used to package food and drinks, is Tetrapack (from the trademark by Tetra Pak® Sweden and Switzerland). These drink cartons consist of a variety of different types of laminates which all contain a thin foil of aluminium, typically with a thickness of ~6–30 μm laminated in conjunction with paper and plastic layers. The thin fragile layer of aluminium foil has caused problems for conventional pyrolytic processes that attempt to pyrolyse the plastic and simultaneously recover the aluminium. On the other hand, in addition to the aforementioned advantages, the microwave pyrolysis process can be operated under gentle conditions and therefore fragile materials, such as the aluminium foil present in the laminate, can be recovered clean and ready for further processing. Details of the studies carried out with the microwave pyrolysis process are presented in Section 3.

2.2.2 Microwave Pyrolysis of Tyres

Considerable attention has been paid over the last few years to the use of microwave pyrolysis for the processing of scrap tyres. Approximately 2.5 million tonnes in North America, 2.0 million tonnes in the European Union and 0.5 million tonnes in Japan, of scrap tyres are discarded per year. As much as 50% of this waste is landfilled which is clearly causing an increasing unsustainable and unacceptable situation. Other recycling methods for waste tyres such as retreading, reuse in other areas (barriers, construction material, etc.), chemical devulcanization and incineration (in cement kilns or power stations), have technical or demand limitations that prevent them from coping with the enormous amount of waste tyres generated [27]. In order to tackle this situation, pyrolysis and gasification of tyres have been studied for a number of years. In the former case, the products consist of mainly oils and a solid residue (carbon and ash). In the latter case the products are a good source of synthesis gas. The solid residue formed during pyrolysis can be further treated in order to produce activated carbon. Many studies concerning the conventional pyrolysis of tyres can be found in the literature [28–44].

Tyres are composed mainly of a mixture of rubbers (50 wt%) and, among many other constituents, they have a considerable amount of carbon black acting as a reinforcing agent. Similar to plastics, rubbers also have low dielectric constants and loss factors and hence are not suitable for microwave heating. However, the presence of carbon black within the tyre formulation, makes this waste a perfect candidate for microwave pyrolysis. The carbon absorbs the microwaves, heating up and transferring the heat to the rubber which pyrolyses, producing more carbon, that in turn absorbs microwaves and heats up. There are no papers in the scientific literature regarding the microwave pyrolysis of tyres; however, further information about the subject is presented in Section 4 since there is substantial information available in published patents.

2.2.3 Microwave Pyrolysis of Other Materials

Examples exist of other processes, in which microwave heating of microwave-absorbents is used as a way to transfer energy to a microwave-transparent material in order to accomplish the pyrolysis of the latter. For example, the pyrolysis of chlorodifluoromethane has been carried out in a microwave-heated fluidized bed with a performance comparable to that of tubular reactors, the best traditional equipment for the pyrolysis of this compound [45].

The simultaneous decomposition of pentachlorophenol and regeneration of activated carbon, using microwaves was reported [46], claiming that the quality of the carbon was maintained or actually increased after several adsorption/microwave-regeneration cycles. Carbon, in graphite form, has also been used as a microwave absorbent for the microwave pyrolysis of urea [47].

Similarly, microwaves have been used for pyrolysis of coal, which is known to have very poor microwave absorption, by mixing it with inorganic oxides (very good microwave receptors) or with carbon. After the initial stages of pyrolysis the coal undergoes some graphitization, turning into carbon black that further absorbs microwaves [48, 49].

Microwave pyrolysis has also been tested with materials that, even though they are dielectric, contain some molecules responsive to microwave fields and can therefore absorb microwaves, heat up and pyrolyse. Example are wood blocks [50–52] and oil shales [53].

Another material treated with microwave pyrolysis has been sewage sludge. Disposal of this material, which is a by-product in wastewater treatment processes, is a considerable problem and currently accounts for up to 60% of the operational cost of wastewater treatment plants. Microwave pyrolysis of sludge provides a rapid and efficient process with reduced process time and energy requirements compared with conventional pyrolysis [54].

Furthermore, the condensables from microwave pyrolysis contain less carcinogenic compounds than those produced in conventional pyrolysis [55] and the noncondensables have a higher concentration of CO and H_2 (synthesis gas) after microwave pyrolysis than after conventional pyrolysis [56].

3 MICROWAVE PYROLYSIS OF PLASTICS IN THE SCIENTIFIC LITERATURE

3.1 MICROWAVE PYROLYSIS EQUIPMENT

3.1.1 Thermogravimetric Microwave Pyrolysis Equipment

Pyrolysis has been used for some time as an analytical technique for the identification of products and the elucidation of kinetics during the degradation of plastics and many other organic materials. In this kind of application, microwaves have been used as the heating source in some of the analytical equipment. Examples include an apparatus to perform thermogravimetric analysis (TGA) which included a novel method for the temperature measurement and control [57], and the so-called microwave differential thermal analysis. The latter works in the same way as conventional DTA, by detecting changes that result from the energetics of the process, but it can also measure differences that result from changes in the microwave heating capacity of the material (changes in dielectric properties) [58–60].

At the same time, a similar system was developed with the specific aim of performing thermogravimetric (TG) experiments during the microwave pyrolysis of plastics and plastic/aluminium laminates [26]. The schematic diagram of the apparatus developed is illustrated in Figure 21.2.

In summary, the apparatus comprised a conventional (domestic) microwave oven with a maximum power output of 1.2 kW (1). The reactor (2) was a fused silica crucible placed in a moulded microwave-transparent insulating brick (3) that was suspended from the

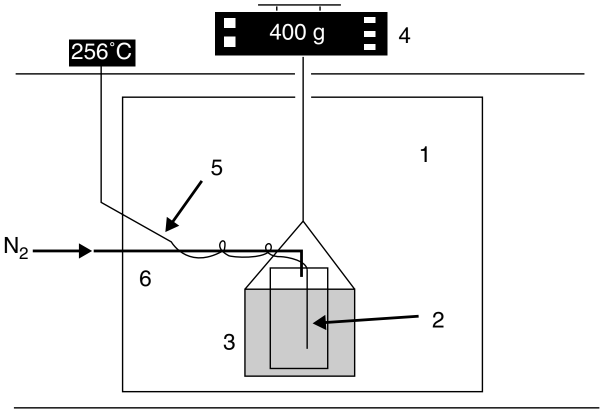

Figure 21.2 Schematic diagram of the microwave pyrolysis thermogravimetric apparatus. First published at the 6th World Congress of Chemical Engineering

bottom hook of an analytical balance (4). Carbon was used as the microwave-absorbent and its temperature monitored using a type-K thermocouple (5). A glass pipe (6) was used to carry a small flow of purging gas (N_2) that was introduced above the carbon bed to limit the presence of oxygen near the reaction zone. The thermocouple and the balance were connected to a computer which ran a data acquisition program in order to record the temperature and the sample weight at a rate of 1 Hz. A more detailed description of the apparatus and the experimental method can be found elsewhere [26]. This equipment was built with the purpose of acquiring initial 'know how' about the microwave pyrolysis process and its characteristics and therefore a number of its components did not provide the same level of accuracy as commercial TGA equipment. Nonetheless, it is believed that further improvements to the apparatus could lead to equipment matching the functionality of many well-known conventional commercial systems.

3.1.2 Semi-batch Microwave Pyrolysis Equipment

The majority of the scientific literature devoted to pyrolysis of plastics is focused on the development of equipment or processes having recycling as their ultimate goal. Many of these have been introduced in previous chapters and include studies using fluidized beds [61–77], cycled-sphere reactors [78, 79], fixed-bed reactors [80, 81], rotary kilns [82], screw reactors [83] and rotating cone reactors [84]. In all these studies the chemical analysis of the pyrolysis products has been an important goal in order to asses the behaviour of the pyrolysis of plastics.

With this in mind a bench-scale semi-batch microwave pyrolysis apparatus was developed. A schematic diagram is shown in Figure 21.3. It consisted of a modified 5 kW catering microwave oven (1). The reactor (2) was a quartz vessel placed in a specially moulded base made of a microwave-transparent/insulating material. The agitation system for the reactor consisted of an impeller, shaft and a motor (3). The temperature of the carbon load was monitored using three thermocouples and automatically controlled using a computer. The reactor was gravity fed using the top feeder (4). The flow rate of purging/carrier gas (N_2) was monitored using a rotameter (5). The products of pyrolysis left the reactor and pass through a system of condensers that had a main collection vessel (6), two water-jacketed columns (7) and two cold traps (8,9). After the two cold traps the uncondensable gases flowed through a cotton wool filter (10) to collect any aerosols present, before leaving the system. Gas samples were collected after the filter. A more detailed description can be found elsewhere [85].

As mentioned above, the main difference between microwave and conventional pyrolysis is the initial source of thermal energy and the way this is transferred to the plastic. Nonetheless, there are other differences, particularly when microwave pyrolysis is compared with fluidized-bed pyrolysis equipment: in the latter, the primary reaction products are carried out of the reactor by a hot gas stream which enables these products to take part in secondary and tertiary reactions. On the other hand, in microwave pyrolysis, once the pyrolytic products leave the carbon bed, they stop receiving heat by conduction from the hot carbon and come in contact with a relatively cold carrier gas. This has an important effect in the number of consecutive reactions occurring and therefore, on the nature of the products, as is shown in Section 3.2.2.

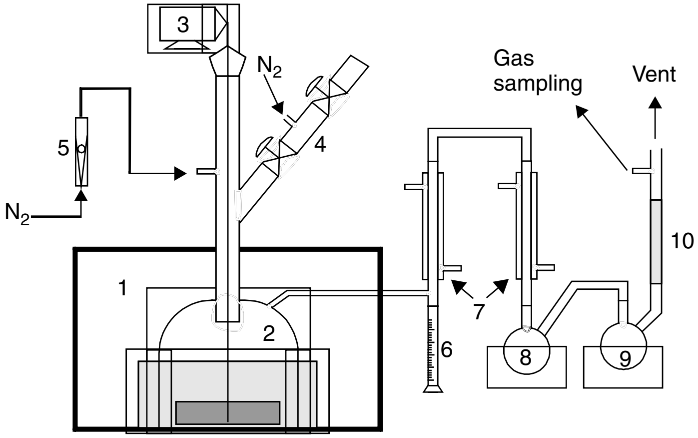

Figure 21.3 Schematic drawing of the microwave-induced pyrolysis apparatus. (Numbers refer to components described in main text) [85]. (Reproduced by permission of the American Chemical Society)

An extra feature of the equipment shown in Figure 21.3 is the design of the condensation train. It is known that under certain conditions, the pyrolytic products when condensed, form a mist or aerosol, similar to the smoke produced by cigarettes or a barbecue. These aerosols, may accumulate as a wax on the walls of condensers, but often they do not settle inside collection vessels. This problem was solved by making the gases flow upwards through a vertical condenser, effectively creating a reflux-like effect, similar to a distillation column. Furthermore, this condenser was operated at a temperature that cooled the products to a point at which they condensed, but did not solidify, and allowed the liquid droplets to coalesce and hence be collected. The optimal operation of the condenser was with water at temperatures between 50 and 60°C [86].

Due to the novelty of the microwave pyrolysis process, there are no other reports in the scientific literature, with details of equipment for the degradation of plastics. However, for the degradation of other materials, details of the apparatus utilized for the microwave pyrolysis of wood have been presented [50, 51].

3.2 RESULTS FROM THE MICROWAVE PYROLYSIS OF PLASTICS

3.2.1 Themogravimetric Experiments

The results for the TG experiments performed with the equipment shown in Figure 21.2, showed typical exponential weight-loss curves that are consistent with the use of the simple power-law model (pseudo-first-order reaction) in order to model the overall process. Figure 21.4 shows the results obtained for the degradation of three kinds of materials, when the experimental weight loss curves were averaged and transformed into conversion curves.

Heat transfer limitations are important restrictions for pyrolytic processes because of the low thermal conductivity of plastics. In general the heat flow from the surface of a plastic particle to its core (internal heat flux) is rather slow compared with the heat flow

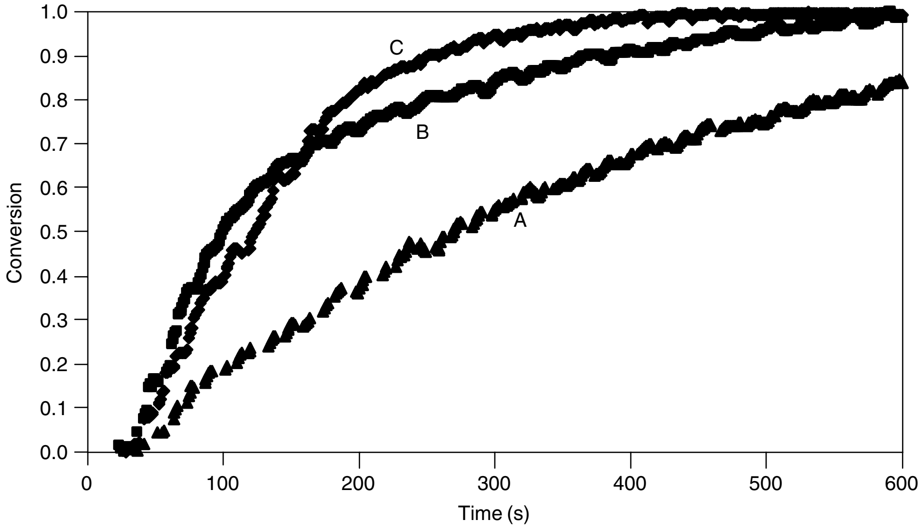

Figure 21.4 Pyrolysis of (A) HDPE pellets, (B) HDPE powder and (C) toothpaste laminate at 550°C using a microwave pyrolysis thermogravimetric apparatus [26]. First published at the 6th World Congress of Chemical Engineering

from the hot medium to the particle surface (external heat flux). Consequently, pryrolytic TGA studies have to be performed with small particle and sample sizes, for example, samples of ~10 mg and 63–90 μm diameter [87]. Moreover, in microwave pyrolysis this difference in heat fluxes is further increased because of the large transfer coefficients for heat conduction between the hot bed of microwave-absorbent and the plastics.

The experiments illustrated in Figure 21.4 however, were carried out with 4 g of material because, as was mentioned before, the aim was not to elucidate the reaction pathway or the kinetics parameters of the pyrolytic reaction, but to provide ‘know how’ about the microwave pyrolysis process. Therefore as can be seen in the figure, the fastest degradation was achieved with the laminate because of its smaller thickness (plastic layer 90–150 μm) in comparison with the average diameter of the HDPE powder (150 μm) and pellets (3 mm diameter, 1 mm high).

As an approximation, the apparent reaction rate constant was calculated, assuming that the temperature was constant once the polymer started to degrade. From the correlated data the apparent reaction rate constant was calculated for the three materials at 550°C. Table 21.1 shows the values obtained and compared with values calculated at 550°C, from kinetic data in the literature.

The results shown in Table 21.1 do not imply that microwave pyrolysis is slower than conventional pyrolysis, but confirm the need to consider heat and/or mass transfer limitations because of the particle and size samples used in the experiments [26].

3.2.2 Bench-scale Semi-batch Experiments

The degradation of HDPE pellets and toothpaste tube laminate was performed at a range of temperatures between 450 and 700°C using the equipment shown in Figure 21.3. Details of the experimental method can be found elsewhere [85].

Table 21.1 Apparent reaction rate constants for the pyrolysis of PE with a first-order reaction model

	k (s^{-1})
Microwave pyrolysis laminate [26]	0.011
Microwave pyrolysis PE powder [26]	0.006
Microwave pyrolysis PE pellets [26]	0.003
Conventional pyrolysis PE powder [88]	0.052
Conventional pyrolysis PE powder [89]	0.208

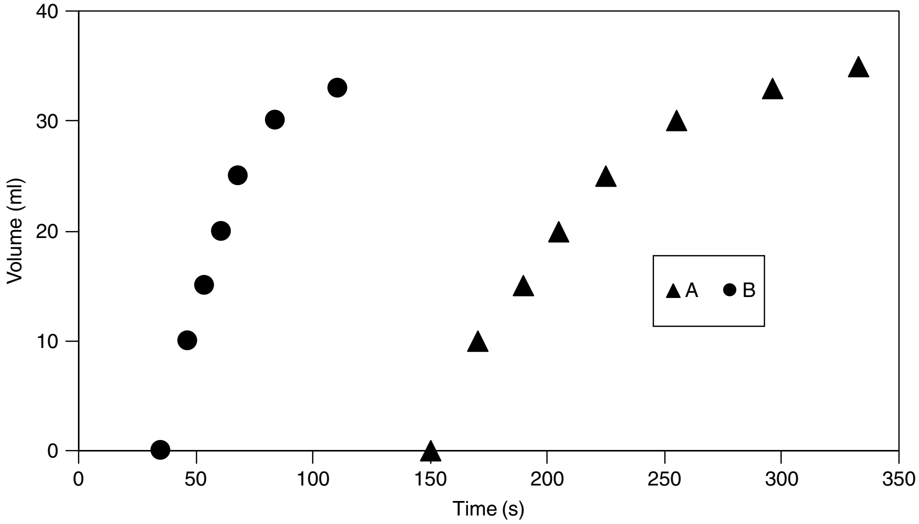

Figure 21.5 Cumulative yield of condensable products for the microwave pyrolysis of HDPE pellets pyrolysis at (A) 500°C and (B) 600°C [85]. (Reproduced by permission of the American Chemical Society)

Figure 21.5 shows the cumulative volume of oils/waxes collected at two temperatures as a function of reaction time.

The temperature had a major effect on the rate of reaction/decomposition, observed by the rate of condensation in the main collection vessel. If this figure is compared with the results in the absence of agitation (Figure 21.4), the same shaped curves are found and the same order of magnitude in the rate of degradation can be noticed. Nevertheless the apparent shorter reaction time demonstrates the effect of improved heat and mass transfer in the semi-batch equipment due to the agitation system.

Table 21.2 shows various results for product (phases) yields for the degradation of PE at 500 and 600°C along with the results obtained using microwave pyrolysis. As can be seen in the table, in the latter case the increase in temperature caused little difference in the yields of the products. These results, which seem to contradict most previous findings, may be explained by the configuration of the microwave pyrolysis equipment.

It is known [90, 91], that the final yield and hence product composition of pyrolysis products are determined mainly by the secondary and tertiary reactions that occur after

Table 21.2 Product yield (wt%) from the pyrolysis of PE reported in the literature (NR = not reported) [85]. (Reproduced by permission of the American Chemical Society)

	500°C			600°C		
	Gas	Oil/wax	Solid	Gas	Oil/wax	Solid
Batch fluidized bed [72]	~7–16	NR	NR	~18–60	NR	NR
Fixed bed [90]	~8–12	~83–90	~2–5	~20–35	~55–74	~6–10
Fluidized bed [74]	10.8	89.2	0	24.2	75.8	0
Microwave-induced pyrolysis [85]	19.0	81.0	0	20.9	79.1	0

the polymer molecules have first been cracked. Considering this and the increase in the reaction rate with temperature, the results in Table 21.2 are explained as follows: for the microwave pyrolysis results, as temperature increased, the reaction rate increased with the consequent increase in the production rate of primary gaseous products. The constant volume of the reactor leads to an increase in pressure in the reactor that resulted in a more rapid flow of gas out of it; the residence time therefore became dependent on the reaction temperature. In other words, with the reactor configuration and dimensions used, the increase in the level of molecular cleavage due to an increase in temperature range shown was counterbalanced by a decrease in the residence time in the reactor [85].

The gas chromatography/mass spectrometry (GC-MS) analysis of the pyrolysis products helped to prove the relationship between reactor temperature and the residence time described in the previous paragraph. Furthermore, the analysis showed that microwave pyrolysis generates the same kind of products as produced in other conventional pyrolysis process. The total ion chromatogram (TIC) for the condensable products was very similar to those obtained with conventional heating systems [85]. The distribution of degrees of polymerization obtained from the GC-Ms analysis also confirmed that at 600°C the effect of higher temperature compared with 500°C was balanced by the reduction of the residence time. At 700°C the temperature effect dominated, causing the same level of cleavage as at 500°C, but in a much shorter reaction time [85].

In terms of the individual compounds found in the condensable products, as with conventional pyrolysis, α-alkenes alkanes and dialkenes were the most abundant compounds. A large number of other aliphatic and aromatic compounds ranging from C_3 to approximately C_{56} were also found, including: methylcyclopentene, benzene, cyclohexene, toluene, ethylbenzene, xylene, propylbenzene and methyl-ethylbenzene. The analysis also showed that the condensables obtained at 500 and 700°C, although possessing similar levels of cleavage, showed important differences in the individual compounds present [85].

The main compounds in the noncondensable gaseous products were linear alkenes and alkanes, ranging from C_1 to C_7 and accounted for almost 90% of the mixture, with the rest consisting mainly of cyclic aliphatic compounds. In terms of individual compounds, the gaseous mixture was composed of compounds similar to those found in the conventional pyrolysis of PE [72, 74, 92], with the difference however that negligible amounts of hydrogen were found [85].

As mentioned in Section 2.2.1, the recovery of clean aluminium from real plastic-containing wastes has been one of the main focuses of the research into microwave pyrolysis. With the semi-batch apparatus shown in Figure 21.3, experiments were performed using toothpaste tube laminate and depulped drink carton laminate (a Tetra Pak®

type of material after a paper recovery process). During these experiments 29.4 and 14.5% of clean aluminium (weight based on the initial load of waste) was obtained with the two laminates respectively, in agreement with the expected theoretical amount (30 and 13.8% by mass). The solid aluminium was separated easily from the carbon by sieving and showed a shiny and clean surface. There were no important differences in the products obtained from the pyrolysis of toothpaste tube laminates compared with the degradation of HDPE pellets [26, 85]. During the degradation of drink carton laminate however, the residual paper present in the material caused substantial differences in the nature of the products: there was a substantial amount of ash formed, the yield of condensables was higher and, as expected, the presence of oxygen-containing compounds (in the condensable and noncondensable phases) such as phenol and acetic acid was observed. Moreover, an important observation was that levoglucosan, one of the main pyrolysis products from cellulose [93, 94] was not detected [95]. Figure 21.6 shows samples of the initial laminate and the recovered hydrocarbon and aluminium products.

3.3 MICROWAVE EFFECT IN MICROWAVE PYROLYSIS?

Although it is possible that some chemical reactions are directly promoted by the presence of microwaves, particularly in organic chemistry [96], there is much speculation on whether this so-called Microwave effect truly exists [97]. In the 1980s, this effect was thought to promote chemical reactions, increase reaction rates by diminishing activation energies and explain other phenomena observed in the presence of microwave fields. Following further investigations, many researchers claimed that microwave-induced

Figure 21.6 From left to right: original laminate, recovered condensable products and recovered aluminium. Top row, toothpaste tube laminate. Bottom row, depulped drink carton

chemistry did not exist. Extensive studies analysed the differences between microwave and other conventional processes in order to establish substantiated conclusions.

Supporting those who believe that there is a nonthermal effect, there are reports claiming that reactions occur at lower temperatures using microwave heating [98] or that there are distinct catalytic effects as a consequence of dipole formation [99]. Likewise its been claimed that the microwave pyrolysis of urea (using carbon as microwave-absorbent) provided advantageous selectivity of reaction routes, promoting favourable chemical reactions and thereby enhancing the yield of desired products [47].

Supporting those who believe that a nonthermal effect does not exist, there are reports that maintain, for example, that claims of the 'microwave effect' were probably due to experimental mistakes when researchers tried to extrapolate concepts of conventional heating into microwave heating [100]. It has been claimed that the possibility of 'reduced' reaction temperatures reported in some cases were nothing but mistakes in the measured temperature due to heat losses that occurred because of conduction through thermocouple guards [101].

The debate continues, but as a result of the research generated so far, it is generally accepted that microwaves do have an important role in promoting chemical reactions, not via a nonthermal effect, but because the heating they induce has the advantages that were described earlier in this chapter: high power density, volumetric dissipation, even heating and good heating control [102]. Examples of modern methods in which microwaves are used routinely in chemistry include a variety of equipment for the performance of organic digestions and, in direct relation to this chapter, the heating of solvolysis agents to achieve the degradation of waste plastics in solution [103–105].

In relation to microwave pyrolysis and taking into account the findings of the studies mentioned above, it is generally believed that microwaves do not pyrolyse organic materials via a nonthermal effect. As will be seen in Section 4, there are a number of patents that claim otherwise, but often lack the necessary evidence to validate their findings. Furthermore, even regarding claims where wastes (such as plastic or clinical wastes) were degraded by microwave energy without the presence of microwave-absorbents, it is highly probable that the reactions occurred initially by thermal effects. As has been mentioned previously, even if plastics have low dielectric constant and loss factors, they still can heat up with microwaves, inefficiently at first, but with increasing efficiency at the glass transition or melting point. This applies even more to other materials such as wood or clinical wastes, that contain within them a considerable number of compounds, many of which are susceptible to microwave heating and that therefore can be 'initiators' of the heating that leads to pyrolysis.

The advantage of microwave pyrolysis over conventional pyrolysis methods do not rely on changes in chemical pathways, but in the advantages that have been mentioned previously.

4 MICROWAVE PYROLYSIS IN THE COMMERCIAL LITERATURE

4.1 PATENTS HISTORY AND COMPARISON WITH SCIENTIFIC LITERATURE

Early patents in the field of microwave pyrolysis were filed in the late 1960s, describing processes for the liquefaction of coal [106, 107] for the production of organic compounds.

Soon after, when waste management became more important, other materials started to be considered for treatment by this kind of process, not only as a source of valuable chemicals, but also as a method to manage production and postconsumer waste. Thus, patent US 3,843,457 entitled ‘microwave pyrolysis of wastes’ presented a process that, regardless of the name, consisted in fact in a gasification process and an apparatus, for the recovery of organic compounds from organic wastes. The explanation given claimed that the wastes would decompose because of cleavages caused directly by microwaves in the carbon–oxygen bonds in the material, but did not provide more detail or experimental proof [108].

In the 1970s, industrial research in the area was led by the tyre industry in the light of the, increasing problem of waste tyre disposal. Consequently processes for the ‘devulcanization of rubber using microwave energy’ were presented [109, 110]. Simultaneously, based on the document mentioned in the paragraph above, Patent US 4,118,282 was the first document to mention the idea of mixing a microwave-absorbent with other materials. The patent talked about a process and apparatus in which ‘high molecular weight organic materials’ were mixed with ‘carbon or other catalysts’ and subjected to microwave and ultrasound energy in order to obtain volatilization products [111]. The document admitted that the ‘chemistry of the process is not completely understood’ and again, wrongly claimed that ‘the microwave energy is sufficient to crack or rupture bonds in the high molecular weight material’. The patent established that cracking resulted because of arcing occurring between carbon particles, which is partially correct; however, it failed to provide accurate explanations of the phenomena involved and often incurred assumptions that at present are believed to be false.

The 1980s saw many more patents filed and published, explicitly using the concept of microwave pyrolysis and with an increasingly obvious environmental drive; for example, a patent entitled ‘recovery process’ describes a method and an equipment for the microwave pyrolysis of the char formed by the initial conventional pyrolysis of waste tyres [112]. However, even though the number of patents increased, many of these still did not describe the nature of the process and the role of the microwave-absorbents. Patent EP 409835 for example, described a method and apparatus for the destructive distillation of organic material; this ‘destructive distillation’ being the pyrolysis of said material [113]. The invention described an equipment to carry out the process with a preheating stage (using the recycled pyrolytic gases) followed by microwave pyrolysis of the preheated waste. The description incorporated more details for the equipment and the process conditions compared to previous patents and presented innovative ideas to help achieving higher process efficiencies. However, it also established that ‘the material being subjected to destructive distillation is such that it contains a substantial proportion of carbon–carbon bonds (such as a hydrocarbon or carbohydrate material)’. Examples mentioned included agricultural waste, sewage and slurry; however, it is known nowadays that some of these wastes do not pyrolyse by the simple action of microwaves and need a microwave-absorbent. Sewage sludge, for example, does not contain on its own enough carbon black to absorb enough energy to pyrolyse and hence, subject to microwave radiation, it dries only by evaporation of water [54, 56]. Similar inaccuracies exist in a number of patents, essentially variations of EP 409835, describing processes for the production of carbon black via microwave pyrolysis [114].

Patent EP 393030 first described with more accuracy the microwave pyrolysis process, defining it as: a method for the destruction of macromolecular waste material which is not itself susceptible to microwave heating, by contacting it with a material susceptible to heating by microwave radiation, in an atmosphere which is such that flame generation is substantially prevented [115]. There are also several patents for several countries that are in essence just variations of this one, for example, Patents EP541641 and GB2,256,435. These, even though they do not appear as equivalents in the patents offices, have been studied and do not provide anything new to the concepts already included in those mentioned above. Furthermore, Patent EP 393030 mentions plastics as an example of the waste material and suggests 'carbon black or other material that upon degradation, produces carbon black such as waste tyres', as microwave-absorbent. Figure 21.7 presents the block diagram described in this patent, showing the typical sequence of operations in an example of the invention for combined microwave pyrolysis of tyres and plastic waste.

However, even if the process definition was better accomplished, the suggestions in the patent for process embodiments (equipment configurations) are nondetailed. Moreover, the patent also contains suggestions that seem inaccurate in the light of current knowledge. For example, a process temperature of 400–800°C was suggested for the pyrolysis of PE or Nylon, but at least 800°C for more 'thermally resistant plastics and halogenated plastics (such as PTFE or PVC)'. There is no evident reason to suggest that higher temperature provides better process efficiency for the pyrolysis of PVC; on the contrary, the use of initial moderate temperatures for the pyrolysis of PVC is an extremely useful way of performing the dehalogenation of the waste prior to the pyrolysis of the polyene backbone [116]. Also, the patent claims that the waste material should be fed to an upper part of the bed of microwave-absorbent in order to maximize contact between the two solid phases, as the former sinks through the bed. The justification for this claim is that the bulk specific gravity of carbon is 0.5 whereas that for plastic is about 0.8–1.0. However, it has now been proved that when HDPE pellets are placed on top a bed of carbon in order to carry out microwave pyrolysis, the process is very inefficient, the plastic does in fact not sink within the carbon bed and a considerable amount of char is left on the surface of the bed [86].

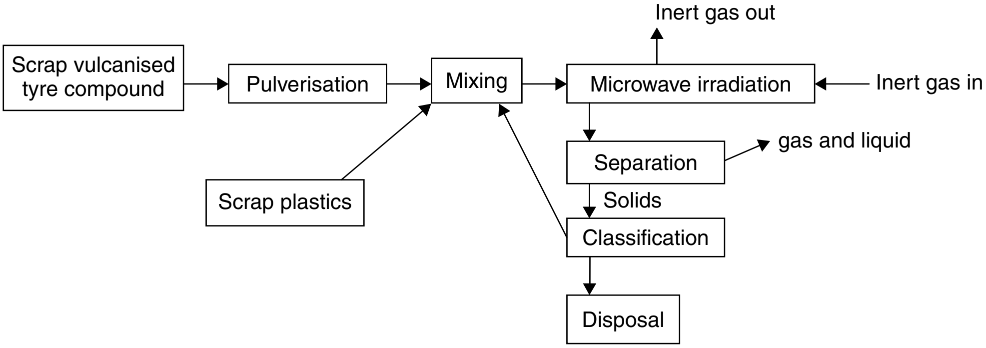

Figure 21.7 Process flow diagram for the destruction of macromolecular waste. Figure 1 in Patent EP 393030

In the 1990s additional microwave pyrolysis patents were filed with special emphasis on tyre degradation. An 'improved' method and apparatus for the destructive distillation of organic materials, tyres in particular, using microwave energy was presented, using a variable-power microwave generator so that the applied power could be increased once the pyrolytic temperature was reached (with an alleged improvement in process efficiency) [117]. A mobile apparatus for the same purpose with a cylindrical rotating reactor which aids the reaction and allows the separation of solid and liquid products during the process is also claimed [118]. Likewise, another rotating devise is claimed through Patent WO01/03474 in which a tyre or tyres are rotated inside an annular enclosure and around two arms that deliver microwave energy to both internal and external surfaces of the tyre [119].

Specifically with regard to the pyrolysis of plastics, new patents have been filed recently containing variable degrees of process description and equipment detail. For example, a process is described for the microwave pyrolysis of polymers to their constituent monomers with particular emphasis on the decomposition of poly(methylmethacrylate) (PMMA). A comprehensive list is presented of possible microwave-absorbents, including carbon black, silicon carbide, ferrites, barium titanate and sodium oxide. Furthermore, detailed descriptions of apparatus to perform the process at different scales are presented [120]. Similarly, Patent US 6,184,427 presents a process for the microwave 'cracking' of plastics with detailed descriptions of equipment. However, as with some earlier patents, this document claims that the process is initiated by the direct action of microwaves initiating free-radical reactions on the surface of 'catalysts or sensitizers' (i.e. microwave-absorbents) [121]. Even though the catalytic pyrolysis of plastics does involve free-radical chain reaction on the surface of catalysts, it is unlikely that the microwaves on their own are responsible for their initiation.

Another patent in which there is some doubt about the underlying chemistry, is US 6,133,500 which shows a method and apparatus for the controlled 'non-pyrolytic' reduction of organic material. The patent presents an innovative design for the application of microwaves to the reactor. Nonetheless, regardless of this potentially efficient idea, the document claims that: 'the microwave energy results in the severing of weaker molecular bonds in longer chain molecules to reduce those molecules to simpler forms. This is in effect a de-polymerization process. The process is controlled to avoid pyrolysis of the organic material'. However, the typical process temperature mentioned was 350°C which is well into the pyrolytic temperature for many organic materials and in particular for the ones mentioned in the patent (tyres, plastics, etc.). Clearly the invention is a pyrolytic process with a different name [122].

Patent US 6,152,306 describes a whole plant for the reduction of municipal solid waste, including plastics. The plant is said to include a microwave reduction chamber in which pyrolysis presumably occurs. However the document did not contain any detail regarding the chemical reactions or the mechanisms involved [123].

4.2 COMPANIES

There are a few companies that advertise on the Internet proprietary processes for microwave pyrolysis of wastes. Not surprisingly, considering what was presented in the previous section, most of these refer specifically or specially to the pyrolysis of waste tyres.

One of the most active companies dedicated to the treatment of wastes using microwave heating has been Environmental Waste International (www.ewmc.com) based in Canada. The company owns the rights to patent US 6,133,500 presented above, commercializing it as a 'leading edge Reverse Polymerization Process where direct microwave energy breaks down organic waste to create profitable and sustainable solutions'. According to the information presented on the website, the feasibility of their waste tyre recycling process was proved using a pilot plant operating from 1994 to 1998. Even though there are no references to installations of full commercial plants for waste tyres, the company has operational plants working with other biological and medical wastes. In May 2004 they finished installing a liquid biological waste treatment process for the United States Department of Agriculture.

Amat, Ltd (www.amat-ltd.com) based in the United Kingdom, presents on their website 'The world's most advanced environmental technology'. Amat stands for Advanced Molecular Agitation Technology. The company's technology is based in their Patent WO01/03474 presented above and has being commercialized as Z3A Process and Technology (from Zero Environmental Damage, 3rd alternative; landfilling and incineration being the first two). The company has received three awards since 2000 that have enabled them to continue their work in the area and are looking for partners for the commercialization of their technology.

Reactive Energy, LLC (www.reactiveenergy.com) is a company based in the United States whose 'mission is to pursue the development and commercialization of processes utilizing chemical reactions facilitated by microwave energy'. Currently, the company is focused on the development of three primary applications using microwave technology. One of these, called Climax PlusTM, is commercialized as a patented a method for converting mixed plastic waste into low-sulphur fuel oil. It is believed that this technology is based on Patent US 6,184,427 described above.

Likewise, another company whose technology may be based on a patent described in this chapter is T.R. Environtech Co. Ltd (www.trrecycling.co.kr). A Korea-based firm, their website mentions that their technology is based on the work performed by the person who some years earlier invented Patent US 4,118,282. However, even though the company claims to have a process for the 'low temperature pyrolysis for tyre waste and rubber waste', the website does not mention microwaves as the heat source for the process.

Finally, Molecular Waste Technologies Inc. is another US-based company developing microwave technology for waste disposal. The website mentions that they have collaborated with Amat (above), but that they have their own proprietary process, covered by patent US 6,152,306. The company establishes that a plant using its process could be optimized to process 600–700 tonnes of MSW per day, producing nearly 400 kg of carbon black and 175 litres of oil per tonne of MSW.

5 CONCLUSIONS

Microwave heating is a process tool that has a number of advantages over other, more traditional, heating methods. These advantages include a more even distribution of heat, high heating rates and easier control over the temperature. Although most existing microwave heating processes are used to heat up materials that have permanent dipoles, mainly water, other materials, such as carbon, can also be heated.

Mixing carbon with microwave-transparent materials, particularly plastics, and subjecting the mix to microwave radiation, is a very efficient way to heat up such materials, increasing their bulk temperature to a point where pyrolysis occurs. In this chapter the main characteristics of a number of microwave pyrolysis processes, for plastics and other materials, have been introduced, showing that these processes combine the advantages of microwave heating with the commercial and environmental opportunities intrinsic to the pyrolysis of wastes.

Scientific studies have found that the differences between microwave and conventional pyrolysis go beyond the obvious difference in the source of heat. Other differences arise from the very high rates of heat transfer from the microwave-absorbent to the waste, the amount heat received by the primary pyrolytic products once they leave the absorbent bed and the highly reducing environment. These three aspects have been shown to have an important effect in the final products since they modify the extent of secondary and tertiary reactions. Moreover, the scientific studies have shown that a nonthermal microwave effect in these processes is unlikely to exist. Tests have showed the potential of the microwave-induced pyrolysis process for the treatment of real plastic-containing wastes and it is believed that a commercial process could be developed, for example, to recover clean aluminium from plastic/aluminium laminates. Other materials, in particular tyres, coal and medical wastes are very good candidates to be treated/recycled using microwave pyrolysis and there have been a considerable number patents filed with this goal in mind.

The research and development carried out so far in has shown that, even though microwave pyrolysis will not be the solution to the whole problem of plastic disposal, it certainly has the potential to help reducing the number of resources currently committed to landfill. Evidence of this potential is the number of companies interested in the development of the process and that are currently active, trying to commercialize proprietary microwave pyrolysis processes. However, this chapter has shown that in order to accomplish a more widespread utilization of this kind of processes a better communication between the commercial and scientific communities is needed. The companies with their patents would be able provide many innovative ideas that may help to increase processes efficiency and the scientific community would provide explanations for the improvements, that would in turn generate even more ideas in a self-sustaining cycle of improvement.

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22

Continuous Thermal Process for Cracking Polyolefin Wastes to Produce Hydrocarbons

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1 BACKGROUND

The viability of obtaining hydrocarbons through thermal decomposition (i.e. pyrolysis or thermal cracking) of polyolefins has been known ever since polyolefins were discovered, more than 70 years ago. However, the ecological and economic needs for this decomposition have only been appreciated when it came to treating huge amounts of wastes of these materials that are increasing every year. Nevertheless, it is necessary to mention an initial application relating to polyolefin thermal cracking for the production of polyolefin wax, but this process used only new materials, as distinct from wastes. The patent 1457575 for Leuna Werke – Walter-Ulbricht was an example of this in 1965.

Contrary to an apparently widespread idea, the reuse of polyolefin wastes after satisfactory cleaning and sorting, as a 'regenerated' plastic material is rarely practical in technical and economic terms. Firstly, polyolefins are easily attacked by oxygen in the air and ultraviolet radiation. When polyolefin waste is left exposed to outdoor conditions for months, as is the case with most wastes, it can become too degraded to provide good-quality plastic material that conforms to the standards (with probably the only exception being films that are highly carbon-filled).

Secondly, the cleaning of the wastes must be thorough, for the purposes of both the final quality of the product as well as for the protection of the injection moulds and extruders that process it. However, such a standard of cleaning is difficult and requires considerable labour such that the waste thus cleaned can cost more than the starting raw material. In conclusion, only the 'new' wastes, such as fabrication scraps, injection runners and gates, etc. can be economically regenerated, which represents a very small percentage of the total waste stream. Hence, if we wish to valorize polyolefin wastes, we are left with only one solution consisting of producing high-quality hydrocarbons by thermal cracking.

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2 INTRODUCTION

Hydrocarbon thermal cracking (or pyrolysis) has been practised in the petroleum industry for more than a century, and the problems raised by such an operation are now largely solved. Thus, this work deals only with the questions specific to the polyolefin cracking based on common practice and procedures.

Polyolefins consist of very long chains of the alkene type with thousands of carbon atoms, but possessing only one final double link in the α position. Theory shows that thermal cracking leads to shorter molecules, but of the same type. These shorter chains generally possess only one final double link in the α position. Most of these molecules are therefore α-olefins.

The energy necessary for cracking the polyolefin wastes is provided in the form of heat, and the most rational way of obtaining it lies in burning a part of the hydrocarbons resulting from the cracking itself. The question is then: 'How much would be consumed for this operation?' The answer, to a great extent, depends on the operational conditions, but this chapter will provide some of its theoretical elements. The solution is in breaking a certain number of links between the carbon atoms in the polymer chain. This number will determine the result obtained. Only cracking leading to the array of liquid and gaseous hydrocarbons most commonly obtained will be dealt with here.

The average energy of the C–C link is considered to be 313 kJ mol^{-1} (75 kcal/mol). A simple calculation shows that to pass from the polymer to the average hydrocarbon obtained during the intended cracking, seven links per polymer kg must be broken, which represents less than 2200 kJ/kg (less than 525 kcal/kg). The energy needed for heating, for the polymer fusion and for the vaporization of the hydrocarbons obtained must be added, making a total of less than 600 kJ/kg. The total is lower than 2800 kJ/kg (670 kcal/kg).

This energy can be easily obtained by burning 0.1 kg of hydrocarbons (taking into consideration the poor heat yield). Therefore, it is apparent that the combustion of 10% of the polymer contained in the wastes is sufficient to guarantee their complete cracking. Some wastes with high water and impurities content may require more energy. While this is so, it is noticeable that cracking yields between 15 and 20% of gas that is noncondensable at room temperature. The combustion of this gas more than adequately provides the energy needed for the cracking (this method of heating is the object of a French patent lodged by the author in 1992 under the French Patent 92 13189).

One important point to be stressed is that, for a given temperature, the longer the molecule the faster is the cracking. On the other hand, in practical terms, it should be noted that in the absence of oxygen, the cracking of alkanes in particular begins at around 300°C and increases sharply at around 360 – 380°C, at which temperatures the output products are converted to the vapour state (except for the tar and the coke). Therefore, boiling of the plastic charge being cracked can be observed.

Whatever the chosen pyrolysis procedure is, we obtain at least 15–20% of $>C_5$ combustible gases where combustion produces a heat that is largely sufficient to undertake the whole pyrolysis process. All the cracking procedures that take into account this fact will be self-sufficient in terms of energy. In addition, the cracking, being undertaken in a closed vessel without a significant pressure, is an operation that is neither polluting nor dangerous and can be undertaken using cost-effective equipment.

Moreover, it should be noted that catalytic cracking can be considered only in the liquid or the vapour phase and only with sufficiently purified hydrocarbons. It is practised according to techniques that are already well known, which can be found in the literature in order to allow the production of some preferred products. In the case of waste pyrolysis, this type of cracking can be undertaken only after a preliminary cracking would have transformed the wastes into liquid or gaseous hydrocarbons. However, the liquids obtained through the cracking of impure wastes are themselves contaminated with impurities and in general too contaminated for a direct catalytic cracking operation. Thus, catalytic cracking is best undertaken with a second phase and only thermal cracking vapour obtained in the first phase.

3 THE TWO PRINCIPAL PHASES OF POLYOLEFIN WASTE CRACKING

Presented here are only the methods that the author has tested in practice on plastics wastes. The first attempts were undertaken in 1986 in a small pilot unit that dealt with wastes of polyolefin films used for packaging. Those wastes were nonpigmented, transparent and rather clean. They were provided by waste collectors in blocks of approximately 30 kg, intended for factories producing ‘regenerated’ granules (recyclate). The intention was to show the potential of producing a polyolefin wax to be used in polish applications or in ‘hot-melt’ glues from those wastes.

The procedure that was developed then was based on the idea that molten polyolefin was totally decomposed at around 360°C, yielding more than 90% of polyolefin liquid wax. The remaining part, being made of combustible vapour whose combustion produced enough heat to ensure this decomposition. The produced wax was collected in a continuous process, rapidly cooled and transformed into powder. It was only slightly coloured and was successfully tested in the fabrication of polishes, as a lubricant for the extrusion of PVC and in compositions of hot-melt glues in combination with petroleum resins. This pilot unit was beneficial for familiarization with the practical problems encountered during the treatment of polyolefin wastes of all sorts, coloured and polluted with food or soil impurities, and to test and develop many efficient continuous operations allowing the pyrolysis of these wastes without precleaning.

The pyrolysis treatment of unclean polyolefin wastes may yield two commercial products:

1. In the particular case of transparent and sufficiently clean wastes, the production of polyolefin wax can be considered as described above. Such products have a higher commercial value than that of the new plastic material itself.
2. In the general case of wastes of all sorts, coloured or printed and filled during the pyrolysis with a variety of harmless impurities (food or soil impurities), also in addition mixed wastes containing EVA or polypropylene, it is no longer possible to stop at the stage of the wax produced in the first phase of the cracking. Indeed, this wax is in this case commercially worthless due to its high level of colours and impurities. Therefore, it must be pyrolysed and transformed into hydrocarbon vapours which will leave the nonvolatile impurities in the wax cracking chamber.

A second phase will follow the cracking of these pyrolysis vapours, involving when needed, catalysts in classical cracking tubes in a way that will favour the formation of the desired products whenever possible. The final vapour obtained is generally rapidly cooled (quenched) at approximately 400°C, before being fractionated in a column where the components are separated and condensed in portions at convenient intervals. This second phase is well known, but it can only be undertaken after the first phase which provides it with its raw material, has taken place with the maximum efficiency and yield.

Therefore, in all the following sections, there is emphasis on the procedures of this first phase which terminates when all the wastes are transformed into hydrocarbon vapours.

4 THERMAL VALORIZATION OF POLYOLEFIN WASTES

The methods that will be dealt with here are those used to obtain hydrocarbon vapours from this first phase. The treatment of plastic wastes of all sorts by pyrolysis, being still in its early stages, workers keeping practised procedures confidential, and often protects them by patents. As a consequence, this chapter deals exhaustively only with the procedures that have been personally tested and developed by the author. The general principle of polyolefin waste pyrolysis consists of heating plastic materials in isolation to a sufficient temperature such that the polymers decompose into small hydrocarbon molecules.

The first problem that is encountered is to study the possibility of continuous operation with various solid wastes. Indeed, from an industrial point of view, a batch process reactor that must be filled, emptied and cleaned after every operation does not allow a rational adaptation of the two pyrolysis phases, since the second (cracking the pyrolysis vapours resulting from the first operation) is essentially continuous. However, it is possible to solve this problem by using multiple reactors operating in parallel; each one is periodically stopped for cleaning and filling while the others are working. This technical solution is absolutely valid, but it still has the drawback of requiring considerable equipment, if huge amounts of waste plastic are to be treated.

The author has developed a totally continuous process while continuing to tolerate the pyrolysis of all sorts of wastes, including those heavily loaded with impurities without any treatment or precleaning. Despite the fact that the processes that are described below tolerate the treatment of all types of polyolefin wastes, they were developed while considering the most common wastes and those accumulated in large quantities in specialized centres. Therefore, there was a special consideration of domestic packing wastes coming essentially from post-consumer domestic waste sorting centres (bags, wrapping sheets, bottles, containers, pots, etc.) as well as from wastes of agricultural sheets (greenhouses and cultivation tunnels). These types of wastes are easily compressible and their impurities are not harmful since they are in contact with food products. However, they sometimes contain considerable quantities of agricultural matter or soiled food impurities. The processes that have been developed by the author enable the treatment of polyolefin wastes containing occasionally up to 70% by mass of humid soil impurities.

5 CONTINUOUS FEEDING OF THE CRACKING REACTORS

The feeding system in continuous operating mode of the cracking reactor is as follows: polymeric mixed wastes are transferred by a moving conveyor, and drop into a feed container (a hopper) with an opening large enough to receive them. At the hopper base, the plastic wastes are taken up by a piston operated by a jack, and compressed into a feeding tube situated at the axis of the piston motion. This tube is of a diameter between 0.3 and 1.2 m, depending on the load to be treated and the downstream process.

The head of the piston is equipped with hollow points, of a trocar type, parallel to the axis of the feeding tube and intended to pierce and to tear the garbage in order to facilitate at the time of compression the evacuation of the maximum possible air and water that it may contain. This water and air is evacuated through perforations in the anterior part of the feeding tube, as well as through the hollow points of the piston.

The feeding tube with a length of 2–4 m, depending on its diameter, opens into a closed reactor where the wastes are heated up to approximately 360–380°C, at which temperature they are transformed into polyolefin wax after being cracked.

The problem of watertightness is solved by the compression mechanism of wastes so that they constitute a hermetic stopper at the outlet of the feeding tube. This compression is undertaken simultaneously by the piston action and by a slight constriction of the feeding tube diameter at the inlet of the rector. Anti-return moving lugs prevent the compressed waste stopper from returning when the piston backs up. It is useful to employ a water radiator for cooling the part of the feeding tube where the plastic ball is formed so that the molten wax in the reactor does not make it melt prematurely. This method of continuous feeding was tested at scaled-up dimensions and yielded satisfactory results. The feeding tube and the reactor extending from it on the same axis are slightly tilted to allow the downward flow of the wax.

6 HEATING METHODS

The classical processes of melting organic solid matter consist of tossing and mixing it, and having intimate contact with the heated wall of the container. However, polyolefin wastes are poor conductors of heat and direct heating by the heated wall leads to overheating that generates coke and char. It is only through vigorous mixing, together with constant scraping that this can be avoided. This requires complex equipment.

To avoid having to resort to this apparatus, the author used a different technique. This consisted of heating wastes arriving in continuous mode to the reactor. Such a method distinguishes the two processes that I will describe below.

The author's first process, still under valid patent, submitted in 1992 under French patent 92 13189, calls attention to the fact that polyolefin is very absorbent in the infrared. This allows it to be heated by the radiation emitted by the bright red-hot walls, at a score of centimetres from a cylindrical grid made of stainless steel and having large rings inside which repel the polyolefin coming through the feeding tube so that it remains confined as long as it is in the solid state. The reactor walls are heated to red-hot by gas burners situated at the exterior of the walls and fed by the noncondensable gases produced by the cracking process itself.

A possible sweeping of the reactor by the superheated water vapour produced by an exchanger using the lost heat of the gas burners constitutes an excellent improvement by realizing a vapo-cracking, minimizing the formation of tar and coke.

The molten wax flows along a receiving channel situated under the grid and is extruded gravitationally outside the tilted reactor through a purpose-made hole, at the same time as the vapour produced during the cracking. This wax is led to a second phase of the treatment. The organic impurities of the wastes are in turn decomposed yielding essentially water vapour and carbon while mineral impurities yield sand and baked clay.

These impurities are swept and released with the wax flowing outside the reactor. This wax is very fluid and can be easily decanted and filtered with traditional equipment, highly heat-proofed after its extrusion from the reactor without being too cooled. Therefore it is sufficiently purified to be treated in a second phase.

The possible heavy impurities that may remain in the receiving channel of the reactor are periodically scraped by a traditional mechanical apparatus and are collected in a container prepared for the purpose of evacuating them easily.

The author's second process, patented in March 2002 under French patent 02 02737, utilizes the same feeding system for the reactor as well as waste confinement in a cylindrical grid with the same diameter of the feeding tube (Figures 22.1, 22.2). The reactor walls are always at some distance from the grid, but now they are thoroughly insulated on their external side and not heated at all. The necessary heating for the primary cracking stage is then undertaken by the steam superheated to around 500–600°C which attacks the wastes directly through the openings of the grid. The effect of the steam thus overheated and coming directly in contact with the wastes is analogous to that of a naked flame. Polyolefin undergoes a very rapid partial cracking during the time that the attacking water vapour cools to around 350–400°C. The nonvaporized part makes a wax that flows through a channel made for the purpose. Then, this wax is evacuated and purified as described in the first process. The impurities are extruded in the same way as described above.

The uniqueness of this process results from the fact that the steam provides the total heat necessary for the primary cracking stage. It is not therefore a simple vapo-cracking. This process intervenes simultaneously while suppressing to the maximum the formation of tars and coke by dilution of steam and partial reduction of the steam pressure resulting from the heavy hydrocarbons produced. Additionally, this process is very flexible and it is suitable for the treatment of highly variable feed rates of waste.

Experience showed that the optimum length of the grid confining the waste can vary from 2 to 3 m and that it is certainly possible to work with several grids mounted in parallel and supplied separately. For example, one can accommodate three grids of 0.5 m diameter and 2.5 m length, side by side in the one reactor, separated by 0.3 m. This example corresponds more or less to a capacity of continuous cracking process of one ton

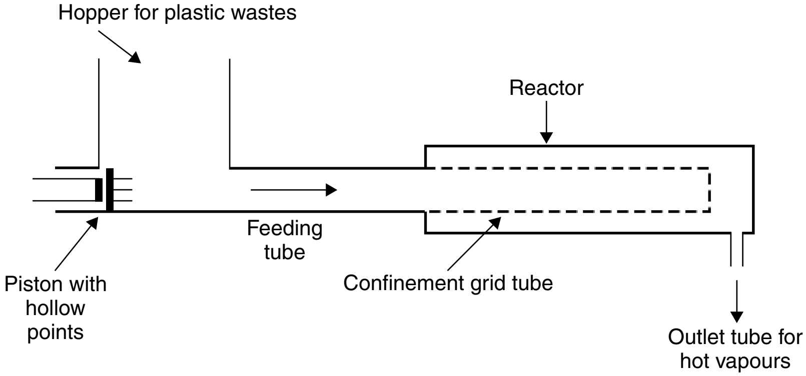
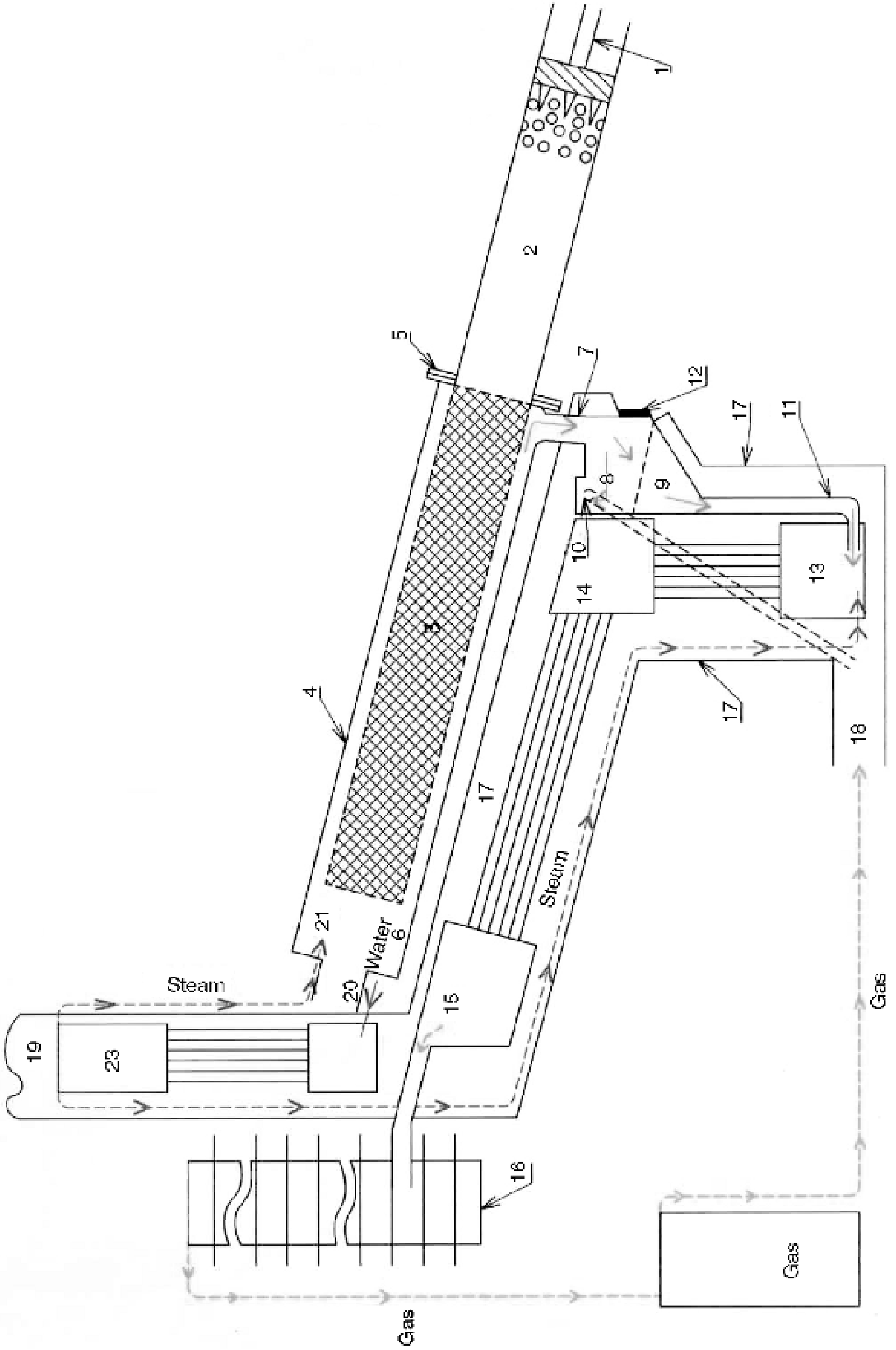


Figure 22.1 Schematic illustration of the principle of cracking of waste by steam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Gas
Gas
Gas

Figure 22.2

Figure 22.2 The initial cracking is done in a closed vessel, sealed from atmospheric oxygen, using heat from direct contact with very hot chemically inert or unreactive gases heated by burning noncondensable gases from the cracking process itself. A classic feed system such as a piston pushes the plastic wastes continuously into a cage in the vessel which keeps them a small distance from the vessel walls. The very hot gases providing the heat are chemically inert or react very little in the cracking conditions. The solid, liquid and gaseous products from this first cracking phase flow freely to the bottom of the vessel in a sealed chamber which acts as a separator. The gaseous products escape from the separator to be burned in the second stage of cracking; the solid products are retained by a sieve and the liquid products are collected in the bottom of a boiler below the separator together with the superheated steam. These collected liquids undergo a second cracking by boiling heated by one or more gas burners fed by the noncondensable gases from various cracking stages. During a third cracking stage vapours from the boiler pass through a tube bundle reactor heated to between 400 and 600°C where the vapours decompose into fractions whose boiling point is not greater than that of diesel (about 360°C). Superheated steam is injected during the second and third cracking stages to obtain steam cracking conditions. The vapours leaving the reactor are sent to a classic fractionation column where they are fractionated into liquid cuts with different boiling points, chosen according to need, and into gases noncondensable at ambient temperature. The latter are sent to a gasometer to feed the gas burners in the various cracking phases, with the surplus gas forming a primary material rich in α-olefins. Steam is injected near the burner flame(s) in the first cracking stage at low pressure superheated to 500°C. The heat lost in the burned gases in the various burners is recovered in a water tube exchanger producing low-pressure superheated steam between 400 and 600°C for use in the third cracking stage. The gases and vapours from the first cracking stage are separated from the liquid and solid products in the separator are burned using additional air in the burners heating the boiler and reactor in the second and third stages. An independent claim is also included for the use of a particular version of this process where the wastes are compressed by a piston (1) in a tube (2) which is several millimetres thick, with a diameter of between 0.3 and 2 m, preferably between 0.3 and 0.5 m and a length three or four times its diameter. The surface of the piston is covered with strong points not more than 0.3 m long, parallel to the axis of the tube and the first third of the tube is perforated, allowing water to flow through. The tube is extended at its end by a mesh cylinder (3) in refractory metal for 2–6 m, closed at the end by a grill. This mesh part is enclosed in a cylinder (4) of refractory steel several millimetres thick, coated externally with a classic insulating layer. The walls of this cylinder are several centimetres from the mesh cylinder except at its end, where the cylinder extends beyond the mesh cylinder by about one diameter to form a cylindrical chamber closed by a flat or dished base with a closeable opening for combustion gases (20) and a superheated steam injector (21). Key: 1 piston; 2 feeding tube; 3 grid; 4 reactor; 5 collar; 6 end of reactor; 7 exit of wax and vapours; 8 decanter; 9 sieve; 10 exit of vapours; 11 tube for extrusion of wax decanted; 12 door to evacuate impurities; 13 boiler-exchanger; 14 second exchanger; 15 exit of exchanger; 16 column; 17 kiln; 18 gas burners; 19 chimney; 20 special case, admission of hot neutral gas (if steam not used); 21 general case, admission of superheated steam; 23 boiler-exchanger for steam per hour of polyolefin contained in waste with a 20% level of impurities. In general, a well-designed grid associated with a good distribution of the superheated steam injectors permits the cracking of 100 kg/h of polyolefin per m^2. Finally, the two described processes lead to the same results. However the superheated steam process on the whole produces a more advanced cracking than the 'radiation' process which provides more wax.

The second part of the first phase consists in converting the formed wax into hydrocarbon vapours. For this, the wax coming from the reactor is heated in a boiler to the boiling point ($\sim$ 380°C), preferably by injection of superheated steam (to a temperature depending on the intensity of the desired cracking) after its purification by decanting and filtration. In general, the cracking vapours produced by this boiling point contain all the hydrocarbons ranging from C_{30} to methane (and even hydrogen) and their fractional condensation gives on average about 10% of noncondensable gas, 35% of a mixture of light and heavy gases, 40% of light fuel oil and 15% of viscous products.

The steam and the hydrocarbons coming out of the reactor at around 380°C simultaneously with the formed wax, can be sent either after reheating or without reheating, to the bottom of the boiler where they will contribute to dragging the steam coming from the boiling wax, or mixed with this steam after its formation so that it undergoes the complementary cracking of the second phase in both cases.

All the steam necessary for the process is produced by plates heated by the remaining heat of the fumes from gas burners after having swept the cracking tubes of the second phase. The superheating of this steam is assured by taking the tubes carrying it past a region close to the burners.

After the first phase, there arises the question of the objective of the second phase. The response depends on commercial considerations. It is important to recall that the cracking is by nature a statistical operation that affects all the existing molecules. This makes it *impossible* to avoid the cracking of some molecules that one would wish to keep, since otherwise it would be difficult to extract them rapidly enough from the reaction environment. At the termination of the process, the whole range of molecules foreseen by theory at a given temperature and time of cracking is obtained. Another consideration is that the elevation of the temperature of cracking increases the formation of coke and light products. Nonetheless, it is possible to favour the formation of some commercial products to a certain extent.

If one tolerates the necessarily marginal wax production, one can estimate that the commercial products obtained can be classified either into fuels or other combustible products, solvents, or products intended for the chemical industry. The author estimates that this last market is the most promising, although it has not yet been investigated seriously. Indeed the hydrocarbons obtained by polyolefin cracking (even from impure garbage) consist essentially of a mixture of a low percentage of alkanes and a large percentage of α -olefins. Importantly, the α -olefins are the raw material of choice for petrochemistry and for the oxo synthesis in particular.

However, as a first step, it will be certainly easier to exploit the energy aspect and to propose use as a fuel or hydrocarbon. In these conditions there are only two possibilities: (i) to encourage the production of fuels for diesel engines (diesel oil); or (ii) the production of LPG and fuels intended to supply generators propelled by gas turbines.

The production of diesel oil will always be limited by the simultaneous formation of other hydrocarbons for which it will be necessary to find uses as well. One can favour the formation of diesel oil by practising cracking at a minimum severity in the presence of water vapour superheated to 450°C with repeated recycling of the products. This will have the effect of preserving to the maximum products ranging from C_{12} to C_{16} of a more advanced cracking.

Of course the hydrocarbon vapours can also be treated catalytically (on zeolites for example), but this will not prevent the recycling of the load component that is insufficiently cracked. In any case, there will always be about 20% of gas whose combustion can largely provide the energy necessary for the whole operation and a fraction of heavy and light gases will remain. This will be very difficult to reduce below 30% of the starting load. But these substrates are excellent solvents, a very good equivalent to the usual degreasing solvents available in the market. This should assure them a ready market. In the domain of fuels, there is also a possibility to encourage the formation of combustible gases solely, without obtaining liquid hydrocarbons (i.e. C_4 at most).

If one makes this choice, it is necessary to resort to cracking at a high temperature with the recycling of the fractions insufficiently cracked after a first process, and to accept increasing formation of coke that may reach 5% or more. However, the required equipment will never require the fractionation of the vapours and the condensation in more or less heavy fractions. It will therefore be possible to get rid of a costly distillation column in the design. The gas obtained must be sent to a gasometer of several cubic meters volume from where it is taken up by a compressor to be stored.

Beforehand, it will be necessary to separate the gas into two categories:

1. A mixture of C_3 and C_4, alkanes and alkenes of LPG type, easily liquefiable and storable in standard containers.
2. A mixture of methane, hydrogen and ethane that can be stored for example under a pressure of 50 bars.

Although the liquefiable gas generally predominates, the respective percentages are difficult to foresee and depend extensively on the cracking conditions. The LPG gas is perfectly adapted to the gaseous fuel used in cars whose engines are designed for gas. The total absence of sulphur is an additional advantage.

With regard to the nonliquefied gas, a part is indispensable to provide the energy necessary for the whole installation. The remaining quantity (typically more than half) can be used to produce electrical energy by supplying a gas turbine generator. The gas turbines operate on heavy fuels in general, but adapt very well to a gaseous fuel. Other processes are being investigated and some have even been the subject of patents, but the time for their assessment has not been sufficient. In any case, the polyolefin waste pyrolysis industry is expected to achieve a significant and rapid development throughout the world, as much to recover precious molecules as to preserve our environment.

23

Waste Plastic Pyrolysis in Free-Fall Reactors

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1 PYROLYSIS

Pyrolysis is an ancient method of decomposing solid matter by heating to high temperatures; examples are production of metals, coke furnaces, and obtaining of chemicals from coal prior to petroleum. There are many kinds of pyrolysis: batch, semi-batch or continuous; catalytic or non-catalytic; out under vacuum or at atmospheric or high pressure. Its medium may be inert, oxidative or reductive. Heating rate, temperature, and time are important pyrolysis parameters.

With regard to the applied temperature and heating rate, pyrolysis may be classified under two groups: (i) pyrolysis at a slow heating rate; (ii) pyrolysis at a rapid or flash heating rate. In the first group, the residence time of the solid in the reaction zone is of the order of minutes to hours. During rapid or flash pyrolysis the corresponding time is milliseconds to seconds.

Free-fall reactors (FFR) are a good choice for rapid or flash pyrolysis. They have been widely harnessed to pyrolyze coal and, more recently, biological mass. A pioneering group at Ankara University was the first to attempt pyrolysis of waste plastics in a FFR. Their results are very promising indeed compared with other alternatives in the literature.

2 PREVIOUS PYROLYSIS WORK

Until fairly recently, no significant publications were produced on rapid or flash pyrolysis of waste plastics harnessing a FFR. A review of FFR developments is therefore given below regarding coal or biomass applications.

Badzioch [1] summarized the volatile yields in the pioneering studies carried out at relatively low temperatures in a publication on rapid pyrolysis containing three introductory

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sections and a collection of twelve papers by various Russian authors. According to Badzioch, Shapatina *et al.* authored the earliest publication on the kinetics of the devolatilization of coal particles in suspension in 1950. Their main interest was the variation of volatile products with heating rates. They showed that the gaseous products from rapid pyrolysis were more useful than in slow pyrolysis.

High heating rates were applied in fluidized-sand-bed experiments by Pitt [2] who studied the kinetics of volatile product evolution from coal. He measured evolution rates in a fluidized carbonizer at temperatures from 300 to 650°C, over a time period 10 s to 100 min.

Loison and Chauvin [3] studied fast heating in the range of 1000°C/s by means of two types of apparatus: a vertical furnace in which a coal flow carried by gaseous nitrogen is heated by radiation; and a belt furnace in which the particles of the coal are introduced into the meshes of metallic cloth which is heated by resistance. The material balance was established for the pyrolysis of seven coals of different ranks. The results showed that volatile matter yield was sometimes greater than that obtained by the standard method and always greater than the change in proximate volatile matter between the original coal and resulting char. Fast pyrolysis gave a high tar/gas ratio. The tar yield was maximum (27%) for bituminous coals having a carbon content of about 86%.

Edinger *et al.* [4] studied rapid decomposition of coal in a transport-type reactor, with residence times 8–40 ms (COED-FMC). They found that pyrolysis atmosphere affects the products. Coal particles never reached the reactor temperature, even at the lowest particle transfer rate; 59% of the coal volatilized when the reactor temperature was 1300°C. This is far above the 41% indicated by the ASTM volatile-matter determination.

Howard and Essenhigh [5] pyrolyzed coal particles, burning them in a one-dimensional plane-flame furnace. They measured the solid composition and the flame temperature along the axis of propagation. Particles attained a temperature of about 1100°C without ignition or significant devolatilization. They found that devolatilization of 0–200 μm particles seems to be a volumetric reaction that is independent of particle size.

Kimber and Gray [6] studied the kinetics of devolatilization of a series of coals at temperatures between 700 and 1200 K with heating rates of 10^4–10^5 K/s. They concluded that the ratio of dry ash-free weight-loss to change in the dry ash-free volatile matter by proximate analysis is greater than one.

Jüntgen and Heek [7] studied ethane release from a finely ground coal (19.1% volume to mass) as a function of heating rate. Their heating rates were between 10^2 and 10^5 K/min.

Menster *et al.* [8] used electrical pulse heating to apply a heating rate of nearly 10^4°C/s to a number of coals. The total volatile yield from low-rank hVC and hVA coals displayed a maximum in the temperature region 700–800°C. The peak volatile yields exceeded the volatile matter contents of the coals as determined by the standard ASTM method.

Badzioch and Hawksley [9] carried out experiments on the pyrolysis of 11 British coals of various ranks in a laminar flow reactor. They studied pyrolysis at temperatures up to 1000°C, heating coal particles to decomposition in 30–110 ms at a rate between 25 000 and 50 000°C/s. The volatile product yield in rapid heating was 1.3–1.8 times higher than that found from the difference between the proximate volatile matter of coal and that of char.

Anthony *et al.* [10] studied rapid devolatilization of monolayers of lignite and bituminous coals supported on wire mesh heating elements in helium. They calculated devolatilization rates by weighing samples before and after experiments of known duration for different residence times (0.05–20 s), temperatures (400–1100°C), heating rates (10^2–10^4°C/s), pressures (0.001–100 atm), and particle sizes (50–1000 μm). They observed that the weight loss from either coal was essentially complete within a fraction of a second, to a few, seconds, depending upon temperature, and increased with increasing final temperature up to 900–950°C. Weight loss (corrected to its value at a fixed temperature) was found to be independent of pressure, heating rate, and particle size, for the lignite, depending only on temperature and time; for the bituminous coal, it increased with decreasing pressure, decreasing particle size, and, to a small extent, increasing heating rate.

Belt and Roder [11] investigated rapid-entrainment carbonization of powdered coal under pressure in a partial hydrogen atmosphere as a means of producing low-sulphur char for use as a power-plant fuel. They utilized a 4-inch diameter and 18-inch high carbonizer. A char containing 0.7% sulphur produced at 1000°C, 400 psig, and 91% hydrogen-in-nitrogen from the 2.55% sulphur-containing parent coal.

Green [12] studied synthetic fuels from coal using the Garrett process. This process produces high yields of volatile fuels from coal through a novel 'flash pyrolysis'. The reactor consists of a ten-foot length of a nominal one-inch pipe. The reactor temperature is maintained by means of electrical heaters. Pulverized coal is fed into a T-connection from a screw feeder where it is picked up by a stream of carrier gas and conveyed through the reactor at high velocity, becoming devolatilized. The hot products first pass through a series of cyclones to recover the char and volatiles and then are cooled to separate the liquid products. High-volatile bituminous Kentucky coals were used in an attempt to determine the optimum pyrolysis temperature for liquid yields in the range 540–650°C. The maximum tar yield reached about 40% on moisture-ash-free basis which is more than twice that obtained in the standard Fischer assay test for this coal. It was proposed that flash pyrolysis to gasify carbon at the higher temperatures tends to reduce the hydrogen/carbon ratio in the char, decrease the tar yield, and increase the hydrogen/carbon ratio in the gas.

Kobayashi *et al.* [13] studied devolatilization of a lignite and a bituminous coal at high temperature under rapid heating conditions. Devolatilization rates were measured in a flow furnace designed to render heating rates of 10^4–2×10^5°C/s (with typical temperatures of 725–1825°C and residence times down to a few milliseconds). The volatile yields were determined by differences in weights of coal fed and char collected, and by use of ash as a tracer. 0.1–0.3 g of graded coal particles (+400–325 Tyler mesh) in an argon carrier gas was injected through a 1.2-mm I.D. water-cooled stainless steel tube along the axis of the furnace into plasma-preheated argon stream, confined by a 50.8-mm I.D. cylindrical graphite muffle tube. At 1825°C both coals yielded 63% volatile which was significantly greater than the ASTM volatile matter of 46% (m.a.f.).

Ubhayakar *et al.* [14] studied rapid devolatilization of pulverized coal in hot combustion gases, varying the input gas temperature between 1525 and 1975°C. They used three particle size distributions for the same type of coal: as received, the fraction which remained on a 200 mesh screen; and that which passed through the screen. The residence time in the gasifier was 7–70×10^{-3} s. The tests were conducted at a pressure of 1 atm, heating rates up to 10^5°C/s, and volatile product yield up to 68% of the original dry-ash-free coal.

Nskala *et al.* [15] studied characteristics of chars produced by pyrolysis following rapid heating of pulverized coal. They used a furnace 5 cm I.D. to study fast pyrolysis of size-graded pulverized coal particles. The study was carried out as a function of isothermal pyrolysis time (0.018–0.025 s), particle size (50–181 μm), and parent coals (three lignites). The following experimental conditions were kept constant throughout the investigation: coal feed rate ~0.5 g/min; volumetric flow rate of nitrogen (which was used as the pyrolysis medium) into the pyrolysis furnace 32 L/min; temperature 808°C; and atmospheric pressure. Under these conditions the heating rate of the coal particles in the pyrolysis furnace was of the order of 8×10^3°C/s, and they calculated the weight loss using ash as a tracer. They proposed that: (i) a monotonic change in the physical properties of chars occurred with increasing pyrolysis time; (ii) there was some dependence of weight loss (i.e. volume per mass yield) on particle size; (iii) the three lignites underwent pyrolysis to a comparable extent, presumably because of their similar initial chemical composition; (iv) there was an appreciable influence of temperature and heating rate on weight loss in the Parr crucible; and (v) there was a significant influence of the mode of pyrolysis (i.e. entrained vs fluidized bed) on the nature of the char produced. From a theoretical treatment of gas–solid interactions they also proposed that all coal particles smaller than 200 μm diameter were heated from their initial room temperature to the predetermined gas temperature of 808°C so fast that no appreciable gradient was established between their surface and their core. They used an empirical equation in conjunction with experimentally determined kinetic constants to calculate the weight loss in the laminar flow reactor. They found that: (i) for pyrolysis times ranging up to about 0.2 s, the agreement between experimental and calculated values of weight loss was good; but (ii) for pyrolysis times greater than 0.2 s, the disagreement between these values became more pronounced. They suggested that: (i) the pyrolysis furnace can be used effectively for studying the pyrolysis of size-graded, pulverized, coal particles under essentially isothermal conditions; and (ii) it may be most important to examine the resulting chars and determine changes in physical and chemical properties due to rapid heating because of the relevance these may have in coal conversion processes.

Torrest and van Meurs [16] studied the rapid pyrolysis and desulphurization of Texas lignite on a laboratory scale. As a reactor they used a pyrolysis tube 100 cm long and 5 cm diameter. Preheated steam or nitrogen entered the bottom of the tube, with flow rates and particle sizes chosen so that particle residence times were of the order of seconds. Particle sizes ranging from 100 to 1000 μm were tested. Most of their work was carried out on 200–350 and 500 μm beneficiated particles. The heating rate for that size was 1000°C/s and the terminal settling velocity was about 100 cm/s. The average velocity of the steam at 760°C was 64 cm/s. They found that rapid heating of lignite particles during free fall, through a counter-flowing pyrolysis gas, was an effective method of producing a low sulphur char. For 200 μm particles with residence times of seconds in steam, the organic sulphur of the lignite was reduced from 1.3 to 0.8% by weight over a temperature range 700– 800°C.

Zanzi *et al.* [17] studied rapid pyrolysis of biomass, wood and agricultural residues using a FFR, and concluded that the char reactivity is very strongly influenced by treatment conditions and may be significantly increased by using high heating rates, small particle sizes of the fuel and short residence time at higher temperature. A longer residence time results in the formation of lower reactivity char. This may be seen both in the gasification tests and in the tests on final char pyrolysis. The char reactivity in steam gasification increased when residence time decreased.

Char is a main product in hydropyrolysis of coal. It is used in general as feedstock to steam gasification to produce hydrogen, which is in turn harnessed for hydrogasification. Thus char reactivity is an important parameter for the design and development of a hydropyrolysis process. Xu and Kumagai [18] investigated nitrogen evolution during rapid hydropyrolysis of coal in a continuous FFR whose length was 1300 mm and diameter 10 mm. They employed three coals in the particle size range 70–90 μm, giving a residence time of 2 s. The temperature varied from 923 to 1123 K and hydrogen pressure was up to 5 MPa. The dominant nitrogen gaseous species was ammonia accompanied by a little HCN because most of the latter was converted to the former through secondary reactions. They concluded that the evolution of nitrogen in coal is caused mainly by devolatilization at temperatures below 973 K, while the evolution of the volatile nitrogen in char is accelerated with increasing temperature and hydrogen pressure. Gas residence time has a significant effect on product composition. Xu *et al.* [19] utilized the same FFR in a similar study raising this pressure to 7 MPa. At a hydrogen pressure of 1 MPa one of the coals gave 50, 48, 47, and 46% C yield in char respectively at 873, 973, 1073, and 1123 K. The corresponding C yields in tar were 26, 19, 12, and 9. Thus temperature has a much more pronounced reduction effect on the tar yield. Tar decomposes at high temperatures to form methane, ethane, and HC. This indicates the importance of operation temperature in flash pyrolysis. The authors present a comparison of different works employing FFR, Curie-point pyrolyser, and rapid heating batch reactors. Both Curie-point pyrolyser and batch reactors apparently give slightly smaller weight loss than FFR despite the shorter reaction time in FFR. They suggest that this may be due to the better solid–gas contact in FFR.

Sugawara *et al.* [20] harnessed a FFR to study hydropyrolysis in a hydrogen stream at atmospheric pressure. They rapidly pyrolyzed five noncaking and two caking coals at temperatures up to 1233 K with a heating rate of 6000 K/s. Both volatile matter yield and internal surface area of char were measured for several treatment times ranging from 0.1 to 0.4 s. Pyrolysis rate was determined from changes in particle temperature, diameter, and apparent density. Rapid-hydropyrolysis char was more favourable for gasification than slow-heating pyrolysis char.

Flash pyrolysis in FFR is a useful means to remove sulphur from coal [19, 21]. As shown by Li *et al.* [22], it can also be utilized to remove heteroatom molecules from biomass. Both the yield and the composition of the resultant gas depend on the biomass composition. The gas output is richer in hydrogen in the case of cellulose and hemicellulose than in the case of lignin. Smaller biomass particle sizes and higher fast pyrolysis temperatures also boost hydrogen content. The total of carbon monoxide and hydrogen content is reported to be 65.4% for legume straw and 55.7% for apricot stone.

3 DESIGN ASPECTS OF FFR TO BE USED IN PYROLYSIS

The literature surveyed above and our own experience [23–27] identify several important aspects for FFR design to be employed in waste plastic pyrolysis:

1. Depending on the reactor length, there is a threshold for particle size to begin to influence free fall or reaction time and hence products. The reactor length should

mesh with the size and density of the particles to be processed. This needs to be investigated with a view to product quality.

2. All possible means, including provision of multiple exit points along the reactor, use of a carrier gas, and application of vacuum must be considered to facilitate fast removal of gaseous products from the reaction medium.
3. The kind of reaction medium, i.e. whether it is inert, oxidative, or reductive, deserves attention because of its substantial effect on the yield and composition of solid, liquid, and gaseous products.
4. Raw material may need some kind of pretreatment. For example, styrene foam can be subjected to heat to make it compact before grinding to fine particles.
5. A direct current screw feeder should help to deliver under control the feed at the precalculated rate. This rate depends on the size and speed of the feeder.
6. It is essential to centralize the feed and keep it away from the reactor walls. Sticking of particles to the inner surface of the walls turns rapid pyrolysis into fixed-bed pyrolysis. The growth of the stuck mass leads to blocking of the reactor. Carbonization on walls is an impediment to drawing a mass balance.
7. Another important point is the attainment of a smooth temperature profile along the reactor. Multiple heaters may provide this smoothness.

4 A FREE-FALL REACTOR SYSTEM FOR FLASH PYROLYSIS

4.1 SET-UP

Figure 23.1 depicts the current version of the free-fall reactor developed and used in a series of pyrolysis researches [23–26] at Ateklab, Ankara University, spanning over

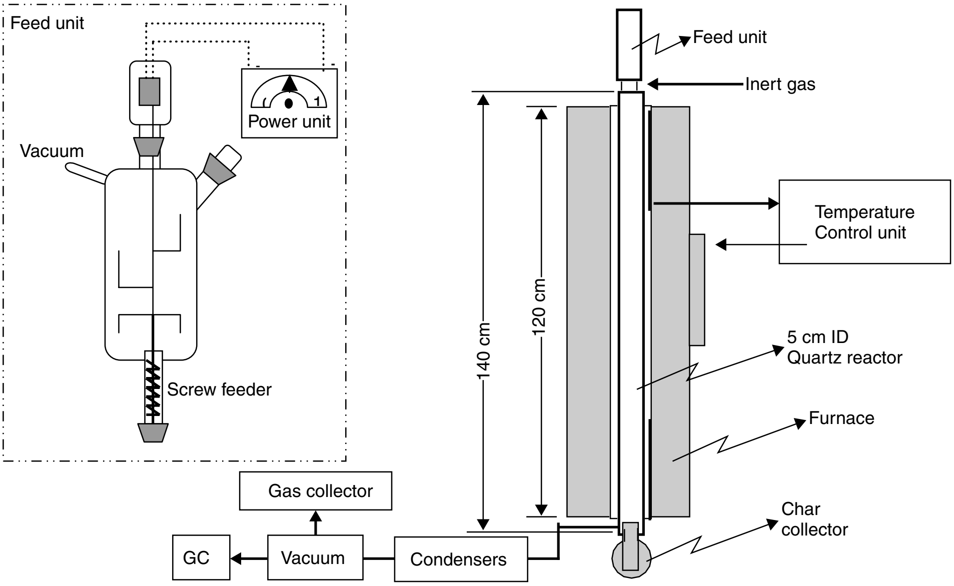

Figure 23.1 The FFR set-up

15 years. The inset shows the specially designed feed unit consisting of a 12 V DC motor, a bladed shaft, and a single-thread screw feeder connected in this order and housed in a three-piece Pyrex casing which is about 400 mm high. A power unit (not included in the drawing) precisely regulates the voltage of the DC motor to vary between 0 and 12 V which in turn fixes the rotational speed of the screw feeder and thereby the (downward) feed rate, depending on the particle size fraction. The motor is seated in the top piece Pyrex. The middle Pyrex has a side entrance (not shown) through which to dump a preweighed lot of raw material. Two extra blades break up and smoothly deliver the lot to the screw feeder underneath. The bottom Pyrex extends about 50 mm downward from the feeder's tip in order to prevent scattering and direct the feed towards the central axis. A conical funnel situated between the feed unit and the quartz reactor also helps to centre the feed particles and thus substantially reduce their sticking at the walls.

A high-temperature furnace jackets the reactor which is connected to a char collector and two water-cooled condensers in series. Each condenser balloon is in a salt–ice bath. The reactor's diameter is 50 mm and height 1400 mm, its heated zone being 1200 mm long. An inert gas (N_2) entrance is also incorporated to purge oxygen. Experiments are carried out under vacuum, the suction being at the exit of the condenser bath series. Vacuum is also connected to the middle Pyrex of the feed unit in order to balance pressure. The application of vacuum helps to adjust the retention time of the pyrolysis products and to remove them from the reaction medium, thereby reducing unwanted further reactions. A possible alternative to achieve these would be the use of a carrier gas, as mentioned above. This is not opted for here because of its undesirable dilution of the products.

Two Ni–CrNi thermocouples measure the reactor temperature at 400 and 800 mm from the top, the upper thermocouple being harnessed for the temperature control by a personal computer.

Free fall time through the reactor is an important factor influencing the reaction extent. The reactor length must match the particle size range to render a suitable retention time. This is exemplified by an Ateklab investigation as follows. Raw material particles (LDPE) were separated by ISO 3310-1 standard sieves into (three) size ranges, namely 150–212 μm, 75–150 μm, and >75 μm diameter. After calibration for each of these ranges, the voltage of the DC motor driving the feeder was appropriately set to render an approximate feed rate of 2 g/min.

4.2 EXPERIMENTAL PROCEDURE

The feed unit is dismounted, charged with a weighed amount of feed particles in the selected size range, and remounted after heating the reactor to the preset temperature with a stopcock in its place. Oxygen is purged out of the system by nitrogen. The vacuum pump is operated until a preset reduced total pressure. The motor of the feeder is started. The reaction causes the pressure to rise. The vacuum connection is shut off and the system is allowed to cool when the feed is completely exhausted. The temperature varied along the reactor's heated zone as depicted in Figure 23.2.

The gases from the vacuum pump are either directed to a gas chromatograph (GC) through an automatic injection valve whose inside loop was 0.250 mL or discharged to gas collection burettes. The GC is a Varian 3400 with a flame ionization detector (FID)

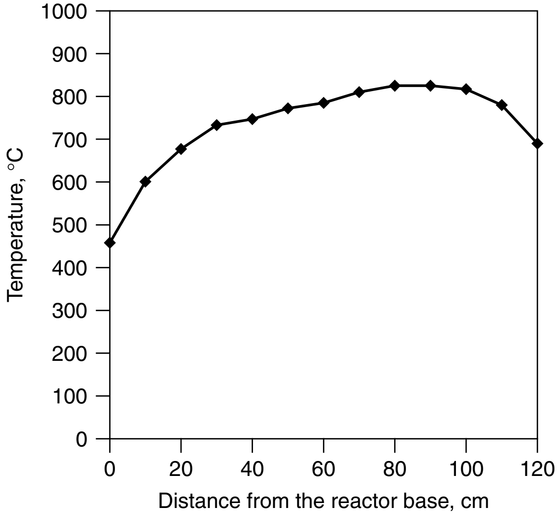

Figure 23.2 A typical temperature profile of the reactor

and a Porapac Q column. It is employed to analyse both the vacuum pump effluent and the gas in the collection burettes. The results are averaged for each run. The liquid product is analysed harnessing a HP5890 Plus GC/MS with an OV-101 column.

The residue in the char collector and the liquid total in the condenser balloons were, respectively, taken to be the solid and the liquid yields based on the feeder charge. The gas yield was then found by taking the difference. The sum of the gas and liquid yield was defined as the total conversion.

5 PLASTIC WASTE RECYCLING

Plastic wastes are generated in Europe at the rate of 15 million tons per annum [28]. Their minimization and recycling are encouraged [28] and legislated [29–30] for economic and ecological reasons. Recycling also serves to conserve natural resources. This is indicated for example by the statement [31] that each ton of polyethylene (PE) and polyvinyl chloride (PVC) respectively requires for its production 18.7 and 8 tons of crude oil.

The 1973 petroleum crisis intensified research on coal liquefaction and conversion processes. The technology developed in this field was later harnessed in chemical recycling of plastics. Mastral *et al.* [32], for example, employed two different batch reaction systems (tubing bomb reactors and magnetically stirred autoclave) and a continuous reactor (swept fixed bed reactor). Chemical recycling techniques such as pyrolysis [28, 33–38] or coliquefaction with coal [39, 40] convert plastic wastes into hydrocarbons that are valuable industrial raw materials.

Generally included in the chemical recycling literature are details such as the plastic waste treated [41], the reactor type [28, 36, 42], the catalyst [33, 35, 43], the operation and its conditions [28, 36, 42], the product constituents [28, 33, 44, 45], the liquid and gas yields and the solid residue [28, 42–44] and kinetics [45, 46]. The most frequently employed type of reactor in polymer pyrolysis is the fluidized bed, despite its inherent disadvantages that a fraction of the products is lost to the inert stream and that substantial extra heat is necessary for the fresh and/or recycled inert gas feed which has to be cooled on exit so as to separate the condensable products.

PE is the overwhelming majority of post-consumer plastic wastes resulting from agriculture, automotive, construction, distribution and domestic use. Polypropylene (PP), polystyrene (PS), PVC and polyethylene terephthalate (PET) are the other significant components. Many workers have studied PE pyrolysis. Scott *et al.* [33] operated a fluidized-bed reactor at atmospheric pressure, with difficulty in the calculation of product phase yields. The situation improved at higher temperatures. At 725°C about 12% of the feed was unaccounted for, the gas yield reaching 42.2% whose ethylene content was 19.3%. In another flash pyrolysis research on PE Williams and Williams [28] also harnessed a fluidized bed. They obtained 10.8% gas, 43.9% oil, and 45.3% wax at 500°C, and 71.4, 24.6, and 4.0% respectively at 700°C. The number average molecular weight of the wax was 494 at 500°C. Moreover, the analysis of the combined wax and oil output at this temperature showed mainly aliphatic hydrocarbons in the range C_{18}–C_{57} with a mean around C_{33}. The monomer content of the gas was 2.19% at 500°C and 26.86% at 700°C.

Milne *et al.* [42] used an internally circulating fluidized bed to study pyrolysis of low-density PE (LDPE) at temperatures ranging from 780 to 860°C and residence times of 400–600 ms. They achieved gas yields in excess of 90 wt% with total alkene yields as high as 75 wt%, demonstrating a waste treatment potential for processes such as flash pyrolysis, distinguished from classical pyrolysis by its high heating rates and low retention times, where these conditions can be maintained.

LDPE was catalytically depolymerized in solution in an autoclave by Scott *et al.* [47] who observed, as expected, that increasing the temperature or decreasing the reaction time resulted in higher liquid yield. At a plastic waste:catalyst ratio of 20:1 and a maximum temperature of 420°C, they reported 52.6% liquid and 47.4% gas yield. The majority of the gas was C_3 and C_4, the monomer being about 5%.

Polystyrene was flash pyrolyzed in a free-fall reactor under vacuum [49, 50] giving yields at the level of fluidized-bed figures [33, 51]. Also investigated [49] was flash vacuum pyrolysis of LDPE whose results are now presented here in this manuscript with an additional experiment using the same system.

6 RESULTS FROM ATEKLAB FREE-FALL REACTOR

6.1 LDPE RESULTS

Additive-free granular LDPE was PETKİM Commercial Code Number F12, obtained from PETKİM Petrochemical in Aliağa, Turkey. The particles were separated by ISO 3310-1 standard sieves into three size ranges, namely 150–212 μm, 75–150 μm, and less than 75 μm diameter. After calibration for each of these ranges, the voltage of the DC motor driving the feeder was appropriately set to render an approximate feed rate of 2 g/min.

The first set of experiments used LDPE particles in the 150–75 μm size range and varied the reactor temperature between 750 and 875°C. As seen in Figure 23.3, both

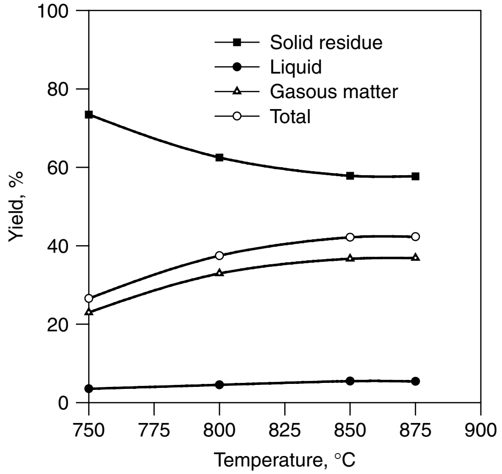

Figure 23.3 Temperature effects on product phase yields for the feed size range 150–75 μm. (Copyright 2003 from Polymer-Plastics Technology and Engineering by A Karaduman, M. C. Kocak and A. Y. Bilgesu. Reproduced by permission of Taylor & Francis, Inc., http://www.taylorandfrancis.com)

Table 23.1 Temperature effects on gaseous output composition (feed size 150–75 μm). (Copyright 2003 from Polymer-Plastics Technology and Engineering by A Karaduman, M. C. Kocak and A. Y. Bilgesu. Reproduced by permission of Taylor & Francis, Inc., http://www.taylorandfrancis.com)

Gas products (%)	Temperature (°C)		
	750	850	875
Methane	11.09	19.92	21.84
C_2	67.20	66.29	64.28
C_3	1.10	4.92	8.58
C_4	20.61	8.87	5.30

the liquid and the gas yield (i.e. wt% of feed) rise monotonically with temperature at the expense of the (unwanted) solid residue, the total conversion gain reaching about 43%. The gas yield alone changes from 22 to 37%. The overwhelming majority (over 99%) of the gaseous product is C_1–C_4. Table 23.1 indicates that high temperature reactions involving C_4 (mainly butene) and C_2 (mainly ethylene) almost double the methane fraction, accompanied by an increase in propene. Milne *et al.* [42] reported a similar temperature effect for an internally circulating fluidized-bed reactor. Williams and Williams [28] also harnessed a fluidized bed at lower temperatures (700°C maximum) and observed a similar trend with some fluctuation in butene fraction.

The substantial increase (more than 50%) in the gas yield more than compensates for the slight drop (from 67.2 to 64.3%) in its ethylene monomer content. Thus operation at higher temperatures is desirable. This work is eminently superior in respect of ethylene yield; the highest literature value given in Milne *et al.* [42] is about 33%. Fluidized bed rendered 2.19–26.86% [28], circulating fluidized bed 27–37% [42], autoclave 5% [47] and steam cracker fluidized bed 8.1–30% [44].

The gas chromatogram of the liquid product at 875°C is depicted in Figure 23.4. The bulk of the liquid product is paraffinic. Derived from Figure 23.4, Figure 23.5 shows that 96% of the liquid product is below C_{40} while over 55% of it is C_{12}–C_{20}. As is known C_{12}–C_{20} hydrocarbons are essential raw materials for the production of fatty acids, fatty alcohols and detergents. In contrast, the liquid output of Williams and Williams [28], as mentioned above, comprised alkadienes, alkenes, and alkanes in the range C_{11}–C_{57} with a mean of C_{33} at 700°C. They observed that, at higher pyrolysis temperatures, the total concentration of aliphatic species above about C_{30} was greatly reduced. This is further evidence that the temperatures employed in the present work are appropriate for LDPE pyrolysis.

Kiran *et al.* [48] pyrolyzed PE in a fixed-bed reactor (Gray–King apparatus) obtaining a gaseous mixture and a green wax whose melting point was about 80°C. (This wax apparently plugged their product lines and condenser tubes.) They heated PE samples up to 600°C at the rate of 5°C/min despite the TGA indication that degradation finished between 440 and 475°C. The batch time was about 4 h. In comparison, the present work is a continuous process whereby approximately half of the LDPE waste is converted to liquid and gaseous products within seconds, albeit at about 875°C.

As portrayed in Figure 23.6, at 875°C, increase in particle size adversely influences the liquid and gas yields and hence the total conversion. In going from <75 to 212–150 μm

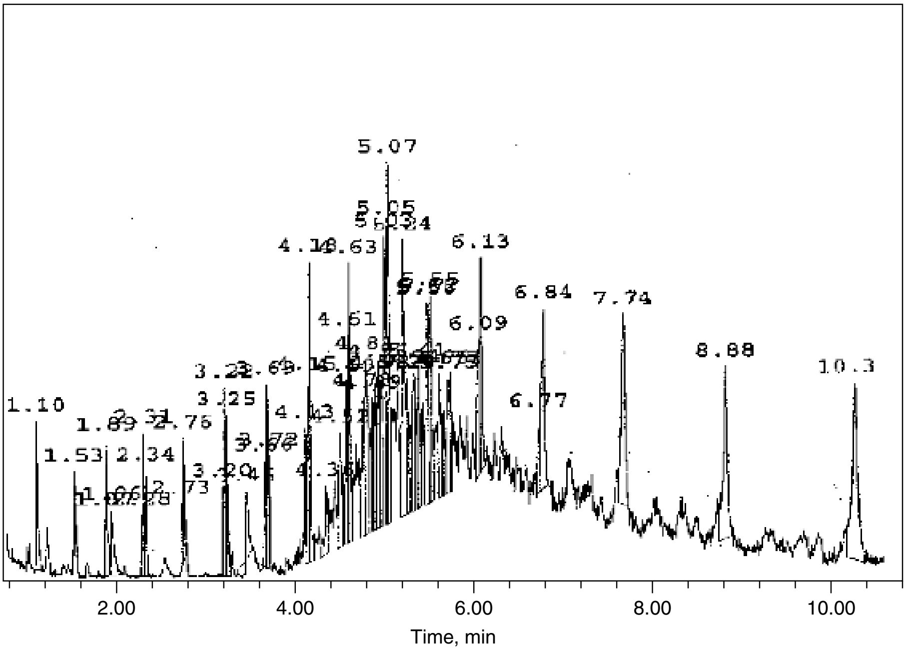

Figure 23.4 The GC/MS analysis of the liquid products at 875°C for the feed size range 150–75 μm

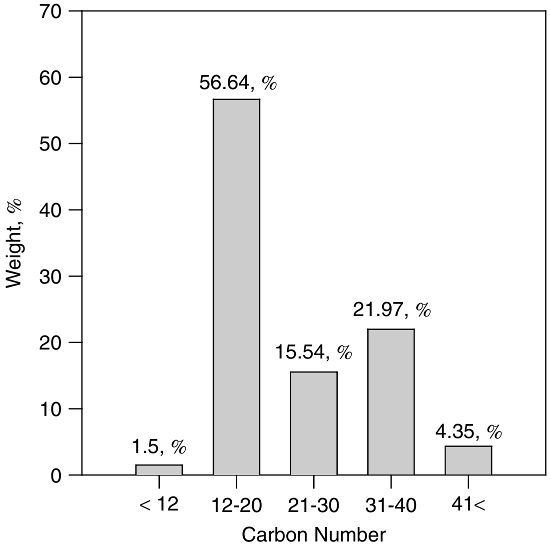

Figure 23.5 The carbon number distribution of the liquid product

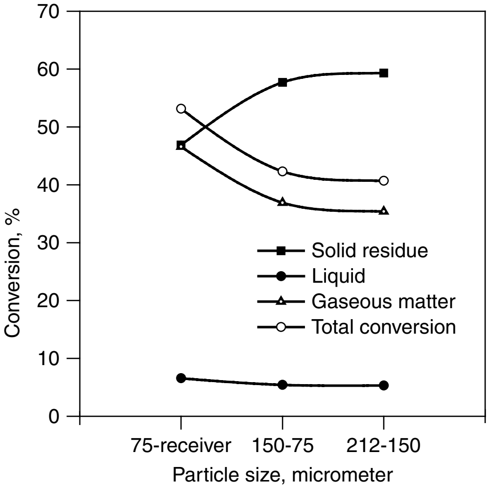

Figure 23.6 The effect of the feed size on the product phase yields at 875°C. (Copyright 2003 from Polymer-Plastics Technology and Engineering by A Karaduman, M. C. Kocak and A. Y. Bilgesu. Reproduced by permission of Taylor & Francis, Inc., http://www.taylorandfrancis.com)

range, they respectively change from 8 to 4%, from 47 to 34%, and from 55 to 38%. Thus the smaller the particles size the better.

The free-fall reactor operating under vacuum has the added advantage over both the sweeping fixed bed and fluidized-bed reactor types that it does not dilute the gaseous products with an inert.

It is interesting to compare flash vacuum pyrolysis of LDPE and PS in a free-fall reactor. Temperature rise causes the solid residues to fall and the liquid and gas yields to increase. The LDPE figures exceed the corresponding PS values in the case of the solid residue and gas yield by about 50 and 10% respectively. In contrast, the liquid yield of LDPE is about one-fifth of PS. These findings are in harmony with the activation energies: 270–331 kJ/mol for LDPE and 126–151 kJ/mol for PS [34].

The most common reactors in polymer pyrolysis are fluidized-bed types, which inherently have the disadvantages that a fraction of the products is lost to the inert stream and that substantial extra heat is necessary for the fresh and/or recycle inert gas feed which has to be cooled on exit so as to separate the condensable products. Free-fall reactors are of course without these disadvantages. This waste treatment study has shown furthermore that flash pyrolysis of low-density polyethylene (LDPE) in a free-fall reactor under vacuum is a promising continuous recycling technique superior to other techniques as regards product quality. The solid, liquid, and gas yield are respectively 60, 4, and 36% at 875°C when the feed is 150–75 μm LDPE particles. The overwhelming majority (over 99%) of the gaseous product is C_1–C_4. Over 64% of this is the ethylene monomer. The bulk of the liquid product is paraffinic; 96% of it is below C_{40} while over 55% of it is C_{12}–C_{20}. As is known, C_{12}–C_{20} hydrocarbons are essential raw materials for the production of fatty acids, fatty alcohols and detergents. Reduction in operation temperature, down to 750°C causes the total conversion (i.e. the sum of liquid and gas yield) to fall from 40 to 25%. This is accompanied by a slight increase (from about 64 to 67%) in the ethylene monomer yield. Thus higher temperatures should be preferred. On the other hand, lowering the particle size down to <75 μm favourably influences the total conversion raising it by about 20%.

6.1 POLYSTYRENE RESULTS

Plastic wastes may be the remains of production or post-consumer wastes, the latter being classified as municipal, packaging, agricultural, automotive and electrical. Packaging wastes are the major category [33, 52–54]. These are mainly thermoplastics such as polyethylene, polypropylene, polystyrene and polyvinyl chloride [28, 33, 55–56].

Plastic waste minimization and recycling are encouraged [28] and even legislated [30, 57–58] for both economic and environmental reasons. Using properly labelled plastics aids separation of mixed wastes prior to recycling either immediately or after remoulding or a chemical treatment, e.g. pyrolysis, rendering various products which may include monomers. Chemical recycling of plastics is an important and challenging task and has led to intensive research. Generally included in the relevant literature are details such as the plastic waste treated [35, 59], the reactor type [33, 36, 42, 51], the catalyst [35], the operation [41] and its conditions [41], the product constituents [33, 51, 60], and phase yields [33, 60]. Information on kinetic and process parameters are scarce, however.

Highly reactive radicals form in pyrolysis due to bond scission. These decompose or react with each other or the polymer giving gaseous, liquid, and solid products [61]. Flash pyrolysis is distinguished from the classical slow pyrolysis by its relatively higher heating rate and lower retention time [23–24]. As in other kinds of thermal degradation, other products such as benzene, toluene, ethyl benzene, and naphthalene accrue in polystyrene pyrolysis when the primaries, namely styrene and its oligomers, are not immediately removed from the reaction medium. Liu *et al.* [51] detected a wider variety of products.

In a study by Sato *et al.* [62], the primaries dissolved in the melted PS or the solvent where the low mass transfer rate lead to significant secondary products. Ohtani *et al.* [61] avoided secondary products by employing helium carrier. They reported monomer, dimer, and trimer of styrene. Flash pyrolysis of PS in a fluidized bed under atmospheric conditions rendered liquid products, mainly containing styrene monomer, toluene, ethyl benzene, and naphthalene [33].

In this study [25], waste polystyrene was flash pyrolyzed in a free-fall reactor under vacuum with the aim to assess the effects of both the operating temperature and the feed particle size on the kinds and relative distributions of products.

While falling in the reactor due to gravity, polymer particles degraded into smaller molecules in a series of reactions, including bond scission. Investigated in this study were the effects of the waste particle size fed and the operating temperature on the type and extent of these reactions. Two sets experiments were carried out. One set employed the 150–75 μm size range at different temperatures, namely 700, 750, 775, 800, 825, and 875°C. The other set harnessed all of the four size ranges mentioned above at 825°C.

Figure 23.7 indicates the temperature effects on the yields in the first set of runs. The gas yield increased throughout the temperature range studied. Up to about 750°C, the operating temperature increase rapidly lowered the solid yield and raised both the liquid yield and the total conversion. Beyond this point, the solid yield continued to decrease, but at a highly diminished rate. The liquid yield, on the other hand, began to fall slowly. This may be due to partial decomposition of the expected product styrene. At 750°C the solid, liquid, and gas yields were 47, 32, and 21%, respectively.

The GC analysis results of the liquid product (Figure 23.8) were focused on styrene, benzene, toluene, and naphthalene components, the often quoted compounds in polystyrene degradation [33, 51, 62–64,]. The run at 750°C showed 48% benzene, 18% styrene, 8% toluene. The benzene content decreased steadily with increasing operating temperature,

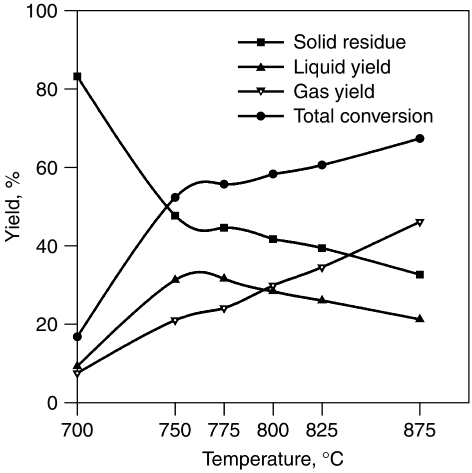

Figure 23.7 The temperature effects on product phase yields of PS. (Reproduced from *Journal of Analytical and Applied Pyrolysis*, 60 (2), A. Karaduman, Flash pyrolysis of polystyrene wastes in a free-fall reactor under vacuum, 179–186 (2001), with permission from Elsevier)

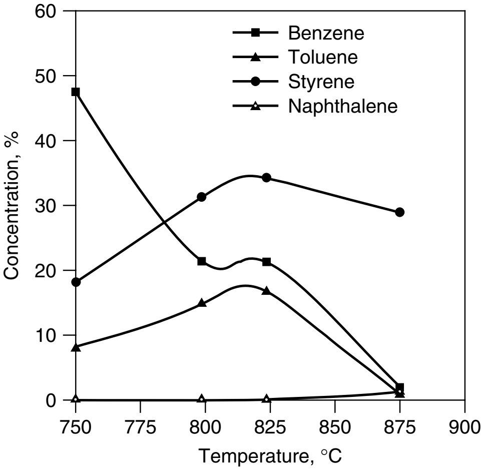

Figure 23.8 The temperature effect on liquid product composition. (Reproduced from *Journal of Analytical and Applied Pyrolysis*, 60 (2), A. Karaduman, Flash pyrolysis of polystyrene wastes in a free-fall reactor under vacuum, 179–186 (2001), with permission from Elsevier)

vanishing at 875°C. Toluene rose initially up to 18%, began to fall at 825°C disappearing at 875°C. The styrene curve resembles in shape that of toluene, reaching a maximum of 34% at 825°C and declining to 30% at 875°C. While negligible at lower temperatures, a little (about 1%) naphthalene appeared at this final temperature.

The C_1–C_4 contents of the gas products are shown in Figure 23.9 for various operating temperatures, disregarding H_2 which the FID detector is known to miss. Apparently generated were about 21–28% methane, 60–70% C2, 5% C_3, and 4% C_4.

How the waste feed particle size influenced the yields were investigated in runs at 825°C, the temperature giving the maximum styrene yield in the first set of experiments. As depicted in Figure 23.10, the coarsest size (300–212 μm) rendered respectively 42% solid, 29% liquid, and 29% gas yields. As the particles became finer the solid yield diminished steadily to about 34% at less than 75 μm. In contrast the gas yield increased monotonically to 38%. The liquid yield seemed little affected by the feed particle size. The total conversion rose from 58 to 66% because of its gas contribution.

In polystyrene degradation, it is desired to maximize the styrene monomer output and hence the liquid yield. The rather low figures of this study were probably related to residence time problems. The generated species and the high gas yield indicate that the primary products decomposed significantly because they remained too long in the reactor. The pressure rise observed after the reaction start certainly reduced the suction and slowed down their removal which may be substantially improved by a continuous N_2 stream throughout the run and/or exploiting a reactor with intermediary exits. In view of the second set of experiments, employment of finer waste feed is advisable since this reduced the solid yield and boosted the total conversion, possibly by increasing the polystyrene residence and hence degradation time as reported in two other free-fall reactor studies [23, 24]. Another alternative is to harness a reactor with a longer heated zone.

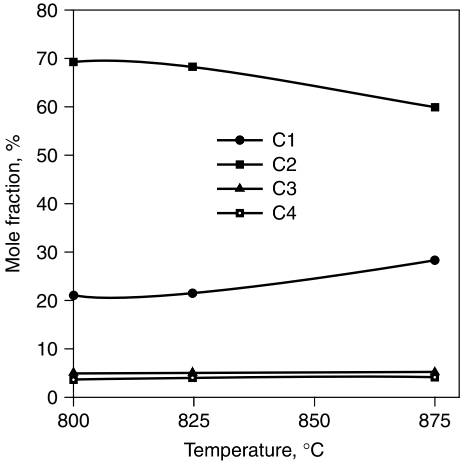

Figure 23.9 The temperature effect on C_1–C_4 contents of the gas products. (Reproduced from *Journal of Analytical and Applied Pyrolysis*, 60 (2), A. Karaduman, Flash pyrolysis of polystyrene wastes in a free-fall reactor under vacuum, 179–186 (2001), with permission from Elsevier)

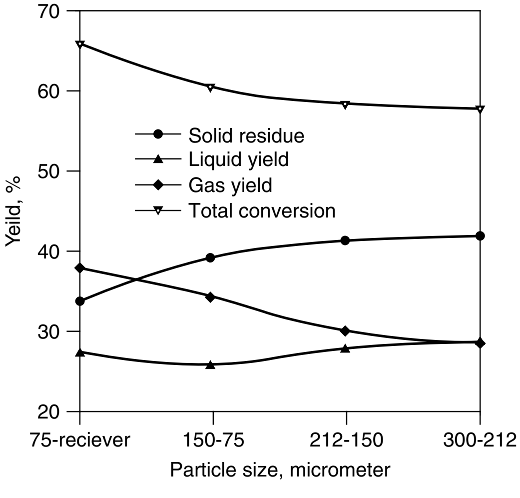

Figure 23.10 The effect of PS particle size on phase yields. (Reproduced from *Journal of Analytical and Applied Pyrolysis*, 60 (2), A. Karaduman, Flash pyrolysis of polystyrene wastes in a free-fall reactor under vacuum, 179–186 (2001), with permission from Elsevier)

GPC analysis of the solid products is needed to elucidate whether or not they contain partially degraded styrene oligomers.

This study showed that polystyrene pyrolysis in a free-fall reactor under vacuum is a promising technique to obtain important liquid chemicals such as benzene, toluene, and naphthalene besides styrene monomer and valuable gaseous output. The liquid yield maximized around 750°C and the styrene yield at 825°C. In general, the higher the operating temperature the lower the solid yield and the higher the gaseous yield and the total conversion. The latter two were also helped by lowering the particle size of the waste feed. Connecting the rather low liquid and styrene yields to residence time problems, suggestions are suggested for improvement and for future work.

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PART V

Monomer Recovery

Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels Edited by
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24

Monomer Recovery of Plastic Waste in a Fluidized Bed Process

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1 INTRODUCTION

The pyrolysis of poly(methylmethacrylate) (PMMA) waste is one of the few technical processes for feedstock recycling of plastics which has been working economically for the last 30 years [1]. The reason for this is the relatively high price of PMMA compared with standard plastics and the possibility to recover up to 95% of the monomer methylmethacrylate (MMA) [2–4]. Feedstock recycling of polyolefins, for example, produces a component-rich mixture of gas and oil and only if the price for crude oil is high, is the economy of such processes viable [5–12]. Other plastics which can be pyrolyzed to high yields of the monomers are polystyrene (PS), polytetrafluoroethylene (PTFE), and polyethyleneterephthalate (PET) [13–17]. The amounts of the monomers with these polymers as feedstock are smaller than using PMMA. If PMMA is heated to a temperature of more than 400°C, it will decompose almost completely into the monomer [18].

For the depolymerization of PMMA, molten metal bath, dry distillation, extruder processes and fluidized-bed processes are used [19]. The depolymerization reactor of a molten metal bath consists essentially of a gas- or oil-heated metal bath. The metals used are those which have a low melting point such as tin and lead. The PMMA regrind is fed from the storage silos onto the stirred metal bath. Bath temperature and a residence time of some minutes are important for good yield and quality of the MMA.

In contrast to this, the residence time of the products in a fluidized bed lies between 1 and 5 s [20]. Buekens [21] studied the influence of the residence times in technical fluidized-bed processes. One of the main advantages in using a fluidized bed reactor for depolymerization is that it involves no contamination of organometallic compounds in the products and less environmental problems [1]. Therefore, companies are looking to use fluidized-bed processes especially for filled PMMA. The filler will contaminate the molten metal bath while in a fluidized bed the often expensive fillers can be recovered.

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Today, PMMA is mainly filled by silica, quartz, aluminium hydroxide and other inorganic fillers. For special uses, the polymer is cross-linked. This, together with the high molecular weight, makes regeneration as a raw material in reprocessing impossible. The feedstock recycling by pyrolysis to recover the monomer is therefore a practical way.

2 FLUIDIZED-BED PROCESS

The experiments for the pyrolysis of PMMA, PS, and PTFE were carried out in a laboratory plant with throughputs of 300 g h^{-1} to 3 kg h^{-1} using the Hamburg process of an indirect heated fluidized-bed reactor. Figure 24.1 shows the scheme of the laboratory plant [22]. The fluidized bed with a diameter (Figure 24.1) of 154 mm and a length of 770 mm, consisting of fine quartz sand with a particle size of 0.3–0.5 mm is heated indirectly from outside by electricity. The gas distributor is a steel plate with 108 tubes (3.2 × 0.75 mm) which were moulded into hooks, thus ensuring that no sand could fall through the plate. Nitrogen was used as a fluidizing medium, but during the experiments it was slowly displaced by gaseous PMMA products. An auxiliary gas stream was led through the feeding system to prevent hot gases and sand from entering the input system. The feeding system consists of two conveyors, the first for a constant feed rate and the

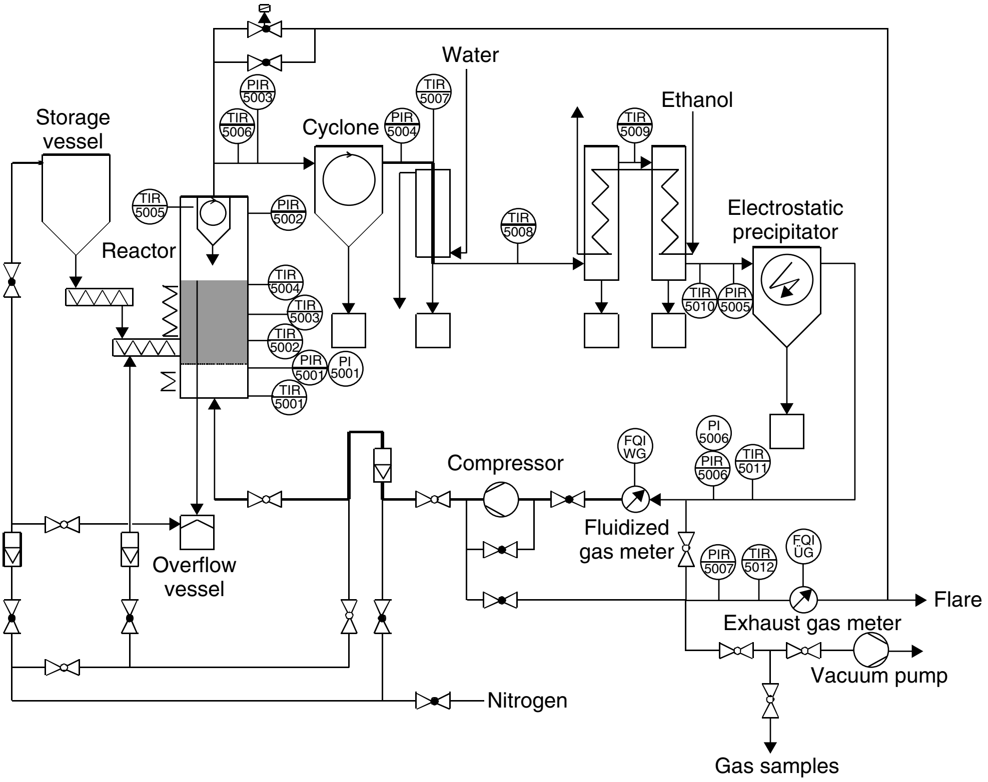


Figure 24.1 Scheme of a fluidized bed process for feedstock recycling of plastics

second for a quick transport into the reactor. In case of filled polymers an overflow vessel is used. The products left the reactor and passed a combined cooling and condensation unit. Fillers and fine sand were precipitated in a cyclone. The gas was cleaned up in an electrostatic precipitator. By a membrane compressor, part of the gas is cycled and used as fluidizing gas for the bed reactor. The oil product is collected below the coolers.

In all experiments, gases, liquids, water fraction as well as solid residue were obtained as products and analyzed on different capillary GC columns and registered with TCD- and FID-detectors. The reactor sand used and the fillers in the overflow and cyclone were combusted in a furnace at 810°C to constant weight. The loss in weight was balanced as carbon black.

Elementary analysis of the feed materials was made with a Carlo Erba Strumentazione CE 1106 CHNS-O. Gases were analyzed with GC-TCD (Chrompack CP 9001; Carboplot P7) and GC-FID (Chrompack CP 9002; Chrompack Al_2O_3/KCl Plot-capillary column). Correlation was based on the methane peak.

After oil distillation, three fractions were obtained. Water and organic fractions were analyzed quantitatively with GC-FID (HP 5890; Macherey & Nagel SE-52). Qualitative analysis of the organic fraction took place by GC-MS (HP 5890; Macherey & Nagel SE-52; Fisons Instrument VG 70 SE). Water was determined by the method of Karl Fischer (Methrom Karl-Fischer-Titrierautomat E547). The third fraction contained high boiling (fluorine cut: bp>295°C) and inorganic components. Like the other solid products it was heated at 815°C to constant weight to determine the organic part. All results of the analysis of the organic product fraction were combined to give a total mass balance.

3 PYROLYSIS OF PMMA

3.1 PURE PMMA

The PMMA pellets were milled to a size of 0.5–1.5 mm. Table 24.1 shows the results of three runs in the fluidized bed with new material, one with tinted product from automobile rear lights.

Raising the temperature increases the amount of gas. At temperatures beyond 550°C, the gas fraction increases rapidly, reaching 42 wt% at 590°C. The gas consists of methane, ethene, propene, carbon monoxide and carbon dioxide (Table 24.2).

Only small amounts of carbon black are formed. The main component in the liquid is methylmethacrylate (MMA). At a pyrolysis temperature of 450°C it is 98.6%, and at 490°C it is 98.3% pure. Even coloured waste PMMA materials such as rear lights gave

Table 24.1 Pyrolysis of polymethylmethacrylate in a fluidized bed (products in wt%)

	Pure pellets			Waste
	450°C	490°C	590°C	490°C
Gas	0.37	2.63	42.46	7.36
Liquid	98.48	97.08	57.27	92.13
(MMA)	(97.16)	(95.48)	(54.88)	(90.99)
Carbon black	0.15	0.29	0.27	0.51

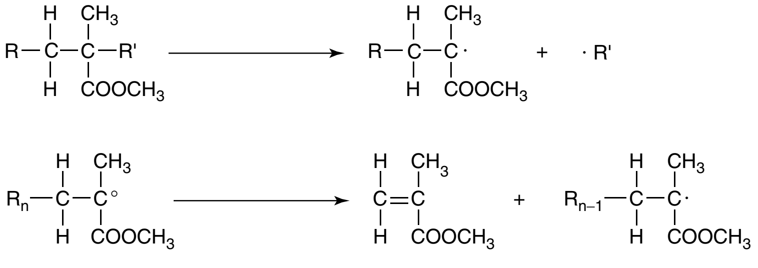
Table 24.2 Gas products of the pyrolysis of PMMA in a fluidized bed: dependence on temperature (components in wt%)

Temperature	450°C	490°C	590°C
Hydrogen	0.47	0.30	0.021
Methane	11.8	10.3	9.2
Ethene	4.7	4.4	5.87
Ethane	3.4	2.6	1.6
Propene	1.3	6.8	16.3
Propane	0.78	1.3	1.9
Propadiene	0.009	0.02	0.09
Propyne	0.014	0.05	0.24
Dimethylether		0.024	0.031
iso-Butane	0.009	0.075	0.088
iso-Butene	0.21	1.85	4.9
1,3-Butadiene	0.19	0.10	0.15
trans-2-Butene	0.05	0.18	0.34
cis-2-Butene	0.03	0.11	0.24
2-Pentene	0.05	0.10	0.46
Carbon dioxide	75.8	55.0	20.4
Carbon monoxide	0.78	14.3	31.9

a really clean monomer with 98.6 wt%. The liquid contains small amounts of methyl isobutyrate (MA), methylacrylate (MA), 1,4-cyclohexane dicarboxylic acid dimethyl ester (dimeric MMA), and methanol (MeOH) as side products. The concentration increases with increasing temperature, but these concentrations are still so low that the liquid could be polymerized to new PMMA after distillation without any further purification. The polymer is totally colourless.

The detailed pyrolysis products are listed in Table 24.3. The influence of temperature on MMA is small between 450 and 500°C, but is drastically increased in the temperature range 500–600°C. The MMA concentration decreases from 97 to 54%.

At the same time there is an increase of carbon dioxide, carbon monoxide, methane, propene, and other gaseous components. The low-boiling components are carbon oxides and hydrocarbon while the higher-boiling components are esters. Mechanistically, the pyrolytic conversion of PMMA to its monomer is a radical process [24]. Two radicals are formed by the action of heat of the polymer chain (Scheme 24.1).



Scheme 24.1

Table 24.3 Products of PMMA pyrolysis at different temperatures (components in wt%)

	Pure pellets			Waste
	450°C	490°C	590°C	490°C
Carbon monoxide	0.01	0.38	13.55	1.05
Carbon dioxide	1.04	1.45	8.67	4.05
Methane	0.16	0.27	3.91	0.76
Ethene	0.064	0.12	2.49	0.33
Ethane	0.047	0.71	0.71	0.20
Propene	0.018	0.18	6.95	0.51
Propane	0.011	0.36	0.82	0.10
Propadiene	<0.001	<0.001	0.038	0.002
Propyne	<0.001	0.001	0.102	0.004
iso-Butene	0.019	0.087	2.10	0.142
1,3-Butadiene	0.003	0.003	0.064	0.007
Butene	0.033	0.068	0.29	0.045
Pentene	0.011	0.031	0.33	0.022
Pentadiene	0.007	0.02	0.063	0.009
Cyclopentene	0.001	0.007	0.053	0.001
Methanol	0.03	0.07	0.06	0.05
Methyl propionate	0.01	0.02	0.03	0.02
Methyl isobutyrate	0.11	0.13	0.31	0.12
Methyl acrylate	0.28	0.33	1.25	0.22
Methyl methacrylate	97.16	95.47	54.88	90.98
3-Methyl-2-butenoic acid methyl ester	0.01	0.03	0.05	0.03
2-Methylene butanoic acid methyl ester	0.03	0.06	0.05	0.07
2-Pentenoic acid methyl ester	0.01	0.06	0.10	0.08
3-Methyl-3-pentenoic acid methyl ester	0.01	0.03	0.05	0.03
1,4-Cyclohexane dicer-boxylic acid dimethyl ester	0.14	0.25	0.29	0.14
Carbon black	0.15	0.29	0.27	0.51

Each of the radicals is then degraded by the repeated elimination of monomeric units. The activation energy of the depolymerization was found to be 105 J/mol at 400°C. The excellent heat transfer in a fluidized bed, the low residence time of the monomers, and the low temperature gradient in the bed explain why so few side products and so little carbon black is formed. After distillation the recovered liquid can be polymerized to new PMMA without any other purification.

3.2 FILLED PMMA

Three different filled PMMA were used. One contains 62 wt% of silica (SiO_2, 10–100 μm), the other 71 wt% of granite (100–1000 μm) and the third contains 67% of aluminium trihydroxide ($Al(OH)_3$, ATH). For the pyrolysis, the laboratory-scale fluidized plant (Figure 25.1) was used and for two runs the pilot plant with a capacity of 10–50 kg/h feeding rate (Hamburg Process)

Silica- and ATH-filled PMMA is an often-used material, for example in bathrooms and kitchens. ATH-filled PMMA is less flammable because the ATH produces water at high temperatures which kills the flame. The question was whether such highly filled PMMA gives similar amounts of MMA and if there is a catalytic effect of the ATH on the pyrolysis process.

The parameters of the pyrolysis experiments are shown in Table 24.4. In the experiments, the pyrolysis temperature was 450°C which was found in previous experiment with pure PMMA to be the optimal temperature. Total mass balances are calculated to the organic content even for the filled PMMA to allow a comparison. The losses (1–2%) calculated to 100% were determined on all product fractions proportionately. The following results should be noted.

The monomer recovery is the highest by feeding pure PMMA pellets (98.4 wt%) in the laboratory plant. But highly filled PMMA yielded monomer concentrations of 83–90 wt%. A short residence time is preferred. The good results of the laboratory-scale experiments were confirmed by the experiments in the technical-scale plant yielding 97% MMA for pure PMMA pellets and 83.5% for silica-filled PMMA.

In all experiments the gas fraction is small. Only 0.4–4.9 wt% of gas molecules are produced. Other ligand compounds were found in a range of 1–95%; filled PMMA affords the higher amounts of oily compounds. In the case of ATH-filled PMMA water is formed as a main product by drying

$$2\mathrm{Al(OH)_3} \rightarrow \mathrm{Al_2O_3} + 3\mathrm{H_2O}.$$

Up to 4.3% of water was found on feeding silica-filled PMMA, mostly deriving from hygroscopic PMMA. For unfilled PMMA in the laboratory plant the carbon black formation is very low (0.01%). This value increased to 1.3% for filled PMMA as feedstock.

Fillers and cross-linking in the PMMA increased the amount of gas, other liquids and carbon black significantly. More detailed information on the product composition is shown in Tables 24.5 and 24.6 in the composition of gas and liquid fractions. The main components in the gas fraction are hydrogen, CO, CO_2, and methane. They are degradation products from PMMA and MMA. All other products appear in low concentration and increase with the pyrolysis temperature and by fillers.

Table 24.4 Process conditions and product fractions for the pyrolysis of filled and pure PMMA in laboratory and mini pilot plants of fluidized beds at 450°C

Plant Fillers (wt%)	Lab 71 SiO_2	Lab 62 SiO_2	Lab	Lab 67 ATH	Pilot 71 SiO_2	Pilot
Throughput (kg/h)	2.0	1.9	0.9	3	34	16
Feed (kg)	5.8	2.8	4.2	12	389	575
Reaction time (h)	2.9	1	1.5	4	11.5	37
Sand in reactor (kg)	8	8	8	9	200	160
Gas flow (m^3/h)	3.9	5.2	3.4	3.9	50	65
Residence time in fluidized bed (s)	1.2	1.0	1.3	1.4	2.9	1.6
Products (wt% of the organic input):						
Gas	2.6	2.0	0.4	4.9	1.6	0.5
MMA	86.6	90.5	98.4	57.9	83.5	96.7
Other liquids	8.1	5.7	0.8	35.2	9.4	1.6
Water	1.4	0.6	0.4	(24)	4.3	0.8
Fillers	(71)	(62)		(44)	(71)	0.3
Carbon black	1.3	1.2	0.01	0.01	1.2	0.1

Table 24.5 Product gases of the pyrolysis of pure and filled poly(methacrylate) (PMMA) (vol% in relation to the organic input; + = traces) a 450°C pyrolysis temperature

Plant Fillers (wt%)	Lab 71 SiO_2	Lab 62 SiO_2	Lab	Lab 67 ATH	Pilot 71 SiO_2	Pilot
Hydrogen	4.1	7.7	15	7.6	12	9.6
Carbon monoxide	23	27	27	25.5	22	28
Carbon dioxide	54	45	36	52.4	43	33
Methane	11	11	17	7.4	11	18
Ethane	0.6	0.6	0.2	0.4	1.0	1.6
Ethene	1.8	1.8	0.6	2.1	4.0	2.3
Propane	0.3	0.2	0.1	0.5	0.6	0.9
Propene	3.3	3.8	1.6	2.3	4.2	3.3
iso-Butane	0.04	0.04	+	0.2	0.05	0.02
n-Butane	0.03	0.04	0.01	0.2	0.04	0.03
trans-2-Butene	0.1	0.2	0.1	0.3	0.2	0.2
1-Butene	0.2	0.6	0.4	0.3	0.3	0.7
iso-Butene	1.2	1.4	0.4	0.2	1.4	0.9
cis-2-Butene	0.1	0.2	0.1	0.2	0.1	0.1
1,3-Butadiene	0.02	0.1	+	0.2	0.05	0.03
1-Pentene	+	0.04	0.01	0.1	0.03	0.02
Other compounds	0.3	0.3	1.5	0.6	0.1	1.3

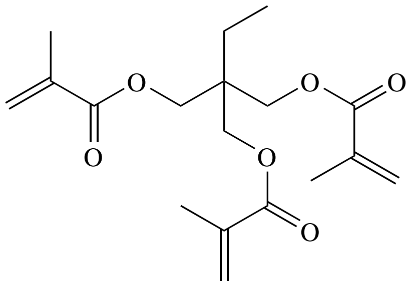
Table 24.6 Liquids of the pyrolysis of pure and filled poly (methylmethacrylate) (PMMA) (wt% in relation to the organic input; + = traces, − = not detectable, temperature 450°C)

Plant Fillers (wt%)	Lab 71 SiO_2	Lab 62 SiO_2	Lab	Lab 67 ATH	Pilot 71 SiO_2	Pilot
Dimethylether	0.02	0.03	−	−	0.03	−
Methanol	0.01	0.01	0.2	8.4	0.02	0.01
Acetone	+	+	+	1.3	0.5	+
Methylacrylate	0.1	0.2	+	1.0	0.2	0.03
Methylpropionate	0.1	0.1	0.02	1.2	0.1	0.1
Methylisobutyrate	0.2	0.2	0.05	1.7	0.4	0.2
Ethylacrylate	0.2	0.1			0.1	
Methylmethacrylate	92	96	99	60.8	92	98
Cyclopentanone	+	+	+	22.4	0.02	+
2-Methylbutanoic acid methylester	0.03	+	+	1.0	0.1	+
Methacrylic acid	1.0	0.9	0.1	11.9	0.9	+
Butylacrylate	+	+	−	1.2	+	0.02
Phenol	−	−	−	+	0.2	−
Dimethylethylcyclohexene	1.0	0.9	0.1	+	0.9	+
Trimethoxymethylbenzene	0.1	+	−	+	+	−
Dodecanoic methyl ester	0.1	+	−	+	0.1	−
Terephthalic dimethyl ester	0.1	+	+	+	0.2	+
TRIM-H_2	−	+	−	−	0.02	−
TRIM	−	+	−	−	0.2	−
Water	1.3	0.6	0.4	1.2	0.8	0.8
Other compounds	4.4	1.9	0.2	7.9	4.2	0.8

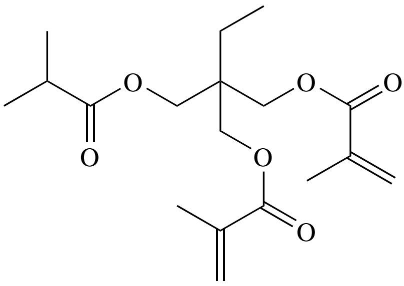
The liquids contain mainly the monomer MMA in the range 92–99% for silica-filled PMMA and 58% for ATH-filled PMMA. Other liquid compounds in higher concentration are methacrylic acid and dimethylethylcyclohexene. After distillation, the MMA is pure enough for new polymerization. Filled PMMA yielded more by-products such as long-chain methyl esters and Diels–Alder products. The reason for their formation could be the higher residence time and some catalytic effect of the filler.

The excellent heat transfer in a fluidized bed, the low residence time of the monomers, and the low temperature gradient in the bed is a reason so few side products and so little carbon black is formed.

The highly filled PMMA (71% SiO_2) was cross-linked. For the cross-linking trimethyl-(3-propane)trimethacrylate (TRIM) and trimethylol-(3-propane)-isobutyrate-dimethacrylate (TRIM-H2) were used. These compounds were detected in small amounts up to 0.2 wt% in the liquid fraction.



TRIM: Trimethylol-(3-propane)-
trimethacrylate



TRIM-H2: Trimethylol-(3-propane)-
isobutyrate-dimethacrylate

They also reduce monomer recovery as well as recovery of other comonomers during pyrolysis because of the disturbance of the step-by-step radical degradation process [29].

It was found that the pyrolysis of the ATH-filled PMMA yielded only 58% MMA monomer instead of 97% found with a pure PMMA feed. Hydrolysis products from MMA such as methacrylic acid, methanol and isobutyric acid were found to be the other main by-products from the thermal decomposition of this composite material. Pyrolysis-GC-MS experiments showed that the yield of the monomer MMA can be increased to 65 wt% by lowering the process temperature to 400°C. Water released during pyrolysis of ATH and the chemical starter/stabilizer in the composite material were found to be responsible for the low monomer yield. The high amount of the aluminium components in this material has almost no catalytic influence on the hydrolysis reaction because the same result was found if steam was used as fluidizing medium instead of nitrogen.

For the pyrolysis, an energy balance was made, too. Between 0.92 and 1.50 kW h kg^{-1} PMMA were needed for heating up the fluidizing gas and for delivering the degradation energy.

The following values were measured for the pilot plant: melting and depolymerization energy (450°C) of pure PMMA: 0.60 kW h kg^{-1}; heating up the fluidizing gas on pyrolysis temperature 0.20–0.40 kW h kg^{-1}, losses of heat by reactor isolation: 0.50 kW h kg^{-1}. The losses can be reduced in a technical plant.

4 PYROLYSIS OF POLYSTYRENE

Polystyrene (PS) is another polymer which can be degradated to the monomer. The required pyrolysis temperature is higher than in the case of PMMA as feedstock. The experiments were carried out in the fluidized-bed reactor (see Figure 24.1) between 515 and 540°C and with different fluidizing gas flows (Table 24.7). The molecular weight of the unfilled PS was 225 000.

The main product is in all cases the liquid. Up to 99.7% can be obtained. The gas fraction is very low and contains mainly methane, ethene, ethane, and propene. The gas content is higher with increasing pyrolysis temperature.

The oil content decreases with increasing pyrolysis temperature and decreasing residence time represented by the fluidizing gas flow rate. A higher gas flow rate gives a shorter residence time of the gases in the fluidized bed.

The whole product composition is shown in Table 24.8. The styrene content decrease with increasing temperature and reaches 74.85 wt% by 519°C and shorter residence time (gas flow rate 6.8 m^3/h). In a pilot plant experiment the pyrolysis temperature was 520°C resulting in a styrene content of 76.8%.

Other main liquid components are dimeric, trimeric, and other oligomeric styrene components. The content reaches 14 wt% of these oligomers. Other components formed by the pyrolysis of polystyrene are toluene, α-methylstyrene, diphenylethane/propane, and other aromatics. The styrene oligomers show secondary isomerization reactions. These make it difficult to pyrolyze them in a following step into higher amounts of styrene. Mainly, other aromatics are obtained by the degradation of the styrene oligomers. This means that the optimum recovery of styrene from PS is about 77 wt% in an uncatalyzed fluidized-bed process.

5 PYROLYSIS OF PTFE

Fluoropolymers are technical polymers with very special properties and applications. Their properties are derived mainly from the strong carbon–fluorine bond energy of 507 kJ mol^{-1}, compared with typical energies of 415 kJ mol^{-1} for C–H or 348 kJ mol^{-1} for C–C bonds. The most important fluoropolymer is polytetrafluoroethylene (PTFE). In

Table 24.7 Reaction parameters for the pyrolysis of PS and the product fractions obtained

Temperature (°C)	515	540	540	515
Gas flow (m^3/h)	3.7	3.7	6.8	6.8
Reaction time (h)	2.0	4.0	2.75	2.0
Throughput (kg/h)	1.25	1.30	1.10	1.05
Feed (kg)	2.5	5.2	3.0	2.1
Products				
Gas (wt%)	0.90	1.88	0.82	0.14
Oil (wt%)	98.87	97.75	99.04	99.71
Soot (wt%)	0.23	0.37	0.14	0.15

Table 24.8 Products formed by the pyrolysis of PS in a fluidized-bed reactor in wt%, + = traces

Temperature (°C) Flow gas (m^3/h)	515 3.7	540 3.7	540 6.8	515 6.8
Hydrogen	0.03	0.05	0.02	+
Methane	0.20	0.52	0.16	0.03
Ethene	0.28	0.63	0.35	0.06
Ethane	0.07	0.24	0.07	0.01
Propene	0.19	0.30	0.15	0.03
Propane	0.02	0.03	0.02	+
Butenes	0.09	0.09	0.06	+
Other aliphatics	0.19	0.34	0.10	0.05
Benzene	0.30	0.12	0.07	0.13
Toluene	2.23	2.91	2.31	2.01
Ethylbenzene	0.66	0.86	0.34	0.36
Styrene	71.94	68.73	73.41	74.85
α-Methylstyrene	2.33	3.19	2.22	2.30
Propylbenzene	0.03	0.06	0.03	0.01
Indene	0.39	0.56	0.50	0.32
Methylindene	0.14	0.08	0.02	0.04
Naphthene	0.06	0.11	0.02	0.05
Diphenylmethane	0.06	0.09	0.06	0.04
Diphenylethane	1.32	2.19	1.66	0.87
Diphenylpropane	1.97	3.07	2.46	1.36
Styrene dimer	6.64	4.28	6.11	4.85
Phenylnaphthaline	1.12	0.67	0.24	0.22
Higher styrene oligomers	4.75	9.08	7.25	9.25
Other components	4.76	1.43	2.23	3.01
Soot	0.23	0.37	0.14	0.15

order to improve the properties of PTFE it is often compounded with glass fibres, carbon fibres, coal/soot, bronze, steel, molybdenum sulphide or polymers such as polyimides or poly(phenylene sulphide).

Slow decomposition of PTFE occurs above the application temperature of 260°C. However, for a noticeable decomposition to occur, temperatures above 400°C are needed. The primary decomposition products are tetrafluoroethylene (TFE) and difluorocarbon diradicals (CF_2). Further products are formed by secondary reactions, depending on temperature, reaction pressure and reaction atmosphere. The typical main products are TFE, hexafluoropropene (HFP), cyclo-perfluorobutane (c-C_4F_8) and other fluorocarbons. Most of these substances are nontoxic, but highly toxic substances such as perfluoroisobutene or fluorophosgene are also formed under some reaction conditions.

Lewis and Naylor reported the first results on the pyrolysis of PTFE in 1947 [26]. At a temperature of 600°C yields of up to 97% TFE were obtained under vacuum (7×10^2 Pa). Under an atmospheric pressure of 1.103×10^5 Pa this yield dropped to only 16%, whereas the yields of HFP and c-C_4F_8 were increased.

Miesowicz [27] used a tube reactor for the depolymerization of PTFE under a nitrogen or steam atmosphere. We have carried out PTFE decomposition in a fluidized-bed reactor using nitrogen as fluidizing gas at different temperatures (Table 24.9).

Table 24.9 Main products of the pyrolysis of PTFE in a fluidized bed

Temperature (°C)	605	650	700
Duration (min)	81	91	55
Feed rate (g h^{-1})	90	83	104
Products (wt%)			
TFE	78.5	75.9	60.2
HFP	4.6	5.2	6.0
c-C_4F_8	3.7	5.9	16.1

Pyrolysis products were mainly TFE, c-C_4F_8, and HFP. Other fluorocarbons and carbon oxides were found only in traces. Reactions of decomposition products with the bed material increase from 5% at 605°C to 9% at 650°C and 13% at 700°C.

Other experiments were carried out with filled PTFE material, using steam as fluidizing gas. Fillers were carbon black, glass fibres, and bronze. Important parameters are listed in Table 24.10. In the first three experiments, the influence of the temperature was investigated, in the following were other fillers used.

The PTFE compounds were production wastes ground down to a diameter around 2 mm. The mass fraction of filler was 25 wt% for carbon black and glass fibres and 60 wt% for bronze. The length and diameter of the glass fibres are 30–70 μm and 10–20 μm, respectively. Carbon particles are 5–150 μm in diameter with an average of 20 μm. Bronze particles were of irregular shape and reached a maximum diameter of 60 μm. All experiments yielded gases, a water fraction, and solid residues as product fractions. Mass balances of all fractions and substances are given in Table 24.11. They are referred to PTFE input. The main products were TFE, HFP, c-C_4F_8, and fluoride (F^-).

The highest yields of monomers such as TFE, HFP and c-C_4F_8 of around 90 wt% were obtained at pyrolysis temperatures of between 645 and 600°C. Formation of oligomeric PTFE waxes can be explained by repolymerization of TFE in the cooling steps where the steam is condensed. The same phenomena occur during industrial production of TFE. Carbon black and glass fibres have nearly no influence on the product composition (compare Table 24.9). For the bronze-filled PTFE the yields of TFE, HFP and c-C_4F_8 were

Table 24.10 Parameters of the main pyrolysis experiments of filled PTFE pyrolysis

Fluidized bed temperature (°C) Compound material	505 Carbon black	545 Carbon black	600 Carbon black	600 Glass fibre	600 Bronze
Input (kg)	5.0	4.8	4.8	3.2	7.1
Duration (min)	145	130	155	225	180
Feed rate (kg h^{-1})	2.1	2.2	1.9	0.9	2.4
Water throughput (kg h^{-1})	3.5	5.5	3.3	3.3	2.9
Steam flow (m^3 h^{-1})	12.6	20.7	12.7	12.5	11.7
Auxiliary nitrogen flow (m^3 h^{-1})	0.6	1.1	0.8	0.8	0.8
Fluidized bed residence time (s)	0.6	0.4	0.6	0.6	0.6
Freeboard residence time (s)	2.4	1.4	2.3	2.4	2.5
Water/PTFE ratio	2.3	3.3	2.4	5.1	3.1

Table 24.11 Mass balance for the pyrolysis of different PTFE compounds

Fluidized bed temperature (°C) Compound material	505 Carbon black	545 Carbon black	600 Carbon black	600 Glass fibre	600 Bronze
Products[a] (wt%)					
Soot	4.7	+	0.18	1.0	+
Fluoride	2.4	6.7	5.9	5.1	16.0
Oligomeric PTFE	11.0	1.9	1.9	0.64	+
Carbon in CO and CO_2	0.51	2.0	1.8	1.4	3.5
Trifluoromethane	0.01	0.18	0.05	0.04	0.24
Difluoroethylene	0.01	0.07	0.07	0.03	0.47
Trifluoroethylene	0.01	0.09	0.05	0.03	0.14
Tetrafluoroethylene	71.0	68.0	71.0	75.0	51.0
Pentafluoroethane	+	+	0.05	0.03	+
Hexafluoropropene	6.3	7.8	7.5	6.6	7.3
Heptafluoropropane	+	+	+	+	+
Cyclo-octafluorobutane	3.9	12.0	11.0	9.9	21.0
Octafluorobutane	+	+	0.03	0.01	+
Hexafluorobutane	+	+	0.16	0.05	+
Not identified	0.42	1.0	0.26	0.12	0.72
TFE + c-C_4F_8	75.0	80.0	82.0	85.0	72.0
TFE + c-C_4F_8 + HFP	81.0	88.0	89.0	91.0	79.0

[a] Referring to PTFE input, + = traces

significantly reduced at the same temperature. There is a catalytic influence, mainly for the formation of fluoride (HF) by reaction with water. The amount of CO_2 and CO also increased.

6 CONCLUSIONS

It can be shown that it is possible to recover high amounts of monomers from special polymers by pyrolysis in a fluidized-bed process. Up to 98 wt% of MMA can be recovered from filled or coloured PMMA wastes. In the case of polystyrene the rate of recovered styrene is limited to about 77 wt%; the rest is oligomers. The high yields of TFE, HFP and c-C_4F_8 obtained from PTFE compounds in the experiments described show that fluidized-bed pyrolysis of pure PTFE or PTFE compounds is a feasible and interesting opportunity for the chemical recycling of this polymer.

In contrast to other recycling processes (mechanical recycling, vacuum pyrolysis), fluidized-bed pyrolysis has a number of advantages. Different kinds of plastics can be degradated into monomers in higher yields than with other methods and without needing to mill wastes into small particle sizes. The most important advantages are that monomers produced can be purified before repolymerization which allows production of a more valuable product and that the process allows continuous operation.

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Feedstock Recycling of PET

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1 INTRODUCTION

PET is one of the most versatile plastics in use today. It can be used for one-dimensional (fibers), two-dimensional (films) and three-dimensional (bottles) applications (Table 25.1). Two-thirds of the PET production is used for filament and staple fibers. These fibers are used for textiles, carpets, tyre cords, safety belts or tent squares. According to the broad range of applications for fibers their properties differ very strongly. Their molar weights range from 10 000 g/mol for low-pilling fibers to 42.000 g/mol for tire cord. Furthermore, these are long term applications and the task of recycling these materials will become urgent in the future. Especially collecting and sorting will be a challenge of increasing interest.

Films and bottles are mainly used as packaging materials in the food industry. Their amounts are increasing rapidly. PET bottles have replaced glass-bottles in many cases. These materials usually have a short lifetime and they are collected by several systems, depending on local conditions. In many countries bottles are separately collected, in Europe as bottles returned to the merchant, in Japan separately collected additional to the municipal waste (Table 25.2). Films used for food packaging are usually mixed with other plastics and wastes. For recycling, mechanical or manual separation is necessary. The effectiveness of recycling depends strongly on the waste management. Countries with large landfill possibilities show a smaller tendency for recycling than other countries. Collected plastics are not always recycled. Often they are used for thermal energy production. According to the wide range of applications PET consumption is increasing rapidly. From 2000 to 2010 a doubling of PET demand from 27.6 million tons to 56.0 million tons is estimated (Table 25.3). While in Europe and America the raise of the PET consumption is mainly maintained by PET bottle production, in Asia the expansion of PET use is correlated to a higher production of fibers, due to the shift of fiber production from the industrialized countries to low-wage countries (Table 25.4).

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Table 25.1 Demand of polyester worldwide according to application, and future prediction [1]

	1990	1995	2000	2005	2010
Fiber	8 900	11 700	18 800	24 200	33 300
PET resin (for bottles)	1 100	3 100	7 100	11 900	18 900
Film	1 000	1 100	1 400	1 400	1 700
Others	700	800	1 100	1 900	2 200
Total	11 700	16 700	28 400	39 400	56 100

Unit : thousand tons in 2000

Table 25.2 Recycling of PET bottles worldwide (2000) [2]

Continent	Country	Recovery	Consumption	Ratio
Asia	Japan	125	362	34.5
	Korea	39	85	46.0
	Taiwan	11.3	91	12.4
	China	6.3	363	1.7
	Indonesia	3.0	26	11.5
	Thailand		38	
	India	15	70	21.4
Oceania	Australia	28	88	31.8
	New Zealand	1.0	9	11.1
Europe	Austria	12	34	35.6
	Belgium	22	80.9	27.2
	Czech	0.1	8	1.2
	Denmark	0.3	5.2	5.8
	Ireland	0.5	10.8	4.6
	Finland	2	8.1	24.7
	France	55.5	254	21.8
	Germany	48	100	48.0
	Greece	1.1	34.5	2.9
	Hungary	0.2	9	2.2
	Iceland	1.0	1.0	100
	Italy	75	420	17.8
	The Netherlands	1.5	67	2.2
	Norway	1.5	4.8	31.2
	Poland	0.5	65	0.8
	Portugal	1.5	32	4.7
	Spain	8.9	159	5.6
	Sweden	7	19.4	36.1
	Switzerland	24	24	100
	Britain	7	227.5	3.1
	Turkey	7.3	35	20.8
North America	Canada	30	76	39.5
	Mexico	20	91	22.0
	USA	356	1 597	22.3
South America	Brazil	20	110	20.0
	Chile	1.0	16	6.2
Total		944.5	4 621	20.4

Table 25.3 Demand for polyester in different regions, and future prediction [1]

Area	1985	1990	1995	2000	2005	2010
North and South America	2 400	2 800	4 300	6 600	9 000	12 000
Europe, Middle and Near East, Africa	1 900	2 800	3 300	4 300	7 000	9 000
Asia	3 300	5 700	9 000	16 700	24 000	35 000
Total	7 600	11 300	16 600	27 600	40 000	56 000

Unit : thousand tons in 1999

Table 25.4 Consumption of PET resin for bottles worldwide, and future prediction [3]

Area	1995	2000	2005	2010
North and South America	1 500	3 000	4 800	6 400
Europe, Middle and Near East, Africa	900	2 400	4 200	6 800
Asia	600	1 600	3 000	5 600
Total	3 600	7 000	12 000	18 800

Unit : thousand tons in 2001

2 PHYSICAL RECYCLING (MECHANICAL RECYCLING)

The collection of PET bottles leads to a pure PET material. After cleaning from contamination and separation of paper labels and polyethylene caps the PET is used to make pellets or flakes. The starting PET material has to be free from polyvinylchloride, because released HCl catalyzes the saponification of PET.

This PET recyclate is used mainly in the nonfood sector, because of hygienic concerns. Small amounts of recyclate are used in bottle-to-bottle applications. In the sandwich process a core of recyclate is coated inside and outside by virgin PET. In this case up to 40% recyclate can be used.

Another possibility to use PET recyclate for food applications is the URRC process (United Resource Recovery Corporation). In this method the cleaned PET flakes are covered with concentrated caustic soda. After evaporation of the water in a rotary kiln the sodium hydroxide etches the surface of the PET at a temperature of more than 200°C. The resulting sodium terephthalate is removed by washing. The remaining flakes are used for the production of bottle preforms. Since 2000 several plants in Switzerland and Germany have been established [1].

3 SOLVOLYSIS (CHEMOLYSIS)

PET is manufactured in a two-step process. In the first step terephthalic acid (TPA) is esterified with ethylene glycol (EG) to form bis-2-hydroxyethylene terephthalate (BHET) and oligomers up to a molar mass of 2000 g/mol. Older plants use the transesterification of dimethylterephthalate (DMT) with EG, because for a long time it was difficult and

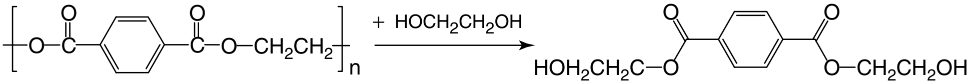


Figure 25.1 Glycolysis of PET

expensive to obtain the necessary purity for TPA. In the second step BHET is polycondensed at temperatures between 270 and 300°C and a vacuum of less than 100 kPa to remove the released EG.

Solvolysis (chemolysis) is defined as a technique which obtains the raw materials, such as TPA, DMT, EG monomers and oligomers as the reverse process of PET production by saponification or transesterification with water, methanol or EG. For the process of PET production raw materials of high purity are obligatory. Polycondensation is not a chain reaction, but a step reaction. Impurities can stop the polycondensation at low molar masses, so high-purity standards are also required for the solvolysis products. The choice of process depends on the starting material and the demand for solvolysis products.

3.1 GLYCOLYSIS

The most important solvolysis process today is the glycolysis of PET with EG, forming BHET as the simplest oligomer of PET. This reaction is performed at 190–200°C and 3.0–4.0 MPa using glycol as solvent as shown in Figure 25.1.

Since, during the production and the glycolysis process diethylene glycol is formed, diethylene glycol is accumulated in the BHET. This diethylene glycol has a negative influence on the properties of PET. Hence, the contribution of glycolysis BHET is limited to 20–30% in the production of new PET.

This process also generates higher oligomers as impurities in BHET. In many cases metal acetic acid salts are used as catalysts in this reaction. Baliga and Wong [5] examined the catalytic effect of acetic acid salts of zinc, lead, cobalt, and magnesium in order to raise the generation of BHET, and reported a catalytic effect in the order $Zn^{2+} > Pb^{2+} > Mn^{2+} > Co^{2+}$. This ranking is in agreement with the effect during polycondensation [6].

Transesterification performed at 170–200°C in the presence of aliphatic carboxylic acids, such as adipic acid, after the depolymerization of PET in EG and propylene glycol leads to unsaturated polyesters. These materials are used in foam production or for the production of polyurethanes and polyester polyol copolymers [7–9].

Since 2003, AIES Co., Ltd. operates a glycolysis and polycondensation plant (Figure 25.2) with a capacity of 27 500 t/y. After a sorting and cleaning process, which is used to separate PET from glass, metal, caps and paper, the PET is depolymerised by ethylene glycol in continuous stirring reactors at a temperature between 200 and 220°C. The resulting BHET is purified by filtration, adsorption on activated carbon, crystallization and vacuum distillation steps. After purification it is directly depolymerised to produce virgin PET.

3.2 METHANOLYSIS

Alcoholysis with methanol (Figure 25.3) is the most general method of manufacturing DMT and EG from waste PET. When PET is treated with an excess of methanol at

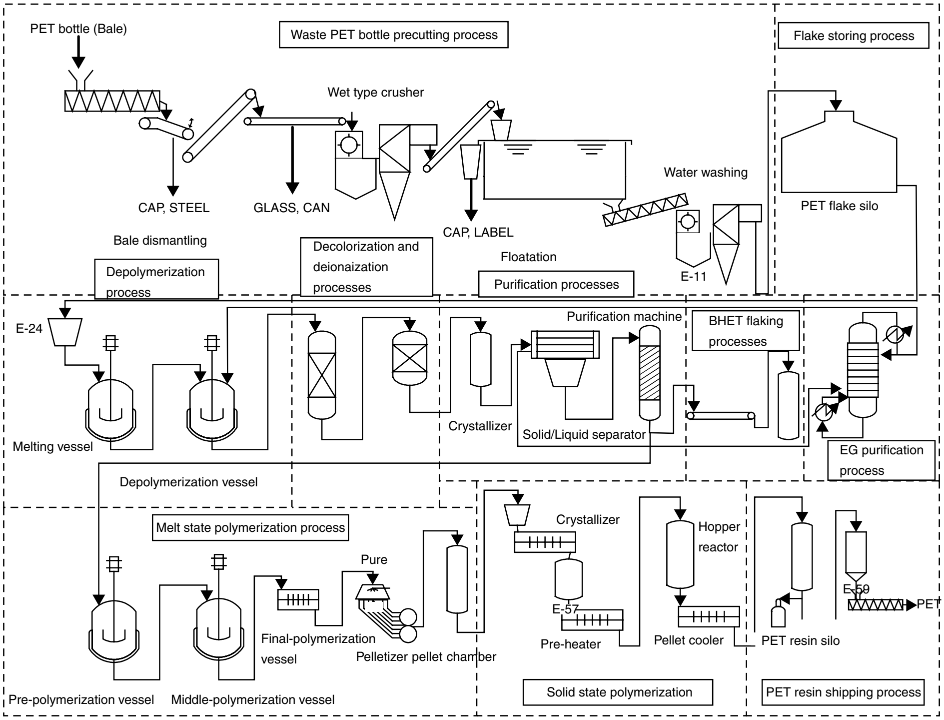


Figure 25.2 AIST glycolysis process

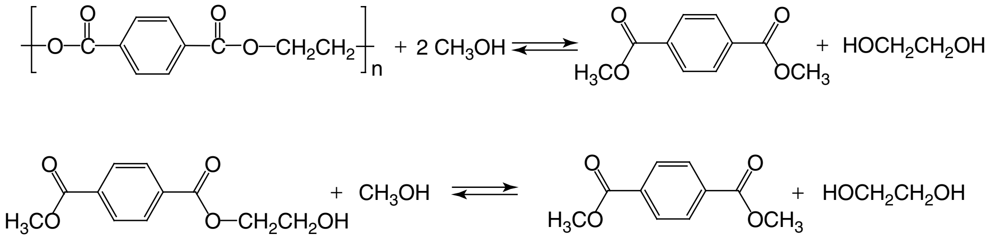


Figure 25.3 Methanolysis of PET

about 200°C and 2.5–4.5 MPa, DMT and EG are produced stoichiometrically. In the methanolysis the same catalysts are used as in glycolysis. The yield of DMT varies between 80 and 85%.

The methanolysis process was patented in 1957 by DuPont [10]. Since 1960 several processes have been developed [11, 12]. The methanolysis process makes use of several steps. At first the PET is dissolved and partially glycolyzed. By this first step the pressure of the subsequent methanolysis can be reduced. The resulting DMT and EG are purified by crystallization and distillation (Figure 25.4).

The methanolysis process can be performed batchwise (Figure 25.4) or continuously (Figure 25.5). In both cases the PET is molten. After that the melt is treated with methanol

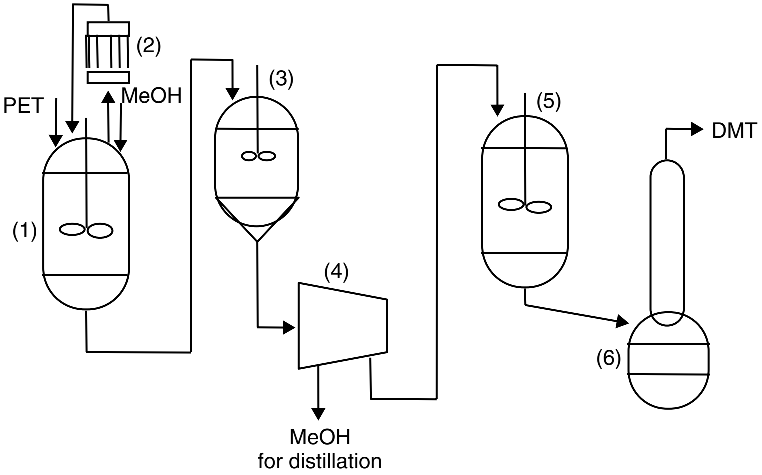


Figure 25.4 High-pressure methanolysis (batch process). (1) Autoclave; (2) reflux condenser; (3) crystallizer; (4) centrifuge; (5) melter; (6) distillation column

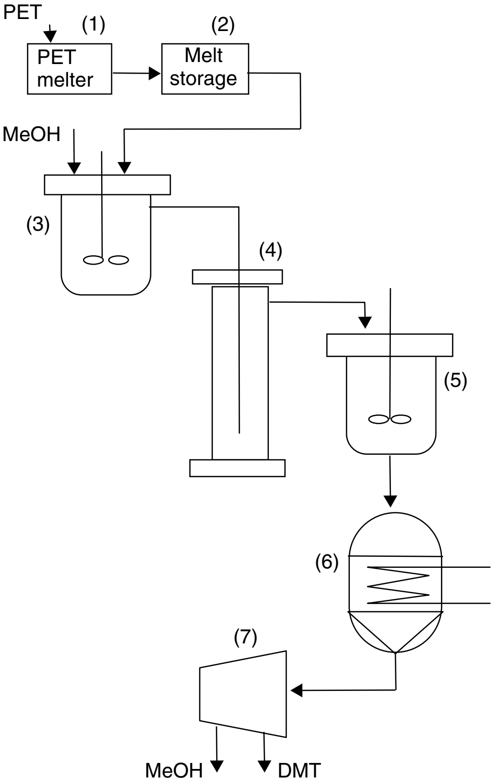


Figure 25.5 Continuous methanolysis. (1) Melter; (2) melt storage; (3) first autoclave; (4) second autoclave; (5) mixer; (6) crystallizer; (7) centrifuge

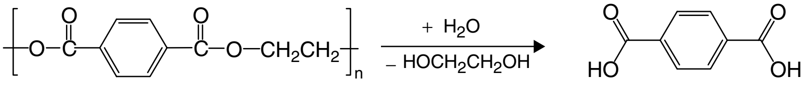


Figure 25.6 Hydrolysis of PET

under pressure and elevated temperature to obtain DMT. For purification of the DMT vacuum distillation columns and crystallizers are used. The purified DMT is usually used for the production of PET in the transesterification process.

Teijin Fiber Ltd introduced a process using the combination of glycolysis and methanolysis. In recent years, this technology has been developed to recycle PET bottles to obtain DMT and purified TPA. The products are used for the production of PET fibers and films. In 2003 Teijin Fiber Ltd. opened a methanolysis plant for the production of 50 000 t/y DMT.

3.3 HYDROLYSIS

Hydrolysis is the saponification of PET with water to TPA and EG as shown in Figure 25.6.

Campanelli *et al.* [13] obtained the initial hydrolysis rate constant of molten PET around 250°C from the concentrations of carboxyl groups, ester bonds and water after the reaction. The results are shown in Table 25.5, together with the results at 100°C [14] and 186°C [15] for solid PET.

Since the hydrolysis rate is small at low temperatures, it is important to raise the rate by increasing the temperature and pressure. Using a temperature higher than the melting point of PET at about 250°C leads to a better distribution of the reactants. At this temperature no catalyst is necessary. At 265°C the reaction leads to a complete conversion in 30 min, with yields for TPA of 97% and EG of 91%. The TPA produced (solubility in water at 270°C = 28.5 wt%) can be obtained by cooling down the solution and following crystallization, because of the almost insoluble character of TPA at room temperature.

3.3.1 Acid-catalyzed Hydrolysis

Pusztaseri [16] and Yoshioka *et al.* [17] describe an improved hydrolysis process using strong sulfuric acid with a good yield of TPA and EG. In this process, it is necessary to purify the EG from sulfuric acid.

Table 25.5 Initial hydrolysis rate constants for PET at different temperatures

Temperature (°C)	Rate constant (g PET mol^{-1} min^{-1})
100	3.0×10^{-7}
186	2.0×10^{-4}
250	0.244
265	0.352
280	0.487

Yoshioka *et al.* [18] describe a process using nitric acid at 70–100°C and atmospheric pressure. The resulting products are TPA and EG. The EG is simultaneously partially oxidized to oxalic acid by the nitric acid:

$$3\ HOCH_2CH_2OH + 8\ HNO_3 \rightarrow 3(COOH)_2 + 8\ NO + 10\ H_2O$$

The nitric acid acts as a catalyst. The NO formed in this reaction is regenerated by the addition of water and oxygen:

$$2\ NO + \frac{3}{2}O_2 + H_2O \rightarrow 2\ HNO_3$$

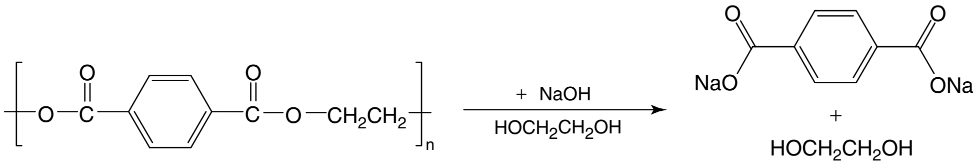
3.3.2 Base-catalyzed Hydrolysis

Base-catalyzed hydrolysis of PET can be used to obtain TPA and oxalic acid [19]. PET is completely hydrolyzed to TPA and EG at 250°C in concentrated aqueous NaOH solution. Then EG is converted to oxalic acid and CO_2 by the introduction of oxygen. Since the sodium terephthalate formed is stable to oxidation, the yield of TPA reaches 100%. EG is converted to oxalic acid by base-catalyzed oxidation with a maximum yield of 61%:

$$HOCH_2CH_2OH + 2\ O_2 \rightarrow (COOH)_2 + 2\ H_2O$$

Oxalic acid is a more valuable product than EG. The final product mixture is a colorless liquid, even when green PET bottles are used as feedstock, indicating that the green dyestuff is effectively oxidized.

Oku *et al.* [20] described an interesting process using a solution of NaOH in EG. PET is completely saponified by the base. The EG formed can be reused as new solvent. EG does not participate in this reaction directly as in the glycolysis process:



The UnPET-process of the United Resource Recovery Cooperation [21] uses a concentrated alkaline solution for the saponification of finely grounded PET. In this process a preceding cleaning treatment is not necessary. The alkaline/PET mixture is heated to 230–290°C in a rotary kiln. After vaporizing the water the PET is saponified. Also EG is vaporized and collected. Impurities such as paper and polyethylene are oxidized by air.

Base-catalyzed hydrolysis always leads to the TPA salt of the cation used. Releasing the salt by neutralization leads to large amounts of waste salts such as NaCl or Na_2SO_4 or a complicated treatment of the sodium terephthalate. Figure 25.7 shows the neutralization scheme for sodium terephthalate with CO_2 for the UnPET process. All components run in cycles. Just TPA, EG, CO_2 and water are released. This product treatment needs five

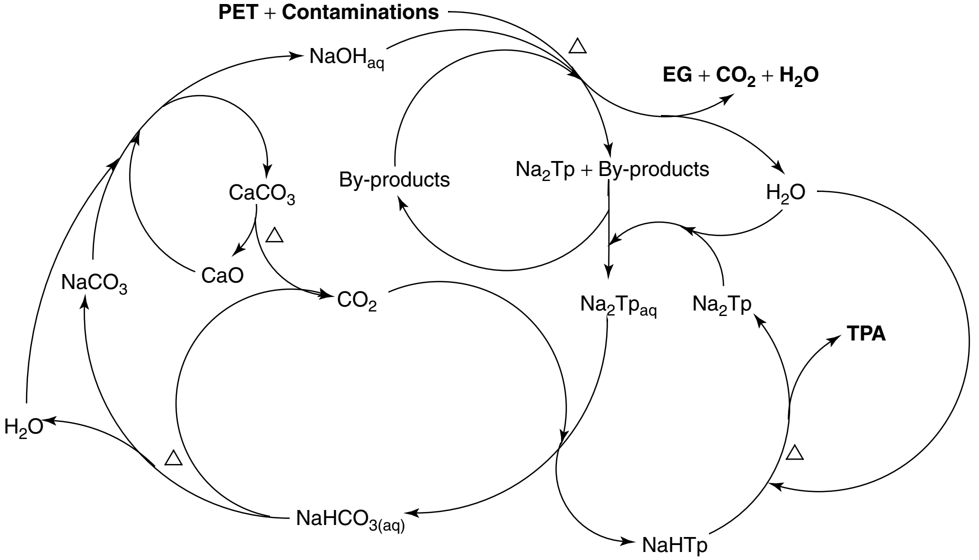


Figure 25.7 UnPET process and neutralization of Na_2Tp (sodium terephthalate) with CO_2 avoiding the production of salts

single steps and is especially energy intensive. After the saponification of the PET in a rotary kiln the products are dissolved in water. Insoluble products return to the rotary kiln. Na_2Tp is neutralized with CO_2 and NaHTp (monosodium terephthalate) precipitates. The NaHTp is heated in water, Na_2Tp dissolves and TPA remains as a precipitate. The solution of Na_2Tp is used to dissolve the products from the rotary kiln. After the neutralization process the $NaHCO_3$ solution is heated to vaporize water and CO_2 to form $NaCO_3$. The $NaCO_3$ is dissolved in water again and treated with CaO. The resulting NaOH solution is used for the saponification of the PET. The precipitated $CaCO_3$ is thermally decomposed to CaO and CO_2. The CaO is used for the recovery of NaOH and the CO_2 for the neutralization of the Na_2Tp solution.

3.4 OTHER PROCESSES

Fundamentally, solvolysis of PET is separated into methanolysis, glycolysis, and hydrolysis. Recently, many processes have been developed, which combine two or three of these techniques, such as the neutral hydrolysis process [22], hydrolysis by reactive extrusion [23], glycolysis–hydrolysis [24], etc.

4 PYROLYSIS AND OTHER HOT PROCESSES

Besides low temperature processes such as solvolysis and alkaline or acid saponification described above, which are usually accomplished in a liquid media at high pressure, there are also high-temperature processes from 300°C to more than 1000°C, at fairly low pressure. In this temperature range products leave the hot reactor zone in a gaseous state. High-boiling products can be condensed. Sublimable products such as TPA or benzoic acid can block pipes and cause corrosion. Especially TPA with a sublimation point of more than 400°C has to be considered as a severe problem in the construction of PET-using facilities. It is necessary to find a safe way to remove them from the gas stream by decomposition, if these products are unwanted or by appropriate filtration methods, if these products are wanted. A special advantage of these processes is that they are carried out under atmospheric pressure in simple reactors.

4.1 DECOMPOSITION MECHANISM OF PET

In contrast to polymerisates, polycondensates can not be depolymerized under inert conditions. Decomposition usually leads to the destruction of the chemical structure and the monomers. The thermal decomposition of PET starts at about 300°C in an inert atmosphere [25]. Between 320 and 380°C the main products are acetaldehyde, terephthalic acid, and carbon oxides under liquefaction conditions. The amounts of benzene, benzoic acid, acetophenone, C_1–C_4 hydrocarbons, and carbon oxides increase with the temperature. This led to the conclusion that a β-CH hydrogen transfer takes place as shown in Figure 25.8 [26]. Today the β-CH-hydrogen transfer is replaced as a main reaction in PET degradation by several analytic methods to be described in the following sections. The most important are thermogravimetry (TG) and differential scanning calorimetry (DSC) coupled with mass spectroscopy and infrared spectroscopy.

4.1.1 Analysis by Negative Chemical Ionization (NCI) Mass Spectrometry

For a long time electron ionization (EI) at 70 eV was the most used method for the identification of pyrolysis products. Unfortunately, in the case of oligomers EI leads to a strong fragmentation, and the molecular ions are difficult to observe. Negative ionization is a softer kind of ionization. The use of negatively charged molecular ions from methane or ammonia leads just to a small fragmentation and to a good observation of the molecular mass of the target molecule.

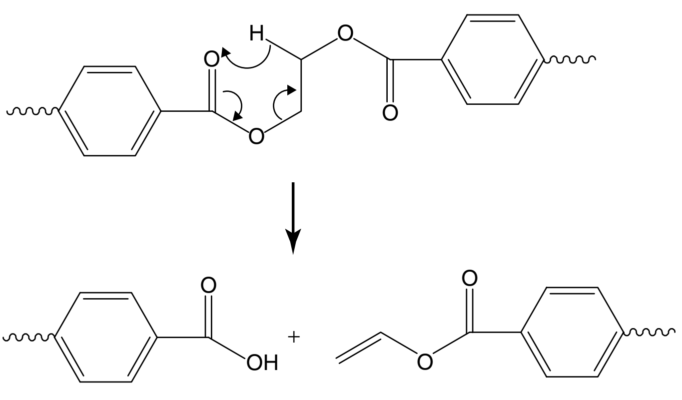


Figure 25.8 β-CH hydrogen transfer

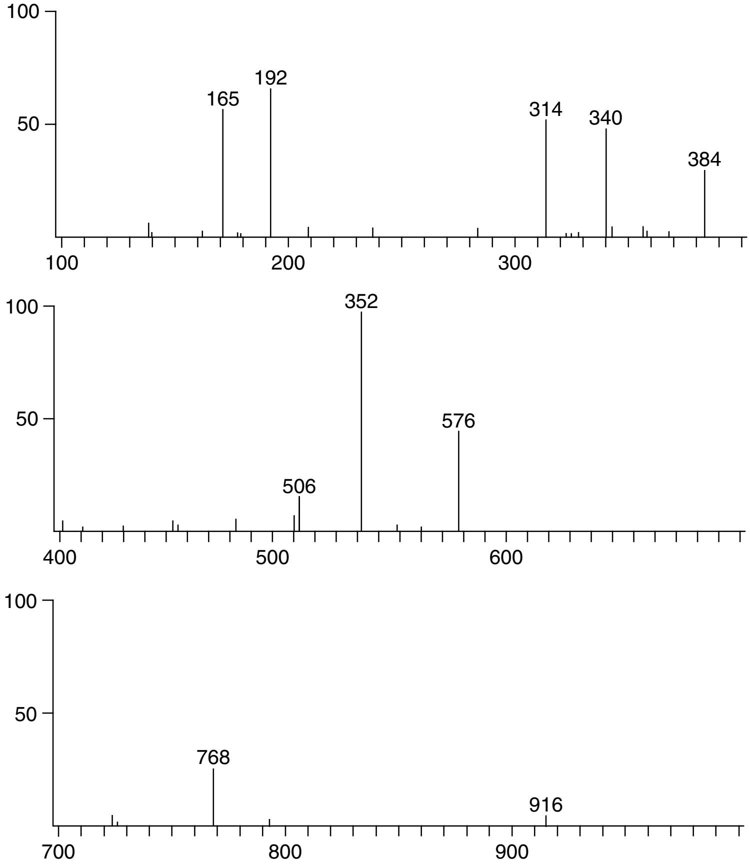


Figure 25.9 Negative chemical ionization mass spectrum of the pyrolysis products of PET at 350°C

Adams [27] and others analyzed the products of the thermal decomposition at 350°C by NCI at 10–15 eV. They found strong peaks for the dimer, trimer and tetramer of ethylene terephthalate (Figure 25.9). It was considered that an intermolecular backbiting process is favored at this temperature and that β-CH hydrogen transfer is not a dominant reaction, because the intensities of β-CH hydrogen transfer products were smaller than those of the oligomers. Montaudo *et al.* [28] found that cyclic oligomers are preferred. They are formed by ionic intramolecular exchange reactions. In a second step the cyclic oligomers decompose by a β-CH hydrogen transfer and form open-chain oligomers with olefin and carboxylic end-groups.

4.1.2 Analysis by Collision-induced Dissociation Tandem Mass Spectrometry (CID-MS/MS)

Montaudo *et al.* [28] used CID-MS/MS to obtain information on the original molecular structure from the cleavage pattern of the molecular ion. In this procedure the ion with

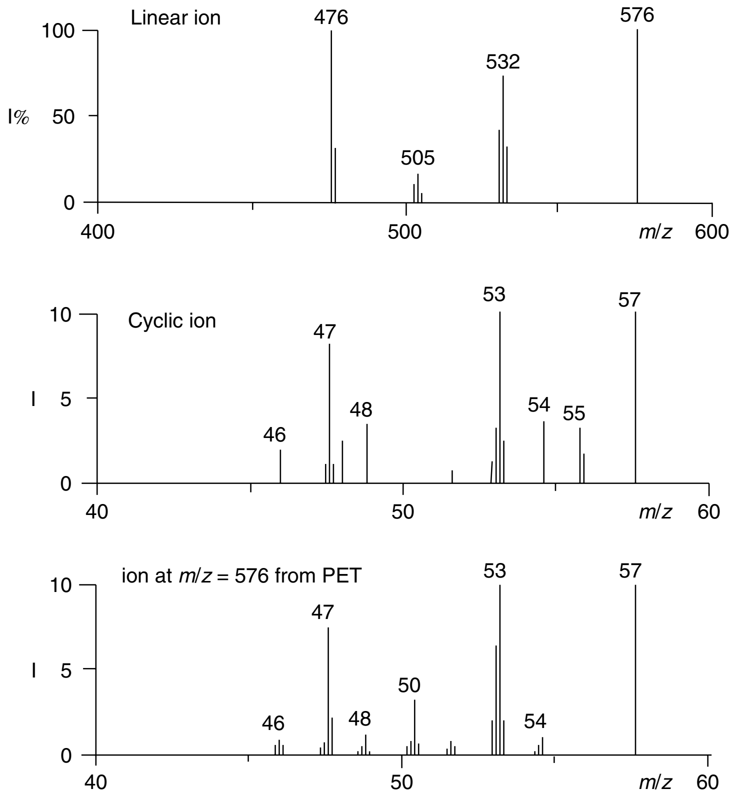


Figure 25.10 CID-MS/MS shows the existence of both linear and cyclic oligomers in the product spectrum of PET pyrolysis. (Reprinted from Polymer Degradation and Stability, Vol. 42, G. Montaudo *et al.*, pp 13–28, 1993, with permission from Elseveir)

m/*z* 576 was chosen to be analyzed by a second MS. The cyclic and the linear trimer were used as comparison in this experiment. According to Figure 25.10, both peaks of the cyclic trimer (*m*/*z* 460, 488, 546) and the linear trimer (*m*/*z* 505) were detected. This suggests that both cyclic and linear trimers are formed during the pyrolysis of PET.

4.1.3 Analysis by Fourier Transform Infrared Spectroscopy (FT-IR)

Holland [29] followed the thermal degradation of PET at 370°C in an argon atmosphere using FT-IR. This method allows one to follow the changes of several functional groups during the decomposition process. The absorbance of three wavenumbers corresponding to the C–H stretching vibration (2960 cm^{-1}), the carbonyl stretching vibration (1730 cm^{-1}), and the ester C–O stretching vibration (1250 cm^{-1}) decreased simultaneously (Figure 25.11) due to the degradation of the material. It was suggested that the main reaction is an intramolecular backbiting mechanism, leading to cyclic oligomers (Figure 25.12).

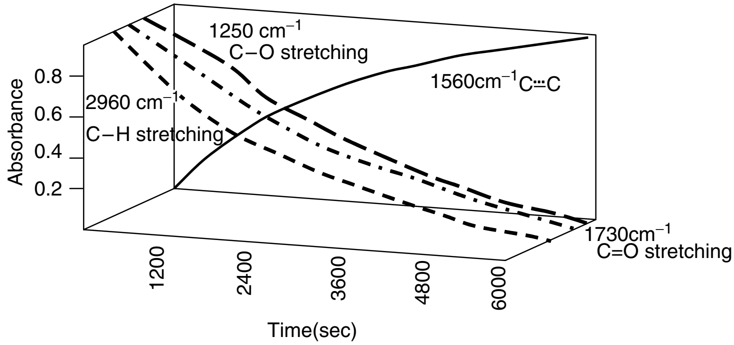


Figure 25.11 Time dependence of FT-IR spectra of PET pyrolysis at 370°C. (Reprinted from Polymer, Vol. 43, B. J. Holland *et al.*, 2002, pp. 1835–1847, with permission from Elsevier)

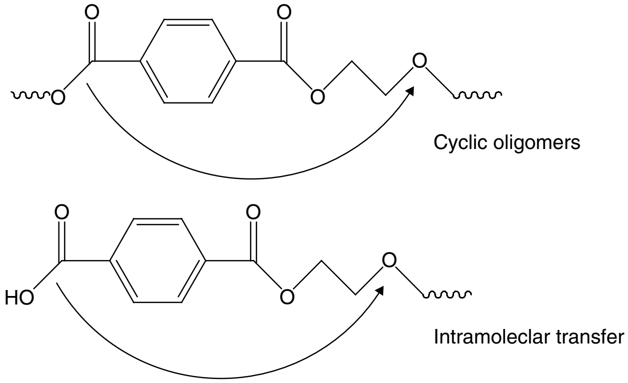


Figure 25.12 Intramolecular backbiting process for the formation of cyclic oligomers from PET pyrolysis. (Reprinted from Polymer, Vol. 43, B. J. Holland *et al.*, 2002, pp. 1835–1847, with permission from Elsevier)

4.2 PYROLYSIS PROCESSES

Pyrolysis can be performed for many different reactors. The product distribution varies markedly between the different reactor types and the reaction conditions, such as temperature, bed materials or catalyst. The aim of the pyrolysis is the reduction of wastes for landfilling and the production of fuels. Especially fuel oil with a high calorific value is an interesting product. Char can be used as a fuel, but is also seen as a precursor for other carboneous materials such as activated carbon. The best way to obtain these products is decarboxylation of the polymer. In this way carbon oxide-rich gas is produced.

4.2.1 Pyrolysis

Most work has focused on the use of fixed–and fluidized-bed reactors. Fixed-bed reactors are commonly used as batch reactors with the disadvantage of long ramp times. The choice of temperature and heating rate leads to strong differences in the product distribution.

Table 25.6 Comparison of different pyrolysis methods for PET

	Williams and Williams [30]	de Marco *et al.* [31]	Yoshioka *et al.* [32]
Reactor type	Fixed-bed	Fixed-bed	Fluidized-bed
Temperature	25°C/min → 700°C	500°C	510–730°C
Gas (%)	34.0	73.4	38–49
Oil (%) and organic solids	41.3	9.1	14–56
Char (%)	15.6	18.5	5–41
Total (%)	90.8	100	100

More than 40% oil can be achieved by heating the polymer at 25 K min^{-1} to a final temperature of 700°C [30]. The oil obtained is rich in aldehydes, ketones, carboxylic acids, alcohols and aromatic compounds; 34% gas and 16% char were also produced. Pyrolysis at 500°C for 30 min leads to 73% gases, 19% solids and 9% liquids [31]. In this case a large amount of sublimed products are observed, which can cause problems by blocking pipes. Table 25.6 shows a comparison of different pyrolysis methods for PET.

The fluidized-bed process shown in Figure 25.13 is a continuous waste treatment process [32]. The polymer can be fed directly into the fluidized bed. Volatile products leave the reactor with the gas stream. Solid products such as fillers and char can be removed by exchanging the bed material. In a temperature range between 510 and 730°C 38–49%

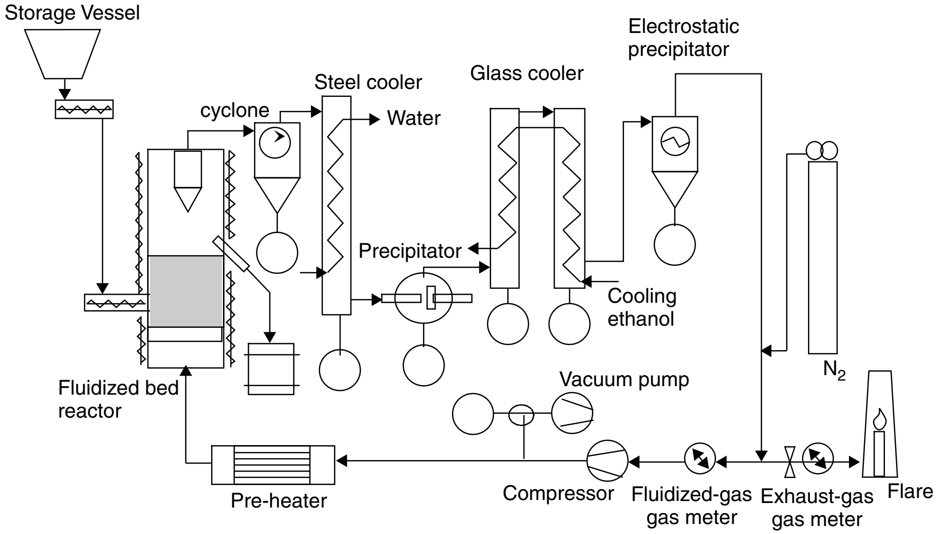


Figure 25.13 Fluidized-bed plant for the pyrolysis of PET with a feed rate of 1 kg PET/h [32]. (Reprinted from Polymer Degradation and Stability, Vol. 86, T. Yoshioka *et al.*, pp. 499, 2004, with permission from Elseveir)

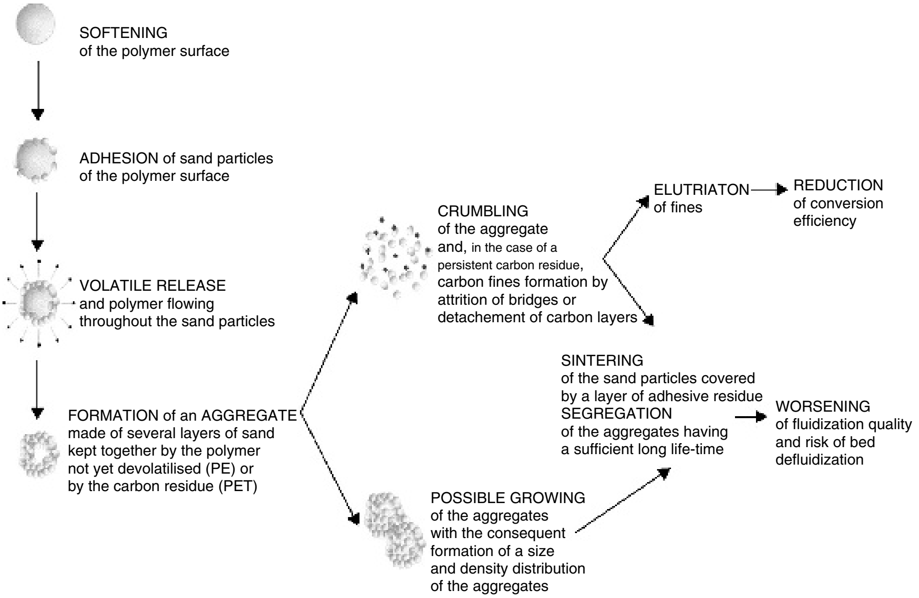


Figure 25.14 Mechanism of the defluidization during the pyrolysis of PE and PET [33] (Reprinted from Chemical Engineering Science, Vol. 55, U Arena *et al.*, 2000, pp. 2849, with permission from Elsevier)

gases (mainly carbon oxides) are produced. At low temperatures high amounts of benzoic acid and TPA are observed. Their yields decrease at higher temperatures in favor of carboneous residues in the reactor. Over the whole temperature range only a little oil was observed.

Indeed, PET shows an effect of defluidization, as shown in Figure 25.14 [33]. Sticky carbon residues formed by PET are covered by layers of sand. In this way larger particles are formed which can not be fluidized by the gas stream. The defluidization time can be increased by reducing the feed rate of the polymer and increasing the reactor temperature.

4.2.2 Catalytic Processes

In most cases the yield of oil produced during PET pyrolysis is very low. But some catalysts can increase the amount of oil and decrease the amount of char. Additionally they show a selectivity for special products.

Calcium hydroxide shows a strong selectivity for benzene [34]. In a steam atmosphere the PET is hydrolyzed and after that the resulting TPA is decarboxylated by the catalyst. At 700°C 36% of the PET can be converted into benzene. This corresponds to a benzene yield of 88% based on PET. Other main products are carbon oxides and char. Organic acids are not observed (Figure 25.15).

One possibility to reduce solid products and obtain hydrocarbons is the pyrolysis of PET together with PP in order to increase the hydrogen content [35]. Pyrolysis at 425°C over a TiO_2/SiO_2 catalyst leads to a high amount of oil with a high C_{18+} hydrocarbon content (Figure 25.16).

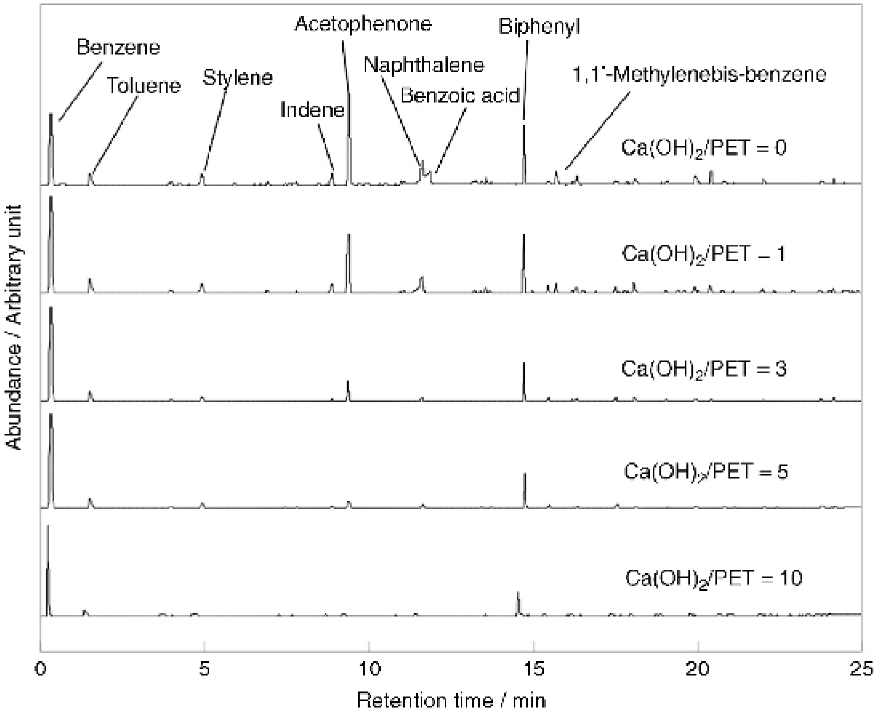


Figure 25.15 GC-MS chromatogram of the liquid products of PET pyrolysis with $Ca(OH)_2$ [34]. (Reproduced by permission of the Chemical Society of Japan)

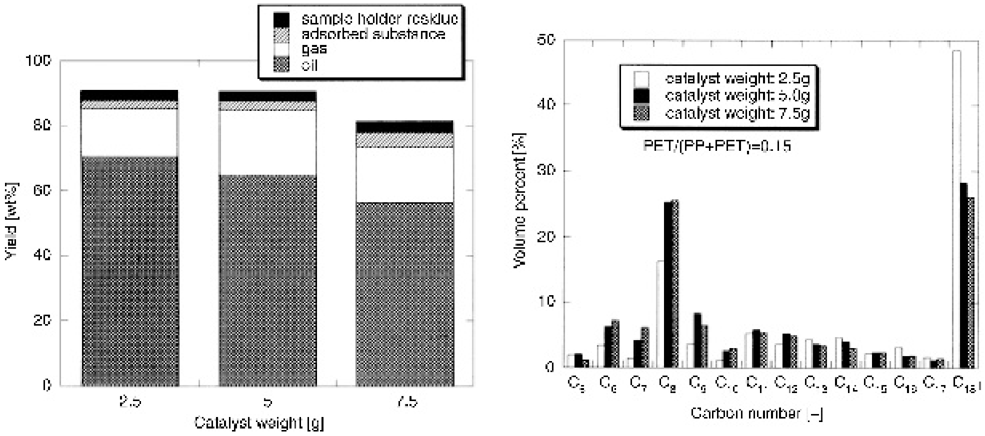


Figure 25.16 Comparison of the product distribution from a mixture of PP and PET over different weights of catalyst at 698 K and the carbon number fractions of the resulting oil [35]. (Reproduced with kind permission of Springer Science and Business Media)

Also copper(II) chloride shows a positive effect on the weight loss of PET during pyrolysis [36]. Between 450 and 500°C the amount of residue can be reduced by half. But the interaction between chloride and polymer leads to chloroorganic compounds, which makes the usage of this method difficult from the point of view of health and environment.

In different processes TPA is an undesired side product. It causes blocking and corrosion problems. It can be decomposed by several catalysts such as CaO/ZnO [37] at temperatures above 300°C. Resulting products are benzene, benzoic acid and carbon dioxide.

4.2.3 Carbonaceous Materials from PET

PET can also be used as a source of activated carbon. The properties of the products are dependent on the process parameters. Surface area, pore size distribution and adsorption behavior are influenced by the heating method and the atmosphere composition. A heating rate of 50 K h^{-1} with a final temperature of 500°C maintained for 2 h leads in different atmospheres to surface areas between 402 and 123 m^2/g [38]. A nitrogen atmosphere gives the best result, while carbon dioxide and steam show lower surface areas. Oxygenated atmospheres show a tendency to increase the pore size. In all these cases a yield of activated carbon of about 17% can be obtained related to PET. Higher temperatures under a nitrogen atmosphere lead to worse results. The surface area decreases from 242 m^2/g at 750°C to 14.7 m^2/g at 1200°C [39] during a stepwise heating process.

The activation of char, obtained from the pyrolysis of post-consumer PET bottles, with carbon dioxide at 925°C leads to highly porous materials. After a burn-off of 76% a BET area of 2500 m^2 is reached. This material shows similar or better hydrogen adsorption properties than high-tech carbon materials such as nanotubes [40]. It was possible to charge the carbon with 2.3 wt% hydrogen at −196°C. This fact opens the way for the use of this low-cost material as hydrogen storage.

4.2.4 Oxidative Pyrolysis and Combustion

Another way of using plastics as fuels is their direct combustion. The oxidative pyrolysis of PET has been investigated in several cases. Oxidative pyrolysis means that instead of an inert atmosphere an oxygen-containing gas was used. In this case pyrolysis can occur, if oxygen can not reach the particle surface due to efflux of volatiles or diffusional resistances at boundary layers, or if oxidative conditions do not affect the kinetics and mechanism of the pyrolytic processes [41].

Senneca *et al.* [41] investigated the oxidative pyrolysis of PET and other materials using a thermobalance. The samples were heated to 800°C at different heating rates and different oxygen contents of the atmosphere. Pyrolysis took place up to a temperature of 415–450°C. A higher oxygen concentration led to a shift of the weight loss to lower temperatures due to the overheating by the combustion of volatile products. At higher temperatures weight loss was generated by char combustion (Figure 25.17).

In fact the oxygen content of the atmosphere has little influence on the pyrolysis [42]. Of course there is more carbon dioxide produced, but the emission of the most products, hydrocarbons and aromatics, remains similar. The combustion reduces primarily the amount

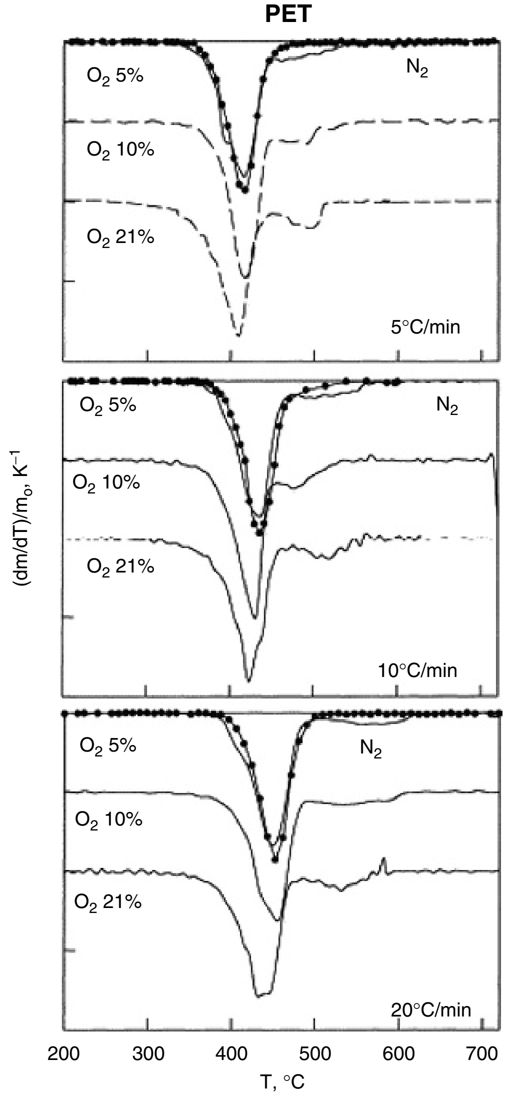


Figure 25.17 DTG curves of PET at different heating rates and oxygen concentrations [41]. (Reprinted from Journal Of Analytical And Applied Pyrolysis, Vol. 71, O. Senneca *et al.*, 2004, pp. 959, with permission from Elsevier)

of residue. However, at 850°C the emission of dibenzofuran increases drastically from 30 μg/g PET during pyrolysis to more than 5000 μg/g PET under oxidative conditions.

4.2.5 Hydrolysis

Another possibility is the saponification with steam to obtain monomers from PET, similar to the hydrolysis in liquid water under pressure. In this way TPA can be obtained, on

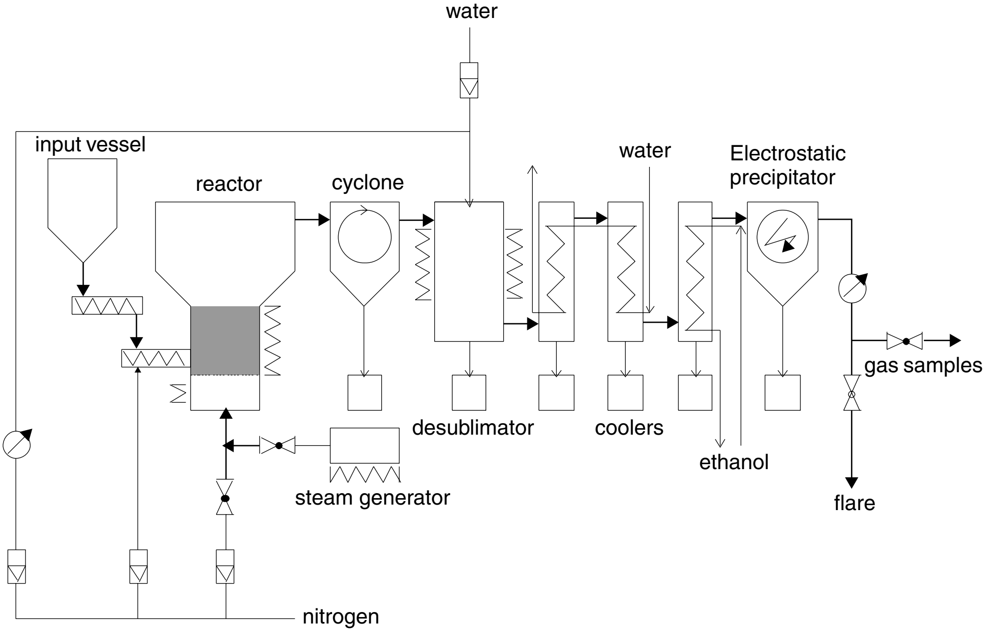


Figure 25.18 Fluidized-bed reactor for hydrolysis of PET [44]. (Reprinted from Polymer Degradation and Stability, Vol. 85, G. Grause *et al.*, pp. 571, 2004, with permission from Elseveir)

the contrary ethylene glycol is usually decomposed. The temperature range of this high-pressure hydrolysis is limited at the bottom by the sublimation point of TPA at 400°C and at the top to 500°C by increasing pyrolytic decomposition of the PET.

Masuda *et al.* [43] have shown that hydrolysis of PET in a fixed-bed reactor at 450°C in an atmosphere of 70% steam and 30% nitrogen led to a yield of 87% TPA and less than 1% carbonaceous residue.

Using a fluidized-bed reactor (Figure 25.18) the results are very similar [44]. For virgin PET with an optimal temperature of 450°C a yield of 72% TPA can be achieved. An additional 24% is fixed in two oligomers. The TPA yield using real bottle materials is still about 61%, and between 17 and 23% TPA remains as oligomers. Fe_2O_3 and NiO fillers in the material reduce the oligomer content rapidly. In this case a yield of 69% TPA can be obtained. Char production is negligible.

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PART VI

Asian Developments

Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels Edited by J. Scheirs and W. Kaminsky © 2006 John Wiley & Sons, Ltd ISBN: 0-470-02152-7

26

The Liquefaction of Plastic Containers and Packaging in Japan

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1 INTRODUCTION

A. Okuwaki and T. Yoshioka

1.1 BRIEF HISTORY OF PLASTICS LIQUEFACTION IN JAPAN

Feedstock recycling of waste plastic is an established method for recycling post-use plastics. Typically, waste plastics are recycled to naphtha, their raw material. This is

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because of the high crude oil price, crude oil price of West Texas Intermediate (WTI) is the highest in the oil market.

The liquefaction of waste plastics is not an entirely new technique, but the challenge to operate commercial plants has been tried in Germany by pyrolysis and hydrogenation. However, the former, operated by BASF was stopped in 1996, and the latter by Veba Oel GmbH in 1999 [1]. It is well known that the reason is not a technical problem, but an economic one; the cost is higher than those of competitive techniques, such as mechanical recycling or blast furnace application.

Economic conditions in Japan are quite similar to those in Germany. Although the feedstock recycling of waste plastics in household waste has progressed since 1997, economic problems still exist in collection, baling, transportation, and feedstock recycling, compared with incineration of household waste that is treated locally on site. The main reason why various feedstock technologies have been commercialized in Japan is that the Plastic Containers and Packaging Recycling Law (abbreviated as Plastic Recycling Law, below) came into effect in 2000. Especially, there is a long history of the liquefaction of mixed waste plastics, as shown in Table 26.1, supported by the Government [2].

The first generation supported by the Government started just after the oil crisis in the 1970s. However, it took a long time for commercialization of liquefaction; until environmental awareness developed in Japan on issues such as problems of the shortage of landfill site and excessive CO_2 emission by simple incineration of huge amount of waste plastics. The Plastic Recycling Law had a big impact.

However, several tens of millions of people's efforts sorting waste plastics in everyday life support the recycling system as well as the financial support of municipalities together with businesses that manufacture or use the containers and businesses that use the packaging.

This section describes the recycling law, the amount of recycled waste plastics, some operating information on three liquefaction processes, and the scope of liquefaction of post-use plastic containers and packaging in Japan.

1.2 THE LAW FOR PROMOTION OF SORTED COLLECTION AND RECYCLING OF CONTAINERS AND PACKAGING [3]

This is simply called the Containers and Packaging Recycling Law, applying to glass bottles, steel and aluminum cans, and plastic containers and packaging. In this law,

Table 26.1 Brief history of liquefaction of waste plastics in Japan

1972	Start of the development of liquefaction (PWMI)[a]
1973	Evaluation of melting, microwave heating, and fluidized bed processes. (PWMI)
1990	Test plant (400t/y) at Okegawa city (SMERI)[b]
1991	Liquefaction of industrial waste plastics (5,000t/y) at Aioi City (CJC)[c]
1995	Pilot plant test for containers and packaging plastics at Kawasaki city. (PWMI)
1997	Liquefaction (6,000t/y) at Niigata city supported by MITI.(Rekisei) Liquefaction (3,000t/y) at Tachikawa city supported by MHW.(JWRF)[d]

[a] Plastic Waste Management Institute;

[b] Organization for Small and Medium Enterprises and Region Innovation, Japan.;

[c] Clean Japan Center.;

[d] Japan Waste Research Foundation

the respective roles of, consumers, businesses, and municipalities, concerned with the recycling system for container and packaging waste are as follows.

Consumers must assume the role of separating waste on discharge, as well as suppressing the generation of waste through the rational use of containers and packaging as described above.

Businesses that manufacture or use the relevant containers and businesses that use the relevant packaging, bear the obligation to recycle. Businesses may also transfer the exercise of the obligation to recycle to the Japan Container and Package Recycling Association (JCPRA), the designated corporate body. Ultimately, they have to pay to recycle their plastic waste.

Municipalities must draw up selective collection plans and devise necessary measures for selective collection of container and packaging waste in their local areas. Thus, they have to collect the plastic waste and to bale it, removing foreign materials, on their budget.

The ratios of recycling for these materials are the highest in the world, especially for plastic containers such as PET bottles. The recycling of PET bottles was started earlier in the USA and EU, but the ratio has decreased in the USA, since enough economic support has not been obtained. However, in the EU, the recycling ratio has increased gradually, supported by the environmental awareness of European people. The increasing ratio in Japan is predominant, since the law became effective in 1997, preceding the other plastic containers and packaging [4].

1.3 FEEDSTOCK RECYCLING OF PLASTIC CONTAINERS AND PACKAGING

The amount and rate of plastic waste and resource recovery is shown in Table 26.2 [5]. Total plastic waste discharged reached 9900 000 t in 2002. The amount of municipal solid waste exceeded that of industrial waste in 2001 and the difference between them tends to increase. Although the amount of feedstock recycling reached 450 000 t in 2002, it still accounts for only 8.9% of municipal solid waste (MSW). Large amounts of waste plastics are treated by incineration with or without energy recovery both in MSW and industrial waste.

In the recycling of plastic containers and packaging, mechanical recycling occupies a major role. Mechanical recycling and feedstock recycling are authorized by the guidelines from JCPRA, but energy recycling is not permitted by the Plastic Recycling Law.

The minimum recycling ratio for each recycling method designated is shown in Table 26.3. A standard method for treatment of bales prepared by municipality is also given there and the ratio is calculated by the designated equation for each method.

All the bales prepared by municipalities according to the guidelines are controlled by JCPRA, and every enterprise permitted by JCPRA having various techniques is able to apply for the tender.

Mechanical recycling has a predominant bidding right over feedstock recycling, since it has an advantage with Life Cycle Analysis (LCA). Practically, however, the mechanical recycling of PE, PP, and PS (3P) needs careful separation by specific gravity separation processes, and only 45% of the minimum recycling degree is permitted. The remaining 55%, composed of PET material, PVC material and PVDC film and accompanying 3P are discarded as industrial waste, though they have been collected, baled, and transported to the recycling sites from various municipalities in Japan.

Table 26.2 Amount and rate of plastic waste and resource recovery in 2002

Total plastic waste discharge 9900 (100%)	Municipal solid waste 5080	Material recycling	260	Material recycling 1520 (15%)	Utilized plastic waste 5420 (55%)
		Liquefaction/gasification/Blast furnace	190	Liquefaction, Gasification, Blast furnace 250 (3%)	
		Densified-refuse-derived fuel	50	Densified-refuse-derived fuel 320 (3%)	
		Incineration with power generation	1,830	Incineration with power generation 2050 (21%)	
		Incineration with heat utilization facility	330	Incineration with heat utilization facility 1270 (13%)	
		Incineration without power generation or heat utilization facility	1,520	Incineration without power generation or heat utilization facility 1730 (18%)	Non-utilized plastic waste 4490 (45%)
		Landfilling	910	Landfilling 2760 (28%)	
	Industrial waste 4820	Material recycling	1,270		
		Liquefaction/blast furnace	70		
		Densified-refuse-derived fuel	270		
		Incineration with power generation	210		
		Incineration with heat utilization facility	950		
		Incineration without power generation or heat utilization facility	210		
		Landfilling	1,850		

[Unit; thousand tons]

Table 26.3 Guidelines for minimum recycling ratio for each method (wt%)

	Year	
Method	**2002**	**2004**
Mechanical	≥40	≥45*
Liquefaction	≥35	≥45
Blast furnace	≥50	≥75
Coke oven	≥50	≥85
Gasification**	≥50	≥65

* For Types I, II, III;
** energy base

Table 26.4 Large-scale feedstock recycling facilities of plastic containers and packaging in 2003

	Method	Company	Location	Municipal mixed plastic waste (t/yr)	Remarks
Mixed plastics	Blast furnace	JFE Steel	Kawasaki	40 000	
			Fukuyama	40 000	
		Kobe Steel	Kakogawa	10 000	
	Coke oven	Nippon Steel Corp.	Kimitsu	50 000	
			Nagoya	50 000	
			Muroran	20 000	
			Yahata	20 000	
	Gasification	Ube-Ebara	Ube	30 000	EUP
		JFE Steel	Chiba	20 000	Thermo select
		Showa Denko	Kawasaki	60 000	EUP
	Liquefaction	Sapporo Yuka	Sapporo	13 000	Toshiba
		Douo Yuka	Mikasa	6 000*	Kubota, March 2004.
		Rekisei Koyu	Niigata	6 000	PWMI

* Stopped.

Liquefaction, iron and steel industry applications, and gasification are authorized as the feedstock techniques. The capacities of recycling via these techniques are shown in Table 26.4.

The capacity of liquefaction is less than that of other techniques since its tender price has been the highest in these as shown in Section 5. However, liquefaction has come into effect in the Plastic Recycling Law, since the Niigata liquefaction plant has demonstrated for the first time in these feedstock techniques, that such mixed and complicated household waste plastics were recyclable as pyrolysis oil.

The liquefaction plant encountered a fire problem towards the end of 1996 under test operation, but it attained commercial operation in April 1998 due to the enthusiastic contribution by Niigata city, PWMI, MITI, and others. Then, the Sapporo Plastic Recycle

Co. Ltd (SPR) was founded to recycle the waste plastics collected in Sapporo city, where 13 500 t has been baled every year. This system has received excellent support by Sapporo city. However, only half of the baled plastics is used in the SPR liquefaction plant located just next to the baling plant due to the tender system controlled by JCPRA. Thus, the operating ratio of the SPR plant is not so high, and this also raises the treatment cost of waste plastics, as does the small scale. The remaining half is used for the iron and steel industry, far from Sapporo. The third liquefaction plant constructed at Mikasa city, Hokkaido stopped this March, since sufficient raw plastic waste could not be obtained.

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2 NIIGATA WASTE PLASTIC LIQUEFACTION PROCESS

A. Okuwaki, T. Yoshioka and M. Asai

The Plastic Wastes Management Institute (PWMI) has started to develop liquefaction technology using plastic containers and packaging, with cooperation among the companies operating original unit processes in the 1994 fiscal year, supported by MITI. As a result of this development, Rekisei Kouyu Co. Ltd started construction of a liquefaction plant that consists of pretreatment and liquefaction processes at Niigata city in 1995, and the test operation started in September 1996.

2.1 PLANT OUTLINE

The plant is shown in Figure 26.1. The official capacity reaches 6000 t/y for sorted bales. Rekisei Kouyu, commissioned by Niigata city, accepts the waste plastics separated domestically and collected in Niigata city (population ∼500 000). The waste plastic is pretreated to remove PET bottles and foreign material and to make fluff for liquefaction,

Figure 26.1 The Niigata liquefaction plant (Reproduced by permission of Plastic Waste Management Institute)

then liquefied by pyrolysis of dehydrochlorinated plastic melt. The product oil is used as fuel in the utilities of Niigata city.

2.2 PROCESS DESCRIPTION

The process is composed of a pretreatment process and a liquefaction process, using pyrolysis of melted dehydrochlorinated plastic, similar to other liquefaction processes.

2.2.1 Pretreatment Process

The separated plastic containers and packaging wastes are collected by 30 packer trucks, capable of carrying 700 kg/truck, and thrown in a pit. The collected waste in the pit is treated by a bag-breaking machine and iron is removed by a magnetic separator, PET bottles by hand picking, grinding, removal of foreign materials such as glass, sand, etc., a continuous feeder, and compacting machine to prepare fluff and stored in a silo. Separation of foreign materials is very important for stable operation, to minimize plugging in the plastic melt line. PET bottles are compacted to a bale of 18 kg.

2.2.2 Liquefaction Process

The flow sheet of this process is shown in Figure 26.2. Prepared plastic fluff is sent to a bag filter set on the top deck (Figure 26.1) by a pneumatic conveyer after treatment by a second magnetic separator and an aluminum separator. Then, the plastic fluff is sent to two series of dehydrochlorinators, specially designed, reciprocally rotating twin-screw-type extruders, through a vertical screw conveyer. This equipment is composed of a melter of plastic fluff and circulator of waste plastic melt. Each is a horizontal type

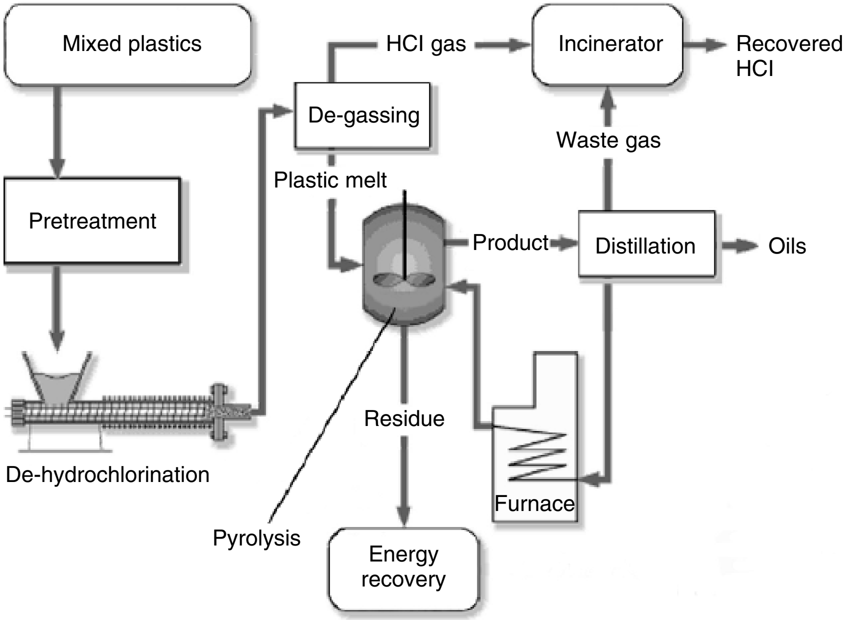

Figure 26.2 Process flow sheet of the Niigata liquefaction plant

Table 26.5 Composition of melted dehydrochlorinated plastic

Total chlorine	1.67 wt%
Inorganic chlorine	1.29 wt%
Organic chlorine	0.23 wt%
Softening point	>180°C
Specific gravity (25°C)	1.04

with an impeller. These are heated at 340°C by a jacket in which thermal medium is circulated.

The evolving gas, composed of HCl and light hydrocarbon, is incinerated at 1000°C or higher and quenched by a water spray to make a 10% HCl solution as well as to control dioxins. The composition of melted dehydrochlorinated plastic is shown in Table 26.5.

The total chlorine consists mainly of inorganic chlorides, which are formed by reaction of HCl gas from PVC and PVDC materials, and metallic materials in the fluff during the dehydrochlorination. This has been reported already from IKV [2]. The degree of dehydrochlorination was almost 95% [3].

The melted dehydrochlorinated plastic is then sent to a vertical tank pyrolyzer, fitted with a scraper for removing carbonaceous material on the reactor wall. Energy for pyrolysis is fed from a jacket heater and a high-temperature gas heater in a circulating furnace, and blown into the bottom of the reactor, holding the temperature at 420°C.

Table 26.6 Composition of plastic containers and packaging (wt%)

	Accepted	Plastic fluff
PE	32.34	21.15
PP	12.98	23.40
PS	18.33	37.40
PVC	7.66	5.23
PET	15,43	5.78
Other	12.77	7.04
Note	Dry basis	Dry basis

June 1996

The carbonaceous material and foreign materials for liquefaction are intermittently extracted from the bottom of the reactor with a part of the reaction mixture and cooled as residue. The pyrolysis gas emerging is carried to a distillation column and condensed as light, medium and heavy fractions.

The light oil from the top is a slightly lighter than kerosene, and the noncondensable light fraction is burned in a waste gas incinerator. The medium oil, corresponding to heavy oil A, is stored as product oil, and partly recycled to the pyrolyzer as a heat source, and heated in a tubular heater of the furnace at 420°C. Initially, plugging with carbonaceous material caused the plant to stop frequently to remove it. However, since October 2002 this problem has been resolved by addition of $Ca(OH)_2$ powder to the fluff. After this improvement, the operation is quite smooth.

The heavy fraction, solid at ambient temperature, has a slightly higher pour point, and requires heating equipment.

2.3 QUALITY OF WASTE PLASTICS

One example of waste plastics accepted is shown in Table 26.6. The composition of waste plastic fluff varies enormously and the accepted value is an average of three samples. PET and PVC materials are predominant, though PET bottles are removed by hand-picking in the pretreatment by Niigata city.

2.4 PROPERTIES OF OUTPUTS

2.4.1 Properties of Oils

The properties of light, medium, and heavy oils distilled from pyrolysis oil. are shown in Table 26.7.

The light oil originally contained relatively high amounts of chlorine, but recently the content has decreased to the 10–40 ppm level. Thus, a packing tower for removing hydrogen chloride from organic chlorine compounds is no longer in use, since the product oil now meets the quality requirement directly. Thus, after addition of $Ca(OH)_2$, the chlorine content dropped to 10 ppm level as shown in Table 26.7.

Table 26.7 Properties of light, medium and heavy oils distilled pyrolysis oil

Reactivity	Light oil		Medium oil		Heavy oil	
Date of sampling	'98/10	'04/3	'98/10	'03/12	'98/10	'03/12
Density (at 15°C) (g/cm^3)	0.8083	0.8019	0.8362	0.8473	0.8634	0.8926
Kinetic viscosity (15°C) (CSt)	0.64	0	1.74	2.712		
Viscosity (50°C) (CP)					44	
Pour point (°C)	<−50		0.0		52.5	
Moisture (ppm)	200	111		72		
Flash point (°C)	<−30		46.0		92.0	
High heating value (cal/g)	10000		10720		10880	
Elemental Analysis						
C (wt%)	88.5		86.5		86.7	
H (wt%)	11.3		11.8		12.1	
O (wt%)	<0.1		0.2		<0.1	
N (wt%)	0.085	0.092	0.12	0.114	0.11	0.112
S (wt%)	0.0012		0.0043	0.0251	0.006	0.0294
Total Cl (wt ppm)	550	11	45	13	43	65.6
Inorganic Cl (wt ppm)	380		15		17	
Organic Cl (wt ppm)	200		33		25	
Bromine value (Br-g/100 g)	42	35.0	25	13.5	16	8.9
Residual C (wt%)	<0.01		0.02		0.45	
Ash (wt%)	<0.01		0.01>		0.04	
pH	2.7		3.4		3.3	
Terephthalic acid (wt ppm)	<10		100		50	
Phthalic acid (wt ppm)	<10		110		70	
Benzoic acid (wt ppm)			1100			
Cetane number			46.0			
Oxidative stability (mgKOH/g)	93.8	0.09	1.90	0.05	0.49	
Type analysis						
Aromatic (wt%)	56.2		32.0			
Unsaturated (wt%)	26.3		27.0			
Saturated (wt%)	17.5		41.0			
Diene value (g/100g)	1.1	1.8	1.0	2.5	0.9	

The medium oil contains quite low sulfur, but has a slightly lower pour point compared with commercial heavy oil A. It is used as a boiler fuel for the sewage treatment plant in Niigata city. The heavy fraction contains quite low sulfur and is used in a paper and pulp factory in Niigata city. The distillation properties of the oils are shown in Figure 26.3.

2.4.2 Hydrochloric Acid

A chlorine balance in the raw fluff has been reported [2] and chlorine recovery had reached 94.95% as 9.6% hydrochloric acid. Recently, calcium hydroxide is added to the fluff as in the Sapporo Plastic Recycling Center to stabilize the operation. The recovery of HCl decreased greatly from 5.4 to 1.2%, as shown in the material balance in Figure 26.3 and is discarded after neutralization.

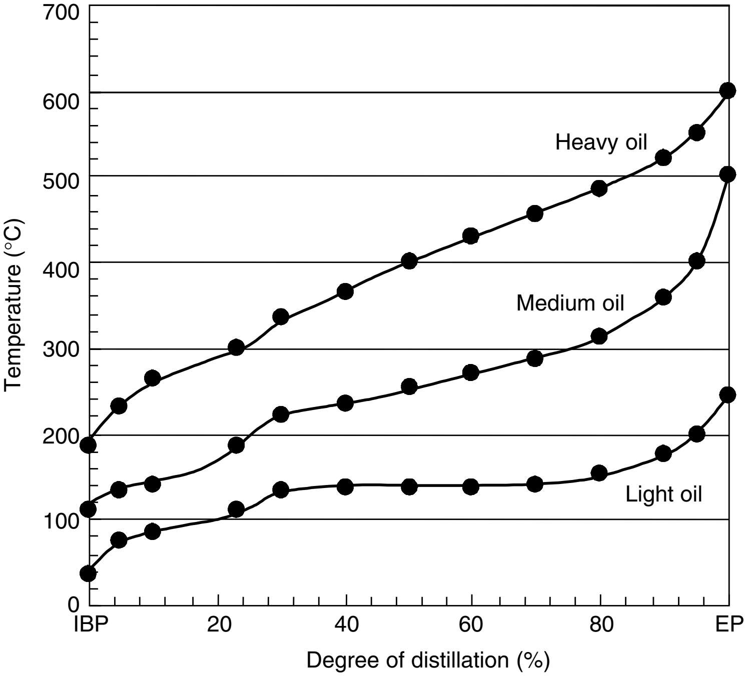

Figure 26.3 Distillation curves for light, medium, and heavy oils

2.4.3 *Pyrolysis Residue*

In Table 26.8, the properties of the residue are also shown. It is notable that aluminum arising from laminated material and foil, and terephthalic acid from PET materials are dominant. The chlorine in the raw fluff transferred some 2.4% or so to the residue [3].

2.5 MATERIAL BALANCE AND CONSUMPTION FIGURES

In Figure 26.4, total material balance is shown, including the pretreatment process, as at 22, October 1998. At that time, since the Plastic Recycling Law had not come into effect yet, large amounts of discharge of the pretreatment was observed. Inflammable residue indicates foreign material, and flammable residue corresponds to paper material.

Pyrolysis oil is produced at 380 kg from 1000 kg of waste plastics. The oil for sale externally amounts to 125 kg, with 255 kg self-consumed as process fuel. After operational, improvements these values improved remarkably, as shown in the following energy balance.

2.6 HEAT BALANCE

Figure 26.5 shows an energy balance on the same date as for the material balance. The product oil for external sale is 167 kg from 1000 kg of waste plastic fluff. The net weight

Table 26.8 Analytical data for residue

Reactivity	
Density (g/cm^3)	1.08 (at 25°C)
Viscosity (CP)	1900
Softening point (°C)	138.5
High heating value (cal/g)	8810
Ash (wt%)	10.3
Elemental analysis	
C (wt %)	75.0
H (wt %)	9.5
O (wt %)	5.0
N (wt %)	0.20
S (wt %)	0.043
Total Cl (wt ppm)	1.08
Inorganic Cl (wt ppm)	0.70
Organic Cl (wt ppm)	0.35
Terephthalic acid (wt ppm)	23 000
Phthalic acid (wt ppm)	<10
Pb (mg/kg)	410
Cd (mg/kg)	13
Cu (mg/kg)	270
Hg (mg/kg)	<0.05
As (mg/kg)	<1
Cr (mg/kg)	24
Sb (mg/kg)	<1
K (mg/kg)	1300
Na (mg/kg)	3700
Al (mg/kg)	16 400
Zn (mg/kg)	300
Fe (mg/kg)	3300

22 October 1998

of pyrolysis oil is 56 kg for sale, since 109 kg of fuel comprises 98 kg of pyrolysis oil and 11 kg of LPG is consumed. These values are greatly improved, as shown in the lower columns, to yield an increased amount of external sale.

The reason for the poor energy balance is that all the residue was landfilled at first and pyrolysis gas was not utilized at all, as well as due to the stoppages of the plant for cleaning the plugging. At present, the energy balance has improved remarkably due to the improvement of oil yield from 501 to 551 kg and the residue has begun to be used partly as fuel.

2.7 APPLICATION OF THE OUTPUTS

The product oil corresponding to heavy oil A, is used as fuel in the sewage plant of Niigata city as well as in a test application for a diesel engine in the Niigata Tekko Co. Ltd (applicable for power plant using diesel engines). The NO_x content in exhaust gas is of similar level to that for heavy oil A, and DXNs contents were 0.0055 ng TEQ/N m^3.

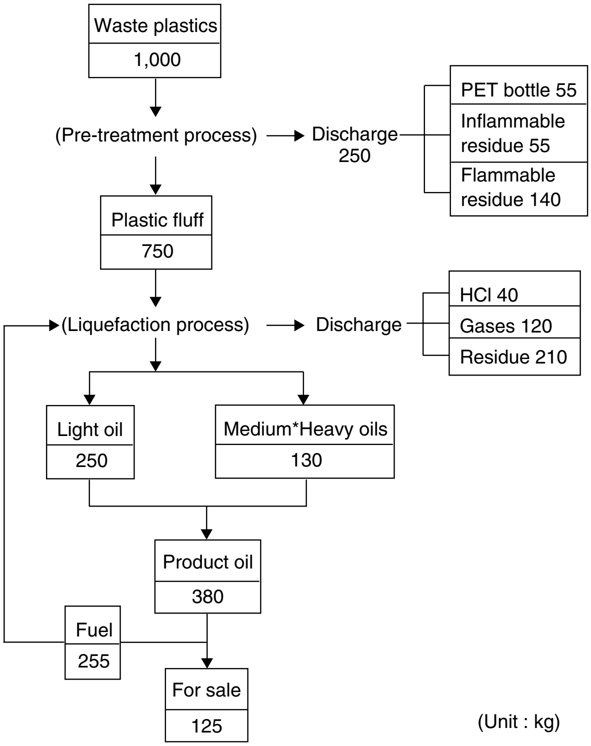

Figure 26.4 Material balance in the Niigata liquefaction plant

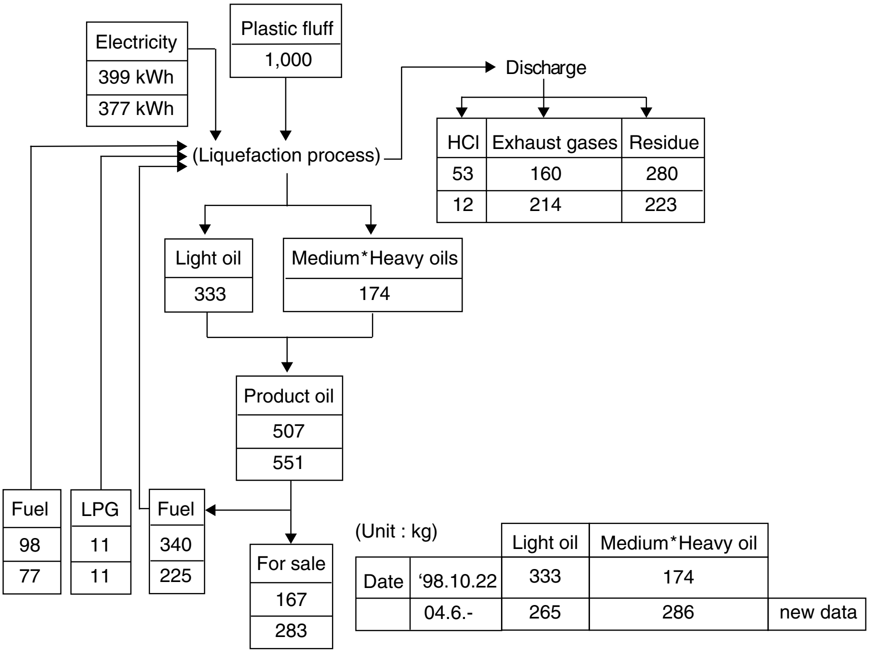

Figure 26.5 Initial and latest energy balances in the Niigata liquefaction plant

A residue used for analysis contained 47% oil. The residue has a higher heating value than that of coal and is suitable for energy recovery. However, it contains chlorine and heavy metals as shown in Table 26.8. Any exhaust gas and fly ash treatment must be carefully considered in its application. Recently, it has been used in a furnace, and has contributed to the improvement of heat balance, as described above.

2.8 ENVIRONMENTAL MEASUREMENT

Exhaust gases from the incinerator, thermal medium furnace, and absorption tower using light oil as fuel, have all met the regulation determined by the law and ordinance for air pollution. Wastewater from two effluents have also met the water pollution law and ordinance [3]. Naturally, the latest values meet these regulations [1].

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2. V. Lackner, Diploma Thesis at IKV, RWTH Aachen, 1991.
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3 SAPPORO WASTE PLASTICS LIQUEFACTION PROCESS

H. Tachibana and K. Wakai

3.1 PLANT OUTLINE

This waste plastics pyrolysis process has been developed by Toshiba Corporation, and a plant with 14 800 tons annual capacity of household waste plastics was constructed in Sapporo by Toshiba Corporation (Figure 26.6). The plant has been in operation since April 2000 by Sapporo Plastics Recycling Co., Ltd (hereinafter SPR) with investment by TERM Corporation, Toshiba Corporation, MITSUI & Co., Ltd. and Sapporo City Government.

The waste plastics utilized at the SPR plant are the household waste plastics specified by the Containers & Packaging Recycling Law and marked as ‘recyclable’ on the each of the products. The waste plastics are discharged at curbside by residents once per week, and collected, sorted, compacted in bale form by the local government, which then supplies the SPR plant.

The SPR plant handles of 43 tons/day on a two-line pretreatment section, 40 tons/day on a two-line pyrolysis and oil distillation section, and operates a 2000 kW × 2 line cogeneration facilities (Figure 26.7) that uses pyrolysis heavy oil as fuel. The pretreatment section is operated by two operators and three forklift operators for 10 hours per day, and the pyrolysis and oil distillation section is continuously operated for 24 hours per day,

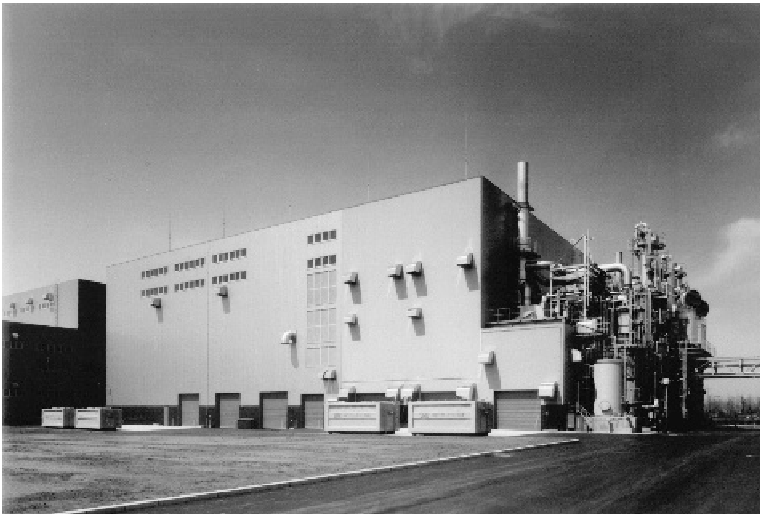

Figure 26.6 SPR plant view

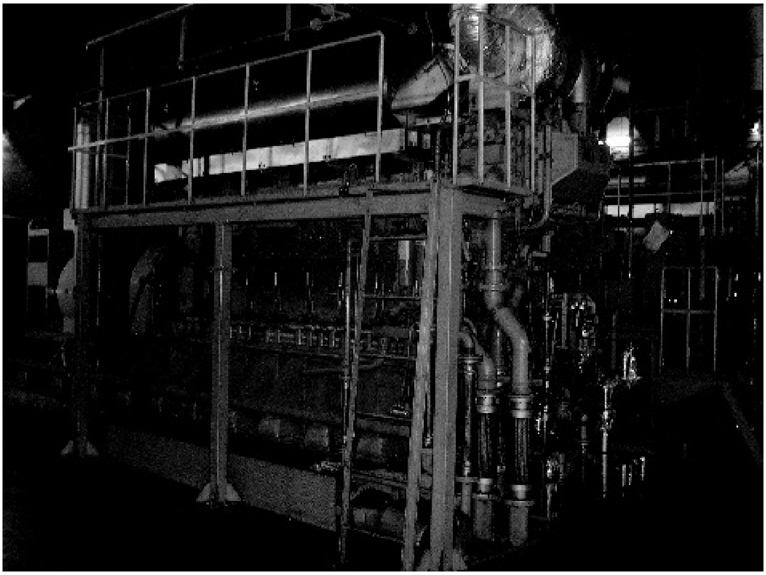

Figure 26.7 Cogeneration system

by four operators per shift. The Whole plant is automatically operated by a distributed control system (DCS). All of the products and by-products obtained from pyrolysis are utilized for feedstock recycling or energy recovery, except for hydrochloric acid obtained from PVC.

The system flow diagram of waste plastics discharged by Sapporo citizens to conversion to oils at SPR plant is shown in Figure 26.8.

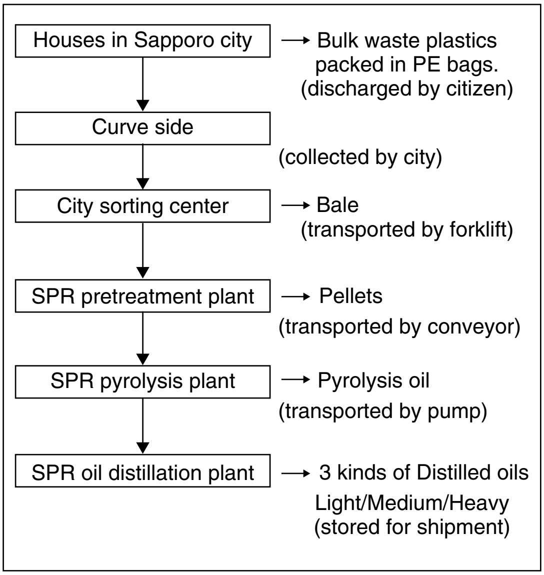

Figure 26.8 Sapporo system flow diagram

Figure 26.9 Waste plastics bale

3.2 PROCESS DESCRIPTION

The waste plastics bales (Figure 26.9) which are 1 × 1 × 1.3 m and weigh 200 kg are transported by forklift in the warehouse of the pretreatment section of the plant and weighed, stored and then continuously shredded, dried, sorted, and pelletized to 6 mm diameter × 20 mm length pellets that are stored in a pellet silo.

The flow sheet of the pyrolysis and oil distillation section is shown in Figure 26.10. The waste plastics pellets are conveyed from the pellet silo to the pellet hopper located on

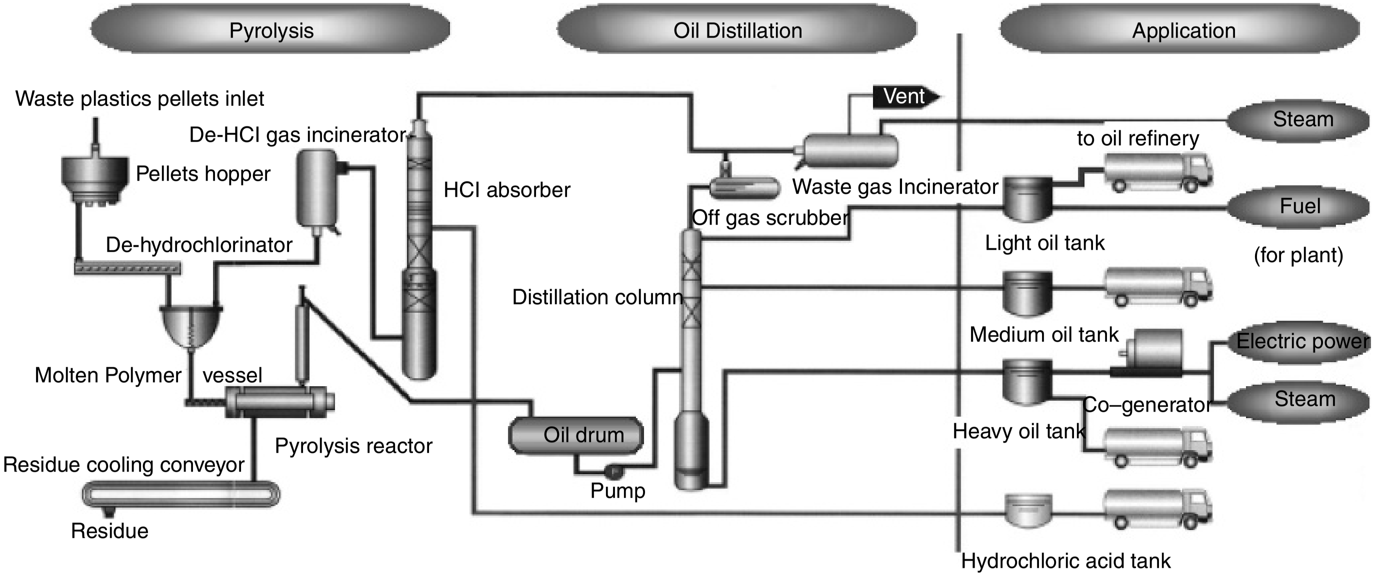

Figure 26.10 SPR process flow for pyrolysis and distillation

the top elevation of the pyrolysis plant and stored. Calcium hydroxide ($Ca(OH)_2$) powder is added to the pellets. Pellets containing $Ca(OH)_2$ are fed into the dehydrochlorinator, which has electric heaters on the cylinder and a specially designed single-axis screw. The waste plastics are melted and thermally degraded in the machine. PVC contained in the waste plastics, is dehydrochlorinated at 300–330°C and ~5 kPa overpressure. The dehydrochlorinated molten polymer and the evolved gases are moved into the molten polymer vessel.

The mixed gas, composed of hydrogen chloride and hydrocarbons, which are separated in the molten polymer vessel, goes into dehydrogen chloride gas incinerator and the hydrocarbons are burnt out at 1300°C. The incinerator and the operating conditions are designed and operated to prevent the generation of dioxin. The hydrocarbon-free exhaust gas from the incinerator is quenched and absorbed into water in the HCl absorber to give 20 wt% hydrochloric acid.

The dehydrochlorinated molten polymer in the molten polymer vessel is quantitatively fed into the pyrolysis reactor (Figure 26.11), which is of rotary kiln type. It has a hot air jacket and ceramic balls inside to prevent coking problems, as shown on the Figure 26.12. Thermal degradation is at 400°C and ~5 kPa overpressure.

The thermally degraded gas discharged from the reactor is liquefied by quenching and is stored in the oil drum. The residue generated in the reactor, which is a dry, fine particle size powder, is periodically discharged from the bottom of the reactor and transferred to the residue hopper through a cooling jacket chain-conveyer. One of the characteristics of the plant design is to move the materials by gravity flow from the waste plastics pellet hopper to residue discharge from the pyrolysis reactor.

The pyrolysis oil stored in the oil drum is fed into the distillation column with reboiler and separated into three fractions; light oil from the top, medium oil from the middle and heavy oil from the bottom of the column. These three types of oils are stored in separate oil tanks and sent to the furnaces and cogeneration system in the plant as fuel through piping, or loaded onto a tank lorry for shipment.

The off-gas, composed of hydrogen and C_1–C_4 hydrocarbons generated in the pyrolysis reactor, goes to waste gas incinerator, in which the hydrocarbons are burnt out and only inert gas is vented to atmosphere through the exhaust gas boiler, where the energy is recovered as steam.

3.3 QUALITY OF WASTE PLASTICS

Figure 26.13 shows the analytical results of waste plastics bales from Sapporo city, as sent to the SPR pyrolysis plant. The content of polyethylene (PE), polypropylene (PP) and polystyrene (PS) which are suitable for the pyrolysis is 71%. Although the consumption of polyvinylchloride (PVC) products is decreasing, PVC content of household waste plastics is still 3.1%. The content of polyvinylidenechloride (PVDC) is relatively high, because PVDC film is used as food wrap in Japan. Polyethyleneterephthalate (PET) bottles used for drinks and soy sauce are collected separately and recycled to feedstock recycling or mechanical recycling according to the Container and Packaging Recycling Low. However, PET waste from nonfood sources is collected together with other plastics and supplied to the SPR plant for pyrolysis treatment. The PET content of household waste plastics

Figure 26.11 Part of the pyrolysis plant

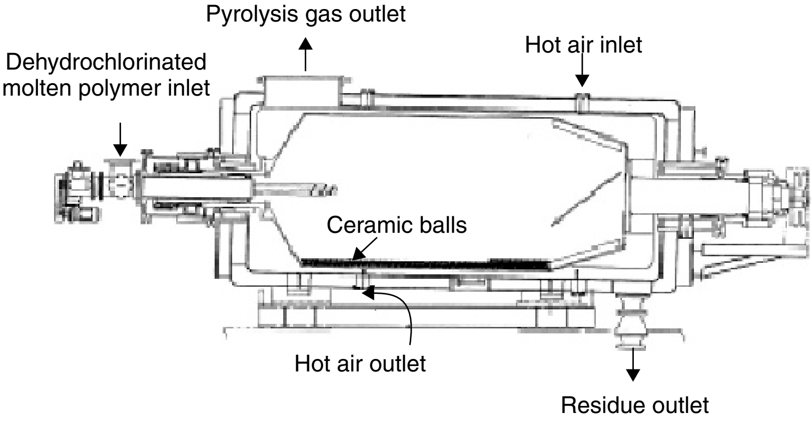

Figure 26.12 Pyrolysis reactor

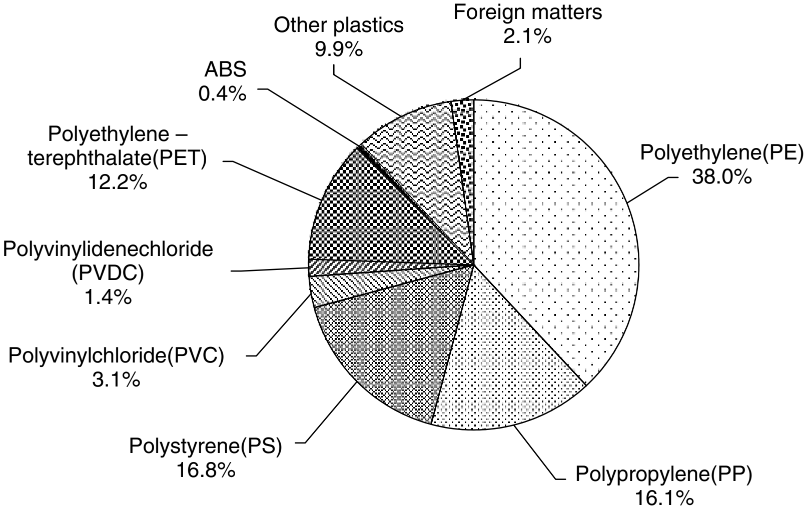

Figure 26.13 Composition of waste plastics bale

is more than 10% and is likely to increase. The amount of foreign matter is relatively low, since foreign materials are previously separated in the city's sorting facilities. The moisture content of the bale is approximately 6%.

3.4 PROPERTIES OF OUTPUTS

3.4.1 Properties of Oils

Table 26.9 shows the properties of pyrolysis oil and distilled oils. The pyrolysis oil is the fully condensed oil before distillation. The distillation characteristics of product oils are shown in Figure 26.14. Figure 26.15 shows the carbon number distribution (NP gram) of the pyrolysis oil and distilled oils. Table 26.10 shows the standard specifications TS Z 0025, that will apply to the waste plastics pyrolysis oils in energy recovery applications, effective in 2005 in Japan. The analysis results shown in Table 26.9 indicate that all distilled oils satisfy the specifications of Table 26.10.

The physical properties of distilled oils corresponded to a mixture of gasoline and kerosene for light oil, diesel oil for medium oil, and crude oil for heavy oil. Light oils contains a high concentration of C_9 aromatic compounds, primarily a styrene monomer and ethyl benzene. Styrene dimer and trimer are not found that much. Medium oils offer the best qualities for fuel application, because of higher flash points and lower pour points. Heavy oils are solid at ambient temperature and must be kept above 60°C for handling in liquid form. Pyrolysis oils contain much ash, including Cl, Ca, Si and other metals, which accumulate in heavy oil and are separated by a centrifuge in the plant. Medium and heavy oils indicate the high cetane index that is suitable for cogeneration fuel (a diesel-driven power generator). Compared with the standard petroleum oils used as fuel, the distilled oil has the same heating value and less sulfur content.

Table 26.9 Analytical results of pyrolysis and distilled oils

Property	Analytical method	Pyrolysis oil	Distilled light	Distil. medium	Distil. heavy
Appearance		Black solid	Yellow liquid	Amber liquid	Black solid
Density (15°C)	JIS K 2249	0.8545	0.8310	0.8377	0.8626
Flash point (°C)	JIS K 2265			92	117
Pour point (°C)	JIS K 2269	35.0	<−50	−25.0	47.5
Carbon residue (wt%)	JIS K 2270	4.18*			0.05
Carbon residue (10%) (wt%)	JIS K 2270		0.08	0.3	
Reactivity	JIS K 2252	Natural	Natural	Natural	Natural
Viscosity (30°C) ($mm^2\ s^{-1}$)	JIS K 2283		0.681	2.615	
Viscosity (50°C) ($mm^2\ s^{-1}$)	JIS K 2283	2.458			19.27
Water content (wt%)	JIS K 2275	0.005	0.031	0.02	0.0085
Ash content (wt%)	JIS K 2272	2.69*	<0.01	<0.01	0.04
Total heating value ($kJ\ kg^{-1}$)	JIS K 2279	44,750	43,750	44,290	45,800
Dry sludge ($mg\ 100\ ml^{-1}$)	Hot filter	6.9*	<0.01	0.02	0.2
Cetane index	JIS K 2280.0	42.3	7.9	48.6	56.6
Total chlorine ($mg\ kg^{-1}$)	TS Z 0025	3,800*	90	47	71
Inorganic chlorine ($mg\ kg^{-1}$)	TS Z 0025		<5	3	38
Organic chlorine ($mg\ kg^{-1}$)	(balance)		90	44	24
Terephthalic acid ($mg\ kg^{-1}$)	GC/MS	100		<10	300
Benzoic acid ($mg\ kg^{-1}$)	GC/MS	<100		42	100
C (wt%)	TCD				85.6
H (wt%)	TCD				12.6
O (wt%)	(balance)				1.58
N (wt%)	JIS K 2609	0.11	0.044	0.191	0.08
S (wt%)	JIS K 2541	0.01	<0.01	<0.01	0.04
Ca ($mg\ kg^{-1}$)	JIS K 0102 50.3	8,200*	17.0	2.2	82
Fe ($mg\ kg^{-1}$)	JIS K 0102 57.4	99	<0.2	7.3	33
Na ($mg\ kg^{-1}$)	AAS	200*	0.8	ND	2.8
Al ($mg\ kg^{-1}$)	JIS K 0102 58.4	150*	<0.2	ND	17
Si ($mg\ kg^{-1}$)	ICPAES	2,000*	<100	4.0	<50
Cu ($mg\ kg^{-1}$)	JIS K 0102 52.4	84*	0.6	0.1	2.3
Zn ($mg\ kg^{-1}$)	JIS K 0102 53.3	18*	0.6	ND	2.1
Mn ($mg\ kg^{-1}$)	JIS K 0102 56.4	13*	<0.2	ND	<0.5
T-Hg ($mg\ kg^{-1}$)	Govern.guide line	<0.01	<0.01	ND	<0.01
R-Hg ($mg\ kg^{-1}$)	Govern.guide line	ND	ND	ND	ND
Cd ($mg\ kg^{-1}$)	JIS K 0102 55.3	0.8	<0.2	ND	<0.5
Pb ($mg\ kg^{-1}$)	JIS K 0102 54.3	37*	<0.2	ND	2.6
T-Cr ($mg\ kg^{-1}$)	JIS K 0102 65.1.4	37*	<0.2	ND	8.2
Cr^{+6} ($mg\ kg^{-1}$)	JIS K 0102 65.2.4	<0.1	<0.1	ND	<0.1
As ($mg\ kg^{-1}$)	JIS K 0102 61.3	<0.1	<0.1	ND	<0.1
Aromatic (vol%)	UOP 501-71		70.7	27.5	
Saturated (vol%)	UOP 501-71		9.3	20.6	
Olefin (vol%)	UOP 501-71		20.0	51.9	

* The ash containing Ca,Cl,Si and other metals is transferred to heavy oil, and separated by centrifuge
ND: not detected

3.4.2 Hydrochloric Acid

Table 26.11 shows the analytical results of hydrochloric acid. The recovered hydrochloric acid shows a 20 wt% concentration and has a good appearance, however, to date it has not been used in a product application because Hg and As content do not meet to customer

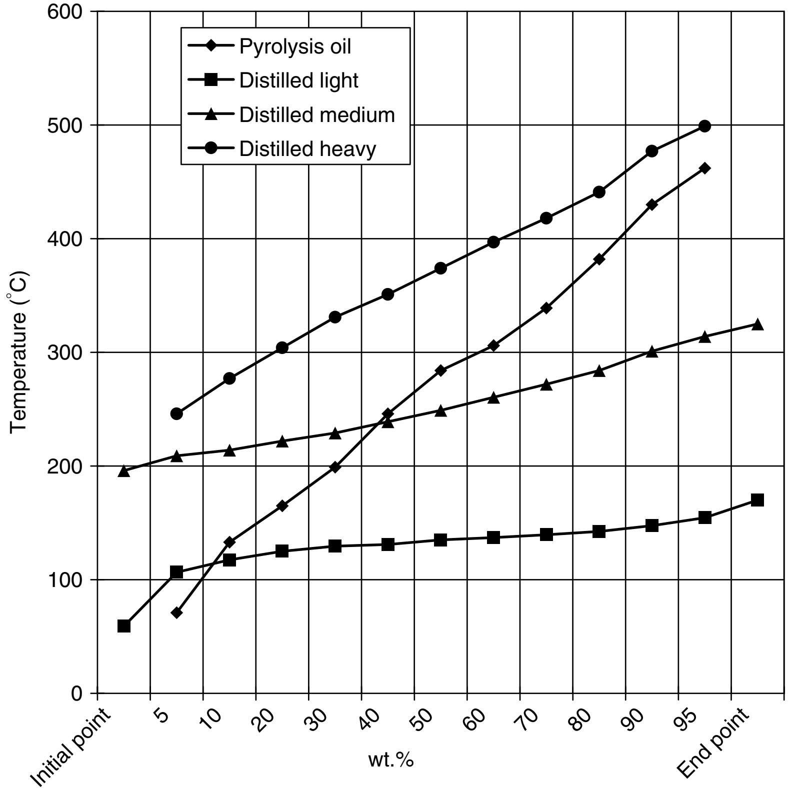

Figure 26.14 Distillation characteristics

specifications. Therefore, the recovered hydrochloric acid is now neutralized by NaOH in the plant and then transferred to city sewage treatment facilities together with other wastewater. Contaminated containers in the waste plastics may contribute the Hg, while As is thought to come from the additives and paints of the waste plastics.

3.4.3 Pyrolysis Residue

Table 26.12 shows the results of pyrolysis residue analysis. The pyrolysis residue is a fine dry powder, black in color. Total Cl and organic Cl contents are 1.4 and 0.1 wt%, respectively. Dioxin content is negligibly small. The higher content of Ca, inorganic Cl and oxygen is due to the presence of $CaCl_2$ and Ca salts of organic acids produced by the addition of $Ca(OH)_2$. SiO_2 and Al from raw materials contained in waste plastics. Although some heavy metals, such as Cd and Pb, are detected, dissolving test results are satisfactory. Therefore, landfill of the residue is possible. The high heating value and high C and H content indicate that fuel application is possible. Recently, the residue has been used as supplementary fuel for the city sludge incinerator at sewage treatment facilities, utilizing the higher heating value.

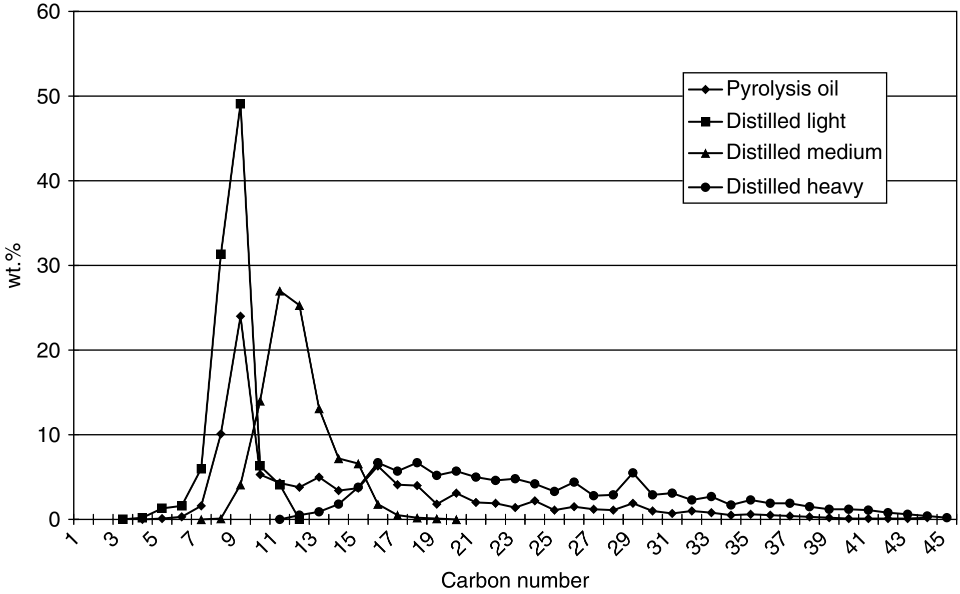

Figure 26.15 Carbon number distribution

Table 26.10 Standard specifications of the pyrolysis oils from waste plastics

Property	Method	Specifications		
		1st category	2nd category	3rd category
Flash point (°C)	JIS K 2265	<21	≥ 21 to <70	≥ 70 to <200
Ash content (wt%)	JIS K 2272	≤ 0.05	≤ 0.05	
S content (wt%)	JIS K 2541		≤ 0.2	
T-Cl content (wt ppm)	Specified*		≤ 100	
N content (wt%)	JIS K 2609		≤ 0.2	
Water content	Observation		No free water contained	

* Specified in TS Z 0025

3.5 MATERIAL BALANCE AND CONSUMPTION FIGURES

Table 26.13 shows the material balance of the pretreatment section based on 100 kg bales, the pyrolysis and distillation section based on 100 kg pellets, and whole plant based on 100 kg bales. The material balance of the whole plant is illustrated in Figure 26.16.

The material balance based on pellets shows a total oil yield of 62.0 wt% for household waste plastics, the composition of which is indicated in Figure 26.13. The light/medium /heavy ratio is 50/7/43(wt%). The yield of medium oil, most suitable for energy recovery, is low. Hydrochloric acid yield is only 1.0 wt%. PVC content in household waste plastics is only 3.1 wt%, and more than 50 wt% of HCl is fixed as $CaCl_2$ by $Ca(OH)_2$ addition. Pyrolysis residue generation was originally 9 wt% and has now increased to 17.5 wt% due to the increase in $CaCl_2$ and Ca salts of organic acids in the residue through the addition

Table 26.11 Analytical results for hydrochloric acid

Property	Analytical method	Analysis data	Specification*
Appearance		Transparent light yellow	
HCl concentration (wt%)	JIS K 8180	20.2	
Ignition residue (wt%)	Weighing after ignition	0.06	
SO_4^{2-} (wt%)	Turbidimetry	0.29	
SS ($mg\ l^{-1}$)	Filtration	89	
Oil ($mg\ l^{-1}$)	n-C_6 extraction	<1	<50
Fe ($mg\ l^{-1}$)	JIS K 0102-57.2	2.6	
Cd ($mg\ l^{-1}$)	JIS K 0102-55.2	<0.005	<0.01
Pb ($mg\ l^{-1}$)	JIS K 0102-54.1	0.032	<0.1
Cu ($mg\ l^{-1}$)	JIS K 0102-52.2	0.04	<0.2
Zn ($mg\ l^{-1}$)	JIS K 0102-53.1	0.25	<1.0
Ni ($mg\ l^{-1}$)	JIS K 0102-59.2	<1	<1.0
Mn ($mg\ l^{-1}$)	JIS K 0102-56.2	0.05	<1.0
T-Cr ($mg\ l^{-1}$)	JIS K 0102-65.1	0.02	<5.0
As ($mg\ l^{-1}$)	JIS K 0102-61.2	0.39	<0.01
T-Hg ($mg\ l^{-1}$)	Govern.guide line	0.018	<0.001
R-Hg ($mg\ l^{-1}$)	Govern.guide line	<0.0005	
Cr^{6+} ($mg\ l^{-1}$)	JIS K 0102 65.2.4	<0.04	

* Specification by HCl customer

of $Ca(OH)_2$. The off-gas comprises the volatile products under the operating conditions, composed of hydrogen and C_1–C_4 hydrocarbons, which are generated in pyrolysis and separated in the distillation column.

As all the pyrolysis and distillation plant outputs are mechanically or thermally recycled except for hydrochloric acid, the total recycle ratio in the pyrolysis process is calculated as 99.0%.

Table 26.14 shows the consumption figures of energy and chemicals necessary for operation of the plant. From the operation cost point of view, electrical power and fuel are the most expensive. In this plant, product oils are used for these purposes: light oil for fuel, and heavy oil for electrical power through the cogeneration system.

3.6 HEAT BALANCE

Table 26.15 shows the heat balance in the plant based on the material balance and consumption figures shown in Tables 26.13 and 26.14, under following conditions:

1. All electrical power and fuel required for operation are calculated assuming an external supply;
2. Enthalpies are 33.5 MJ kg^{-1} for waste plastics bales, 44.0 MJ kg^{-1} for pyrolysis distilled oils, off-gas and fuel, and 18.0 MJ kg^{-1} for residue;
3. Power generation efficiency is 38%.

Table 26.12 Analytical results for pyrolysis residue

Property	Analytical method	Residue	Dissolving test
Appearance		dry powder	
C (wt%)	TCD	46.5	
H (wt%)	TCD	3.3	
O (wt%)	IS	18.2	
N (wt%)	TCD	0.37	
S (wt%)	JIS K 2541	0.08	
Ca (wt%)	JIS K 0102 50.3	10.0	
SiO_2 (wt%)	CIP	4.5	
Al (wt%)	JIS K 0102 58.4	1.5	
Na (wt%)	AAS	0.33	
Fe (wt%)	JIS K 0102 57.4	0.32	
K (wt%)	AAS	0.11	
T-Cl (wt%)	TS Z 0025	1.4	
Org.Cl (wt%)	(T-Cl)-(Inorg.Cl)	0.1	
Inorg.Cl (wt%)	TS Z 0025	1.3	
Terephthalic acid (wt%)	HPLC	0.049	
Benzoic acid (wt%)	HPLC	0.021	
Oil content (mg kg^{-1})	N-C6 extraction	490	
T-Hg (mg kg^{-1})	Government guide lines	ND	ND (<0.005)
R-Hg (mg kg^{-1})	Government guide lines	ND	ND
Cd (mg kg^{-1})	JIS K 0102 55.3	3.3	ND (<0.01)
Pb (mg kg^{-1})	JIS K 0102 55.4	33	ND (<0.01)
Cr^{+6} (mg kg^{-1})	JIS K 0102 65.2.4	ND	ND (<0.01)
As (mg kg^{-1})	JIS K 0102 63.1	ND	ND (<0.01)
Se (mg kg^{-1})	JIS K 0102 67.3	ND	ND (<0.01)
T-Cr (mg kg^{-1})	JIS K 0102 65.1.4	28	
Zn (mg kg^{-1})	JIS K 0102 53.3	350	
Mn (mg kg^{-1})	JIS K 0102 56.4	160	
Ni (mg kg^{-1})	JIS K 0102 59.3	32	
Total heating value (kJ kg^{-1})	JIS K 2279	17,830	
Incandescence loss (wt%)	Government guide lines	58.5	
Flash point (°C)	ASTM E659	>510	
Bulk density		0.38	
Mean particle size (Nm)		6.0	
DXN (pg TEQ g^{-1})		0.0033	

ND: not detected

Table 26.13 Material balance

	Pretreatment	Pyrolysis	Whole plant (wt%)
Waste plastics bale	100.0		100.0
Residue in pretreatment	2.0		2.0
Water in the bale	6.0		6.0
Pretreated plastics pellet	92.0	100.0	(92.0)
Distilled light oil		(31.0)	(28.5)
Distilled medium oil		(4.5)	(4.1)
Distilled heavy oil		(26.5)	(24.4)
Whole pyrolysis oil		62.0	57.0
Hydrochloric acid as HCl		1.0	0.9
Pyrolysis residue		17.5	16.1
Off-gas		19.5	18.0

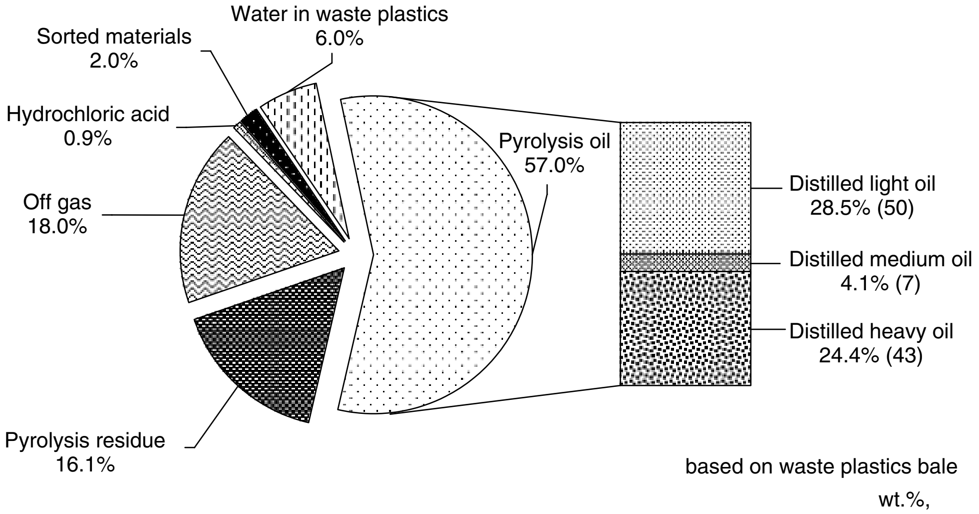

Figure 26.16 Material balance

Table 26.14 Consumption figures

	Pretreatment per bale	Pyrolysis per pellet	Whole plant per bale
Electric power (kWh t^{-1})	230	1200	1334
Fuel (kg t^{-1})		200	184
NaOH (kg t^{-1})		8.5	7.8
$Ca(OH)_2$ (kg t^{-1})		40	36.8
Water (t t^{-1})		10	9.2
LPG (Nm^3 t^{-1})		0.1	0.09
Wastewater (t t^{-1})		2.5	2.3

Table 26.15 Heat balance

Input	(MJ/kg bale)
Enthalpy of waste plastics	33.5
Electric power	11.3
Fuel	8.8
Total	53.6
Output	
Heating value of oils	27.2
Heating value of off gas	8.6
Heating value of residue	3.1
Total	38.9

Input total/output total = 72.6%

Table 26.16 Output applications

	Yield (wt%)*	Applications	
Distilled light oil	20.0	Fuel for furnaces and incinerators in plant	ER
Distilled light oil, remainder	11.0	Feedstock recycling in petroleum refinery plant	FSR
Distilled medium oil	4.5	Fuel for boiler in outside factory	ER
Distilled heavy oil	21.0	Fuel for cogeneration in plant	ER
Distilled heavy oil, remainder	5.5	Fuel for boiler in outside factory	ER
Hydrochloric acid	1.0	Wastewater after neutralization	W
Pyrolysis residue	17.5	Supplementary fuel for outside sludge incinerator	ER
Off-gas	19.5	Burnt in incinerator and recovered as steam in the exhaust gas boiler	ER
Total	100.0		

ER energy recovery; FSR feedstock recycling; W waste
* Yield per waste plastics pellet

The total energy efficiency of the plant, which is determined by the total available output energy and total input energy, reaches 72.6%. These heat balance data are available for LCA (life-cycle assessment).

3.7 APPLICATION OF THE OUTPUTS

Table 26.16 shows the applications of outputs in the pyrolysis and distillation sections. Recently, a portion of light oil is being sent to a petroleum refinery plant as feedstock recycling. All other outputs, such as oils, off gas, residue are used for energy recovery. Only hydrochloric acid is not recycled because of the conditions described in Section 3.4.2. Table 26.16. indicates that 11.0% of output is applied for feedstock recycling, 88% is for energy recovery and 1% is for waste. On the other hand, 60.5% of output is thermally used in plant, 38.5% is shipped outside, and 1.0% is waste.

3.8 ENVIRONMENTAL ASPECTS

3.8.1 Wastewater

All plant wastewater, including the neutralized hydrochloric acid, is transferred to city sewage treatment facilities. The results of the wastewater analysis at the border between the plant and its surroundings, and the city regulation data are shown in Table 26.17. The table shows that all city regulations are met.

3.8.2 Waste Gas

All waste gases from the pyrolysis plant and distillation section generated by burning the off-gas and distilled light oil in furnaces and incinerators are finally vented to the

Table 26.17 Analytical results for wastewater

Property	Analytical method	Analytical data	Regulation*
pH	JIS K 0102 12.1	7.7	5–9
SS (mg l^{-1})	JIS K 0102 14.1	11	<600
BOD (mg l^{-1})	JIS K 0102 21 & 32.3	38	<600
n-C_6 extraction			
Mineral oil (mg l^{-1})	JIS K 0102 20	<1	<5
Other oils (mg l^{-1})	JIS K 0102 17	<1	<30
I_2 consumption (mg l^{-1})	Government guide lines		<220
Cd (mg l^{-1})	JIS K 0102 55.3	<0.005	<0.1
CN (mg l^{-1})	JIS K 0102 38,1.2,3	<0.1	<1
Pb (mg l^{-1})	JIS K 0102 54.3	<0.005	<0.1
Cr^{+6} (mg l^{-1})	JIS K 0102 65.1.4,2.1	<0.04	<0.5
As (mg l^{-1})	JIS K 0102 61.3	<0.005	<0.1
T-Hg (mg l^{-1})	Government guide lines	<0.0005	<0.005
Cu (mg l^{-1})	JIS K 0102 52.4	0.01	<3
Zn (mg l^{-1})	JIS K 0102 53.3	0.07	<5
Soluble Fe (mg l^{-1})	JIS K 0102 57.4	0.05	<10
Soluble Mn (mg l^{-1})	JIS K 0102 56.4	0.45	<10
T-Cr (mg l^{-1})	JIS K 0102 65.1.4	<0.01	<2
F compound (mg l^{-1})	JIS K 0102 34.1	<0.1	<8
Dichloromethane (mg l^{-1})	JIS K 0125 5.1,2	<0.002	<0.2
CCl_4 (mg l^{-1})	JIS K 0125 5.1,2	<0.0005	<0.02
1,2-Dichloroethane (mg l^{-1})	JIS K 0125 5.1,2	<0.0005	<0.04
1,1-Dichloroethylene (mg l^{-1})	JIS K 0125 5.1,2	<0.002	<0.2
cis-1,2-Dichloroethylene (mg l^{-1})	JIS K 0125 5.1,2	<0.004	<0.4
1,1,1-Trichloroethane (mg l^{-1})	JIS K 0125 5.1,2	<0.1	<3
1,1,2-Trichloroethane (mg l^{-1})	JIS K 0125 5.1,2	<0.0006	<0.06
Trichloroethylene (mg l^{-1})	JIS K 0125 5.1,2	<0.003	<0.3
Tetrachloroethylene (mg l^{-1})	JIS K 0125 5.1,2	<0.001	<0.1
1,3-Dichloropropene (mg l^{-1})	JIS K 0125 5.1,2	<0.0005	<0.02
Benzene (mg l^{-1})	JIS K 0125 5.1,2	<0.001	<0.1
Seren (mg l^{-1})	JIS K 0102 67.3	<0.005	<0.1
Phenols (mg l^{-1})	JIS K 0102 28.1.2	<0.1	<5

* According to Sapporo city regulation

Table 26.18 Analytical results for waste gas

Property	Analytical method	Waste gas from plant		Waste gas from CG	
		Analysis data	Regulation*	Analysis data	Regulation*
Fuel used		Distilled light oil and off-gas		Distilled heavy oil	
Dust(6%O_2) (g/N m^3)	JIS Z8808	<0.001	<0.15		
Dust(13%O_2) (g/N m^3)	JIS Z8808			0.02	<0.10
SOx (ppm)	JIS K0103	<14	<322	2	<98
NOx (6%O_2) (ppm)	JIS B7982	111	<150		
NOx (13%O_2) (ppm)	JIS B7982			850	<950
HCl (12%O_2) (mg/N m^3)	JIS K0107	<3	<49		
HCl (13%O_2) (mg/N m^3)	JIS K0107			1.3	
DXN (ng TEQ/N m^3)	WHO-TEF	0.0026		0.023	

* According to Japanese national regulation

atmosphere through a central vent stack, while the waste gas from the cogeneration facilities, which burn distilled heavy oil, is vented to a dedicated stack. Table 26.18 shows the analyzed results of both waste gases. All items clear the national regulation, and dioxin content in the waste gases is below 0.1 ng TEQ/N m^3.

3.9 CHARACTERISTICS OF THE PLANT

3.9.1 Pyrolysis of Waste Plastics Containing PET and PVC

The pyrolysis process for polyolefin wastes only is simple and operation is easy. In addition, oil yield is high and operation costs are low. However, the SPR plant is designed to be operated using household waste plastics, which contain PVC, PVDC, PET and many other kinds of plastics, as shown in Figure 26.13. After plant start-up in 2000, it became clear that the organic acids, such as terephthalic acid and benzoic acid, generated by the hydrolysis and pyrolysis of PET, can cause operational instability due to corrosion at higher temperature ranges and blocking problems in the equipment and pipes.

To overcome these problems, $Ca(OH)_2$ powder was added in waste plastics input [1]. As a result, stable process operation was attained because the organic acids generated in the dehydrochlorinator and pyrolysis reactor were converted to chemically stable Ca salts. The problematic terephthalic acid changed to calcium terephthalate, which is a solid and is stable up to approximately 600°C [2]. The HCl separated from PVC is also fixed in $CaCl_2$, and the phthalic anhydride generated from the plasticizer contained in flexible PVC is also stabilized. The blocking problems on dehydrochlorinating gas line by terephthalic acid due to its sublimation temperature of 300°C and crystallization of phthalic anhydride at 230°C have also been solved.

Thus, stable operation of the pyrolysis plant for household plastics was successful, although the residue volume increased with higher chlorine content and the oil yield decreased.

In addition, the HCl content of oil decreased, moreover the off-gas scrubbing system, in which light oil was washed by NaOH aqueous solution, was out of operation; NaOH consumption decreased, and process wastewater also decreased. Reactivity (pH in extracted water) of the oils was improved from 'acid' (pH: below 4.6) to 'natural' (pH: above 4.6).

3.9.2 Quality of Oils for Energy Recovery Applications

The three types of distilled oils have a good reputation and have not created problems in energy recovery applications. The higher pour point and higher viscosity problem of heavy oil was solved by keeping the heavy oil above 60°C using steam tracing. At this temperature, heavy oil is liquid and has a low viscosity for processing, tank storage, transportation by truck, or burning in furnaces and incinerators. Therefore, no catalyst is used for the cracking of heavy oil.

3.9.3 Feedstock Recycling of the Distilled Light Oil

After research and development was conducted with Japan Energy Corporation (JEC), the remaining distilled light oil has been applied at JEC's petroleum refinery plant as feedstock recycling since April 2004. To date, JEC has not reported operational problems.

3.9.4 Utilization of Pyrolysis Residue

The residue consists of mainly carbon and has a high heating value, as shown in Table 26.12. However, applications could not be found and the residue was landfilled as waste, after costly packaging in a flexible container because the residue was a fine dry powder and caused dust problems upon handling. The codevelopment work with Sapporo city successfully utilized the residue in the sludge incinerator as supplementary fuel. However, dust was still a problem in this application. To resolve the problem and to find better applications, pelletizing facilities for this residue were installed in April 2004. As a result, the dust problem was solved and better applications are expected.

3.9.5 High Recycling Ratio

As mentioned above, the only wastes discharged from the plant are hydrochloric acid, pretreatment residue, and moisture contained in the waste plastics. Therefore, the recycling ratio is calculated as 99.0 wt% in the pyrolysis and distillation sections, and 91.1 wt% in the whole plant as shown in Table 26.13. The heat balance shown in the Table 26.15 indicates that the total heat recovery ratio is 72.6%.

3.9.6 Low Running Cost

The running costs has been remarkably improved by the following developments:

1. Operating capacity was increased to 110–120% of designed capacity;
2. Energy costs are very low, because the heavy oil is used for the generation of electrical power supplied by cogenerator, and light oil is used for the furnaces and incinerators;

3. Waste costs are also very low because the only waste requiring disposal is the residue from the pretreatment section and hydrochloric acid, and these represent only 2 and 0.9% of the waste plastics bales, respectively.

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4 MIKASA WASTE PLASTIC LIQUEFACTION PLANT [1]

K. Tada

4.1 PLANT OUTLINE

Development of liquefaction of waste plastics via thermal cracking by Kubota Co. Ltd was started during the oil crisis in the 1970s, but the yield and quality of reclaimed oil as well as cost were unsatisfactory. At the beginning of the 1990s, a catalytic cracking process was developed by joint research among IIT, Fuji Recycle Co. Ltd, and Mobil Oil Co. Ltd, and the output of reclaimed oil has been markedly improved. Kubota, with Fuji Recycle, has started to operate a liquefaction plant for industrial waste plastics with output 5000 t/yr at Aioi. A test operation has finished at Saga city, pretreating plastic containers and packaging waste. As a result of such extensive development, the Douo Liquefaction Center was founded in April 1999 under the leadership of Kubota in Mikasa city. The capacity is 6000 t/yr of sorted waste plastics, and 3000 kl/yr of product oil. Commercial operation was began in April 2000, but stopped in the end of March 2004. The plant is shown in Figure 26.17.

4.2 PROCESS DESCRIPTION

The flow diagram of the pretreatment and liquefaction processes is shown in Figure 26.18.

4.2.1 Pretreatment Process

Foreign materials such as metals, sand, etc., are removed from domestic waste plastics in the pretreatment process. Mikasa does not have a large population and thus waste plastics have to be collected from various municipalities in Hokkaido.

Figure 26.17 Liquefaction plant at Mikasa

The waste plastics are put into the receiving hopper and conveyed to pretreatment machines, i.e. first and second crushers, vibration separator, air separator, dryer, magnetic separator, aluminum separator, and pelletizers. Plastic pellets having bulk density of 0.35 are obtained.

4.2.2 Liquefaction Process

Plastic pellets conveyed from the pretreatment process are fed into molten plastic tanks by the feed conveyor. The pellets including PVC are melted and agitated in the tank at 300°C for 2 h. At this stage, the dehydrochlorination reaction is sufficient to remove chlorine in the fluff. This is a characteristic of this process, since the modification catalyst of ZSM-5, sensitive to chlorine, is used in the cracking step. The generated gas is collected, and can be reused to produce hydrochloric acid, but it is currently neutralized with sodium hydroxide and discarded in the sewage water.

The molten plastic is then sent to a thermal cracking tank from the dehydrochlorination tanks, and heated to 400°C for gasifying. After gasification, hydrocarbons containing heavy fractions are treated by a neutralization tower to remove hydrogen chloride, completely. Then, the hydrocarbon gases are sent into a decomposer where they are cracked and turned into light gas by the catalyst. The decomposed gas is recondensed by the two condensers so that gas oil and naphtha fractions are obtained. The naphtha and noncondensed gases are self-consumed as fuel for furnaces in the plant. The gas oil is sold as fuel for many uses such as boilers and diesel generators.

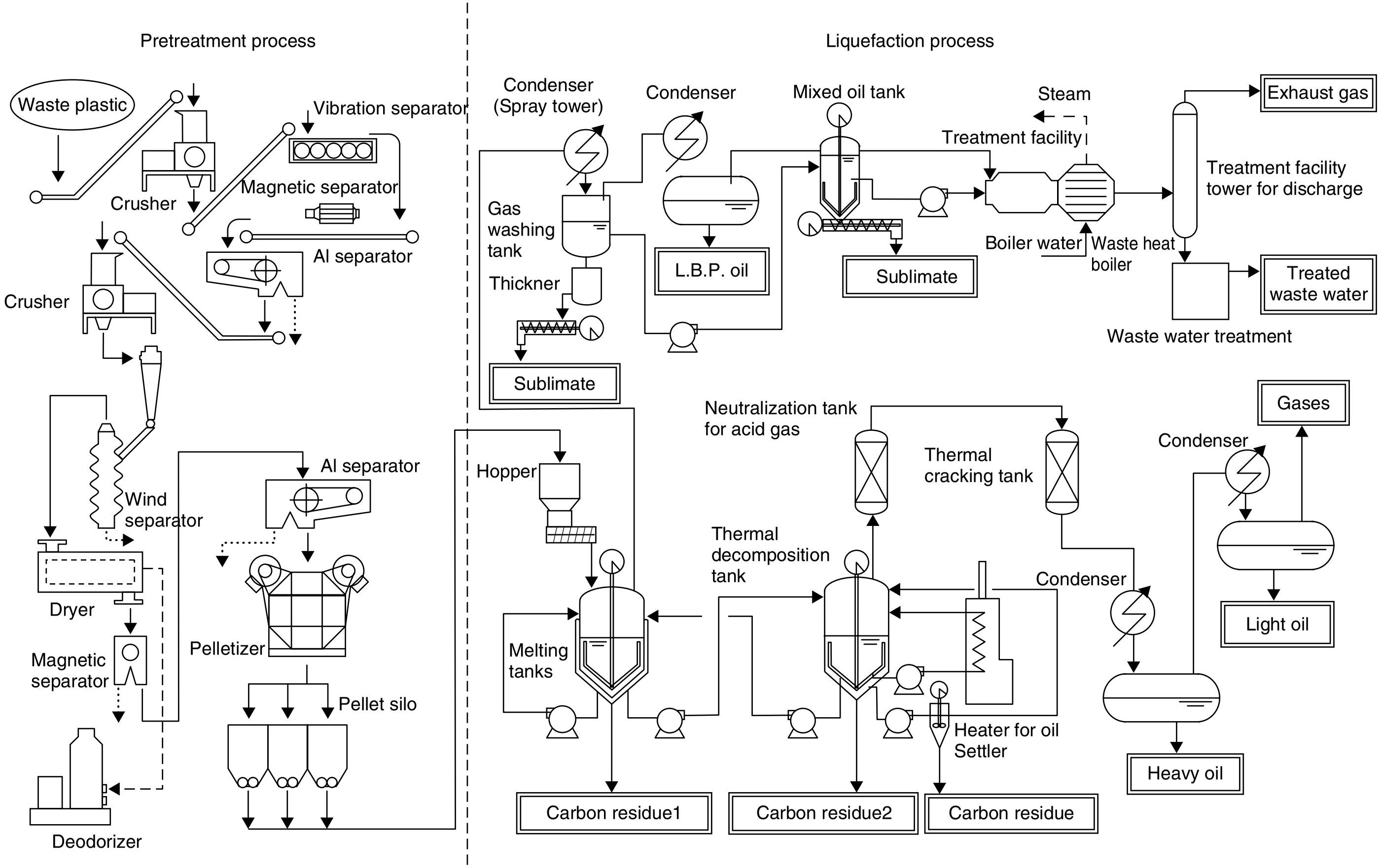

Figure 26.18 Flow diagram of the pretreatment and liquefaction processes. (Reproduced by permission of the Kubota Corporation)

Table 26.19 Properties of light and heavy oils

Reactivity	Light oil	Heavy oil
Density (15°C) (g/cm^3)	0.7816	0.8375
Kinetic viscosity (30°C)(CSt)	0.63	
Kinetic viscosity (50°C)(CSt)		2.31
Pour point (°C)	<−45	12.5
Moisture (vol%)	0.00	0.00
Flash point (°C)	<−20	25
Heating value (cal/g)	9687	10778
pH	neutral	neutral
Cetane number	27.8	
Elemental analysis		
N (wt ppm)	820	800
S (wt ppm)	540	1510
Total Cl (wt ppm)	5	23
Inorganic Cl (wt ppm)	<1	2
Organic Cl (wt ppm)	5	21
Hydrocarbons		
Saturated (vol%)	30.9	54.9
Unsaturated (vol%)	18.0	22.8
Aromatics (vol%)	51.1	22.3
Ash (wt%)	<0.01	<0.001

4.3 QUALITY AND APPLICATION OF RECLAIMED OIL

The cracking product oil is condensed to two fractions as light and heavy oils. Their properties are shown in Table 26.19.

The light fraction of the reclaimed oil has the property of gasoline in its density due to an effect of the catalytic treatment. In addition, the very low chlorine content both in light and heavy oils indicate another characteristic, but sulfur content seems to be relatively higher compared with those for the other pyrolysis oils. Clearly, these low chlorine contents have been achieved by high removal of chlorine in the dehydrochlorination process and the gasification process of primary cracking oil. Thus, the oil has the potential to be fed into refinery plants as a global recycle system. The distillation properties of these oils are shown in Figure 26.19. The distillation curves of light oil indicate the effect of modification by the catalytic process.

4.4 MATERIAL BALANCE

The material balance is shown in Figure 26.20. The collected waste plastics are not satisfactory as fluff raw material, with relatively large amounts of plastics being selected and removed at the pretreatment process.

Although the residence time of plastic melt in the dehydrochlorination process is very long, the amount of HCl gas evolved is less than in the liquefaction processes of Niigata and Sapporo. This may indicate that PVC and PVDC materials are removed effectively

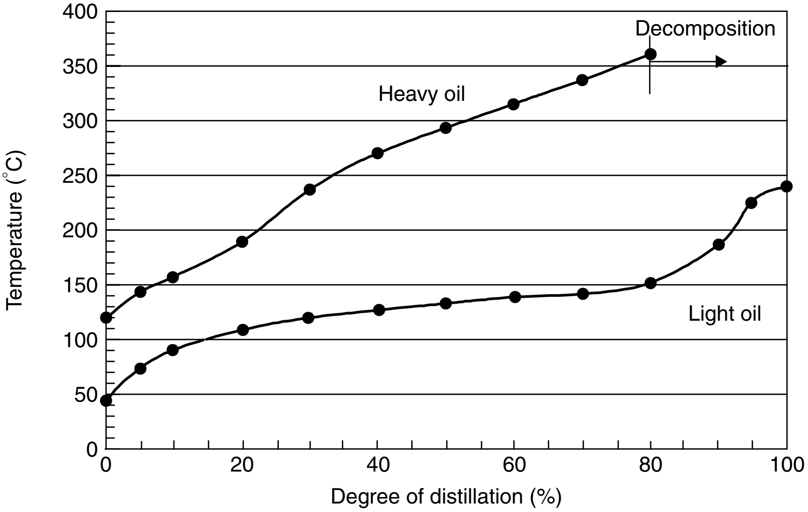

Figure 26.19 Distillation curves of light and heavy oils

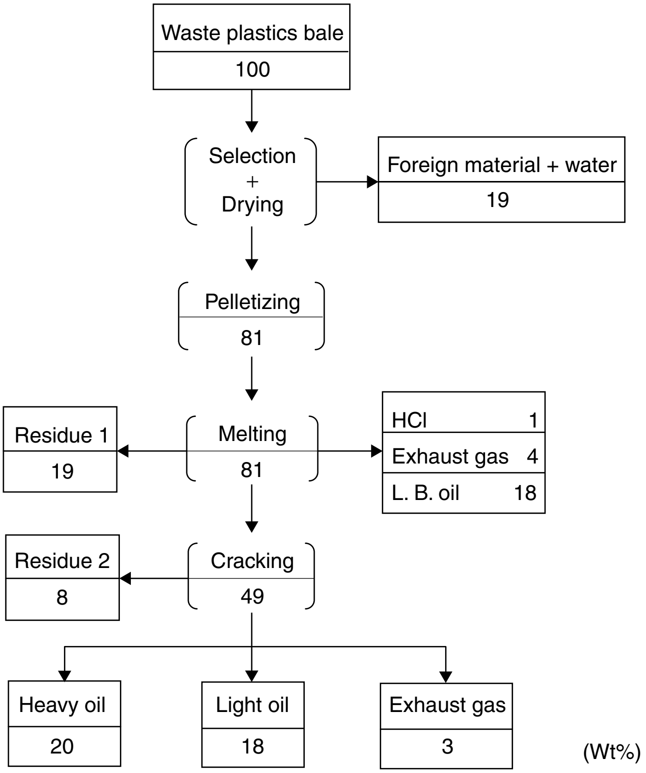

Figure 26.20 Material balance

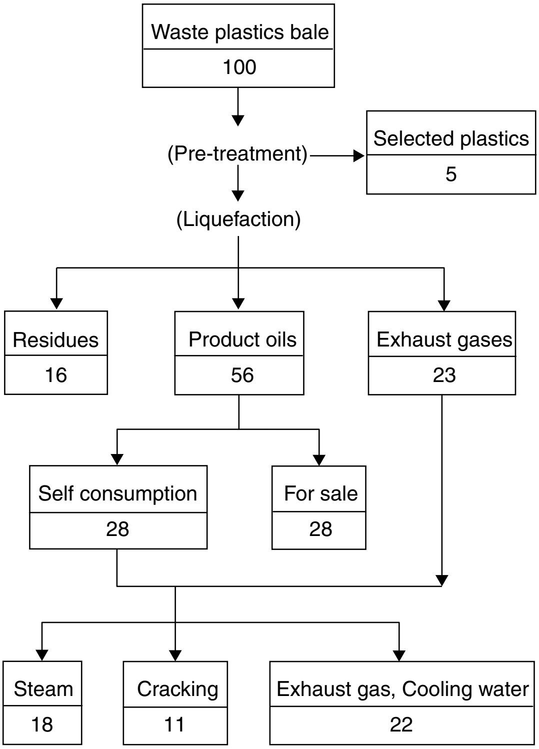

Figure 26.21 Energy balance

on pretreatment, especially, in the air separation. Practically 19% of foreign materials including waste plastics is removed during the pretreatment.

4.5 HIGH ENERGY COLLECTION

The energy balance is shown in Figure 26.21. The heating values of removed plastics are low compared with their weight, 19%. This shows that the quality of collected plastics is not appropriate for liquefaction since it contains PVC, PVDC, PET, etc., which are low in heating value.

Conversion performance of reclaimed oil and hydrocarbon gases reaches 70% or higher. Two kinds of carbon residues are formed in the dehydrochlorination and thermal cracking processes. They can also used as solid fuel for industries. Their compositions are shown in Table 26.20.

The heavy metal and chlorine contents seem to be lower in the thermal cracking residue. They are expected to remain higher in the dehydrochlorination residue, since they are fixed in it as inorganic chlorides.

4.6 CHARACTERISTICS OF THE PLANT

The process is operated at relatively low working temperature (~400°C) and nearly atmospheric working pressure. Further melting and cracking processes are both heat-absorbing

Table 26.20 Composition of carbon residues

	Residue	Residue
Hg and/or Hg-compounds (mg/kg)	<0.01	<0.01
Cd and/or Cd-compounds (mg/kg)	<2.0	2.5
Pb and/or Pb-compounds (mg/kg)	<20	<20
As and/or As-compounds (mg/kg)	<0.5	<0.5
Cu and/or Cu-compounds (mg/kg)	<20	<20
Zn and/or Zn-compounds (mg/kg)	42	91
Fluorine compounds (mg/kg)	8	
Fe (mg/kg)	810	640
Mn (mg/kg)	30	71
Cl (wt%)	1.38	0.92
S (wt%)	<0.01	0.06
C (wt%)	75	78.6
N (wt%)	0.36	0.5
H (wt%)	9.05	7.8
Ca (mg/kg)	1000	2500
Al (mg/kg)	<400	2200
Ignition loss (400°C, %)		25.26
(800°C, %)	91.6	91.41
(Date)	May 2000	September 2000

Table 26.21 Composition of carbon residue

Total Cl (wt%)	1.38
C (wt%)	75
H (wt%)	9.05
N (wt%)	0.36
S (wt%)	<0.01
Ca (wt ppm)	91
Cd (wt ppm)	
Pb (wt ppm)	640
Cu (wt ppm)	71
Zn (wt ppm)	0.92
Mn (wt ppm)	0.06
Fe (wt ppm)	78.6
Al (wt ppm)	0.5
Hg (wt ppm)	7.8
As (wt ppm)	2500
Ignition loss (800°C, %)	91.6

reactions. This guarantees safer operation of the plant. This is a common advantage with liquefaction using pyrolysis, but is very important for the municipality and its residents.

4.6.1 De-hydrochlorination Treatment

The chlorine in the fluff is sufficiently removed from the melted plastics in the molten plastic tanks during the long holding time of 2 h. However, total chlorine in the melt is present as inorganic chlorides as shown in Table 26.21, and only 0.25% Cl_2 remains in this process. It is well-known that the chlorine in pure PVC is removed easily within a few minutes at 300°C [2]. This chlorine is partly caught as inorganic chlorides by reaction of HCl gas released and inorganic materials and metals, that stay in the plastic melt. But, it has been also disclosed that the chlorine in PVDC is removed to only 50–60%, even at 400°C [3]. Thus, the remaining organic chlorine in the dehydrochlorination residue may originate from the residual chlorine in PVDC film, which is one of the major wrapping films in Japan and is present in the waste plastics.

The removal of foreign plastics and the long heating time on dehydrochlorination produce a similar effect to $Ca(OH)_2$ addition in the other liquefaction plants. Consequently, corrosion by hydrogen chloride can be kept to a minimum. This means that maintenance costs of the plant are remarkably less.

4.6.2 Neutralization of Gas Oil

The capture of HCl gas just before the thermal cracking is another characteristic of this process. The two tanks are alternatively used to protect the catalyst from HCl attack. Activated charcoal prepared from palm shell is applied at a loading of 13% K_2CO_3.

4.7 APPLICATION OF THE SYSTEM

Air and water pollution are sufficiently managed according to the law and ordinance, as in other liquefaction processes. In addition, this process can be applied to treat waste plastics from households, from industry and from agriculture, since the composition of plastic containers and packaging is well known (i.e. they contain PVC, PVDC, and ABS, and sometimes thermosetting plastics).

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5 THE SCOPE OF LIQUEFACTION IN JAPAN

A. Okuwaki and T. Yoshioka

5.1 PRESENT STATUS OF FEEDSTOCK RECYCLING [1]

The amounts of collection planned by the municipalities, the contracted amount with municipalities, the amount of acceptance by JCPRA for the recycling of plastics into

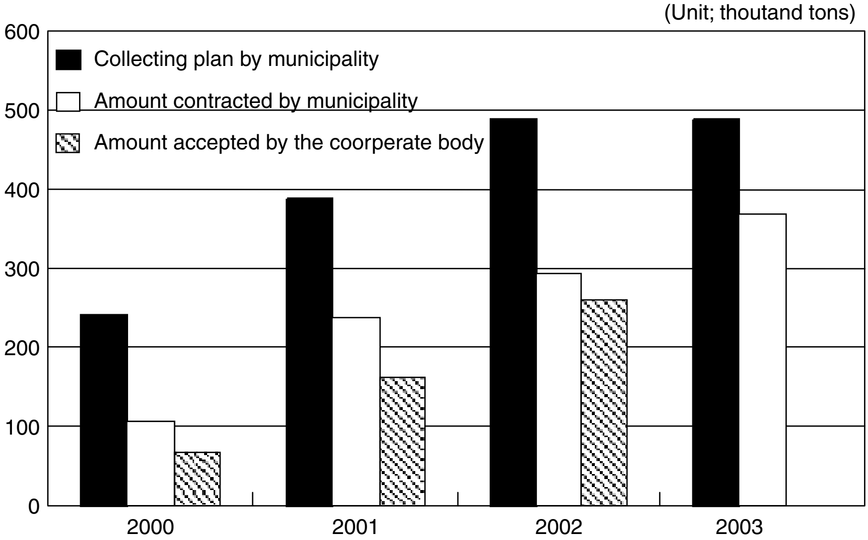

Figure 26.22 Collection plan, municipality contract and acceptance by JCPRA

containers and packaging are shown in Figure 26.22, since the Plastic Recycling Law came into effect in 2000.

The planned amount of collection and sorting by municipalities increased rapidly to 2001, but tended to saturate by 2002 at 487 000 tons, even though the rates of both numbers of the municipalities and the population engaged in the plastic waste recycling are projected to increase until 2007, to 82.1 and 83.5%, respectively. This is caused by the fact that the collection and sorting costs that are payable by the municipality are quite high, compared with the total incineration cost, composed of collection and incineration of mixed garbage, with landfill of ash. As a result, many municipalities do not seem to want to progress the recycling of plastic containers and packaging.

On the other hand, the facilities of feedstock recycling plants have been constructed corresponding to the planned amount, and the amount accepted has increased sharply. This indicates that there is competition among the technologies and the recycling plants and results in the sharp drop in the tender price [2].

Total cost for feedstock recycling of plastic containers and packaging consists of the collection and baling costs, which are paid by the municipality, and the recycling cost paid by businesses that manufacture or use the containers and businesses that use the relevant packaging. The present status and scope for feedstock recycling are discussed below.

5.1.1 Municipality Expense

In Table 26.22, the costs for collection and baling of post-use plastic containers and packaging paid by the municipality in 2000 are shown [3]. The recycling cost in the third column corresponds to the expense paid by the municipality instead of small businesses.

Table 26.22 Municipality expenses for the collection and baling for post-use containers and packaging plastics in 2000

	Collection	Baling	Recycling*	Total
Number of municipalities	20	27	27	26
Maximum ($\times 10^3$ Yen/t)	358	679	10	761
Minimum ($\times 10^3$ Yen/t)	19	12	0.3	6
Number average ($\times 10^3$ Yen/t)	84	91	6	196
Weight average ($\times 10^3$ Yen/t)	69	42	5	104

* For small businesses

The high total cost has to be paid by municipalities. This high cost is the greatest obstacle to expanding the feedstock recycling of waste plastics.

Japanese people understand and cooperate significantly with the spirit of the Plastic Recycling Law and separate the plastics containers and packaging from garbage in everyday life. But the collection of waste plastics involves quite high initial costs, at least two to three times that for mixed garbage, since the waste plastics alone are quite light compared with mixed garbage.

Second, the baling cost add to the collection cost, since the collected waste plastic has to be baled after removing foreign materials such as metals, glasses, etc. for recycling. Usually, these total costs, including collection and baling far exceed the total incineration cost, including collection and incineration of garbage, and landfill of ash. As a result of these economic conditions, almost all local governments are reluctant to progress the recycling of waste plastics.

An example of collection and baling costs in 2002 in Sendai city with a population over one million, is shown in Table 26.23 compared with that for the total incineration cost. In 2002, about 10 000 tons of bales were prepared from plastic containers and packaging. The major use was blast furnace application in JFE Steel at Kawasaki.

Evidently, the total incineration cost is much lower than the feedstock recycling cost. The average waste treatment cost in Japan attained 50 Yen/kg or higher in 2001 [4]. The old incineration plant and landfill site, of course, contribute significantly to the lower cost. The total incineration cost in Sendai is lower than the average cost in Japan. Sendai city, however, has started a new incineration plant, 600 t/d in capacity which should elevate incineration cost at least 50% over the present one.

Rationalization of the collection system by the municipality may reduce the cost a little, but the most important way of reducing collection cost is to develop an innovative

Table 26.23 An example of collection and baling cost (Yen/t)

Plastic recycling in 2002	Collection	Baling and recycling		Total
	24 000	33 000		57 000
Garbage incineration in 2001	Collection	Incineration	Landfill*	Total
	9 024	15 283	8 325	25 519

* Ash 14.56%

collection method to densify the light weight plastic containers and packaging in situ during their collection.

One method available to reduce baling cost is to locate the recycling plant beside the baling plant. This is absolutely important for every process, especially for liquefaction operated on a relatively small scale, but does not necessarily harmonize with the Plastic Recycling Law.

Baling has been introduced according to the bid system by JCPRA to ensure equity for all enterprises permitted by JCPRA, having material and feedstock recycling techniques. At present, this equity is preferential, but this system is not always effective or favorable for reducing the baling cost and progressing feedstock recycling. So, some strange phenomena are associated with the recycling of bales. For example, there is a large baling plant adjacent to the SPR plant, with only 10 m distance between them. A lot of bales prepared by Sapporo city have been shared between an iron and steel company and SPR. The company's bales are carried a long distance from the baling equipment. On the other hand, the SPR bales are transferred only 10 m and are broken into plastic fluff to form pellets. If all the waste plastics collected were liquefied at SRP, the baling cost will be reduced by half. At Niigata, half of the collection to their baling facility is directly fed to the liquefaction plant as described in Section 2. This process aids the reduction of cost for both Niigata city and the company.

5.1.2 Business Expense

The costs of recycling for different feedstock techniques in 2003 are shown in Table 26.24, which includes the transportation cost from municipality to the recycling plant. These costs are all paid by businesses, except for small businesses of (paid for by municipalities and 8% in the case of Sendai city).

The high cost for mechanical recycling method is due to the priority for feedstock recycling. The cost reduction for businesses depends to a great extent on improvement of feedstock recycling technologies. Another method could easily save the expensive transportation cost, namely, the light plastic containers and packaging should be recycled as near as possible to where they are collected.

Table 26.24 Recycling costs* for different techniques

Method	Cost (Yen/kg)
Mechanical recycling	108
Liquefaction	98
Blast furnace	83
Coke oven	78
Gasification	80
Average	88

* Includes transportation from municipality to plant

5.1.3 Status of Liquefaction in Feedstock Recycling

Feedstock recycling process, other than liquefaction, involve large-scale basic industrial equipment, blast furnaces and coke ovens for iron and steel applications and ammonia plants for gasification. Thus, their recycling process can be evaluated as a pretreatment for such basic industries. Actually, no chemical treatment is performed in the blast furnace application at present.

However, liquefaction of waste plastics dose not have such a combination with a petroleum refinery at present. Clearly, small liquefaction plants producing pyrolysis oil in isolation necessarily incur a high treatment cost. Unfortunately, sufficient quantities of bales for maintaining a high rate of operation is not feasible under the bid system. This brings about a vicious circle of high operating cost–low operating rate.

The other issue is the carbon number distribution of pyrolysis oil containing low carbon number hydrocarbons. This affords a relatively high yield of gasoline component. The light oil is subject to the expensive gasoline tax for external sale.

The final factors on operational of a liquefaction plant are stoppages and corrosion problems caused by the decomposition products from pyrolysis of PET material, yielding terephthalic acid and benzoic acid.

5.2 SCOPE FOR LIQUEFACTION

The characteristic features of liquefaction described above necessarily result in unstable operation and high cost of liquefaction via pyrolysis. Recently, the operational problems have been solved by adding calcium hydroxide to control the evaporation and decomposition of terephthalate components such as calcium terephthalate [5].

5.2.1 Cost Reduction

This is a vital problem for liquefaction and has failed in the advanced German trials. In Japan, liquefaction has first to defeat incineration, the technique that has prevailed in most municipalities. The rate of incineration in municipalities has reached 80% or so and 40 million tons of garbage are incinerated every year. From this point of view, the reduction of collection and baling costs as described above is an easy way to achieve this. Second is the question of how to reduce the liquefaction cost compared with those for the other feedstock recycling methods, such as application in the iron and steel industry and gasification for ammonia synthesis. These methods have the merits discussed above. On the other hand, liquefaction has many weak points, it is small in scale, complicated with a mixed raw material for fine technology, and has a low degree of operation, 50% or so.

Simplification of the present liquefaction processes by removing several pieces of equipment (for example, the distillation column) will be one important solution. The present complex facilities are necessary to treat chlorine-containing plastics and PET materials from plastic containers and packaging. They provide only small amounts of oil on pyrolysis, but cause various difficulties. The amount of the former materials tends to decrease due to the replacement of PVC and PVDC materials with polyolefins, but the latter is increasing gradually, due to recycled PET sheet which is used, for example in egg cartons. Removal of such materials is not so difficult by present separation methods, as used in mechanical recycling, though PE, PP and PS are present to some extent.

Such simplification will make it possible to reduce the high operating cost through the reduction of investment to the liquefaction plant, to one-half, or to a maximum of one-third of the present values [6].

5.2.2 A New Recycling Route for Light Oil

The characteristic distribution in the pyrolysis oil is a low yield of medium oil, for diesel or boiler fuel, but a high yield of light oil. The light oil has similar properties to naphtha from crude oil. If this is used in the recycling process as fuel, no volatile oil tax (gasoline tax) is imposed. However, in the case of external sale, the user has to pay the tax. As a result of regulation by the volatile oil tax law, the light oil is not appropriate for outside sale at all.

Recently however, a breakthrough has emerged in the cooperative research between Japan Energy Co. Ltd and the joint group of liquefaction enterprises. The project has run a trial for introducing the light oil into the pipeline in the equipment (see Section 3). The results indicate that a small amount of chlorine, several tens of ppm, contained in the light oil will have no effect on the operation in the main stream.

The result of this trial has been taken into account. In the case of recycling the light oil to naphtha, the gasoline tax or kerosene tax is not imposed on self-consumption in the liquefaction process. Light oil produced in Sapporo and Niigata, has been fed 1000 KL to the Mizushima refinery of Japan Energy Co. Ltd. [7].

5.2.3 Activation for Local Business

The local economy in most districts in Japan has been in a deep recession since the 1990s and unemployment continues to be problems. The present recycling system well meets the Plastic Recycling Law. However, from the standpoint of view of the local citizen, there is a major contradiction. This might lead to a tendency to saturation of the amount of plastic being recycled.

Many local governments have to pay such high recycling costs, including those of small businesses, to prepare bales. The company recycling these bales is not always located at the same municipality; they often have to be transported to the recyclers, far from the municipalities that prepared the bales. Consumers in a municipality separate the waste plastics from garbage, and the municipality collects and sorts the material to prepare bales, but the recycling business is located in another district, or prefecture. This seems to be one problem in the Plastic Recycling Law that needs to be improved to lower the environmental load as well as to bring about an activation of local industries and to provide employment for local citizens. In addition, most local governments have enough capacity to incinerate their garbage, and waste plastics give no ash on incineration.

Under such considerations of the merits and demerits of recycling plastic containers and packaging, with the liquefaction plant in the municipality where the bales are prepared will become an interesting enterprise for many local governments as a tool for activating the local economy and providing employment opportunities.

The system research division of the Research Association of Feedstock Recycling of plastics, Japan (FSRJ) has proposed candidate cities, such as Sendai, where there are no basic industries, such as iron and steel industry and ammonia synthesis [7].

The shortage of plastic containers and packaging should be solved easily by commencing the collection and baling in mega-cities as Tokyo, Yokohama, Nagoya, Osaka, etc., where a lot of factories of big industries are operating. Surely, this will contribute to the lowering of transportation costs and result in reducing somewhat the load on businesses having to pay the recycling cost.

ACKNOWLEDGEMENTS

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27

Process and Equipment for Conversions of Waste Plastics into Fuels

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1 INTRODUCTION

Plastic waste is becoming a serious global issue, thanks to extensive plastic usage all over the world, the treatment of waste plastic has gained the utmost importance. Scientists and experts all over the world are concerned over this major environmental problem which is expected to attain mammoth proportions by the year 2010, with an expected annual increase of global plastic consumption crossing the 5.5% mark.

There are various methods for reutilizing the polymers, each one having its shortcomings or limitations. Yet, thermal and catalytic degradation of plastic into fuel is considered to be the most effective way of reusing polymers. Of late, experts have begun to pay attention to pyrolysis, especially thermal or catalytical degradation of plastics.

2 PYROLYSIS

2.1 DEFINITION

Pyrolysis is defined as a chemical degradation reaction that is caused by thermal energy in the absence of air (oxygen). It is supposed to be one of the most effective methods for preserving petroleum resources, in addition to preserving the environment by decreasing the volume of nondegradable waste. Degradation of plastic is achieved by heating at high temperature, with macromolecules breaking into smaller fragments, consisting valuable mixtures of hydrocarbons (gas, liquid and solid).

The degradation of different types of waste plastics has been studied in the presence and absence of a catalyst. It is found that the properties of the products depend significantly on

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the characteristics of the applied catalyst. A catalyst also reduces the reaction temperature. The pyrolysis process, requiring high temperatures up to 1 000°C can be carried out at much lower temperature (400–500°C) with the use of a proper catalyst. Recycling of waste plastic by pyrolysis can yield excellent results, even with heterogeneous waste plastic materials, where segregation is not economic.

2.2 PLASTICS SUITABLE FOR PYROLYSIS

Polymers are structurally made up of carbon atoms linked by single or double bonds. Hence, each polymer has a specific heat value. For example: Polyethylene and Polypropylene have calorific values of 18 720 BTU/lb and 18 434 BTU/lb, respectively. These organic molecules have a low decomposition temperature compared with inorganic matter. Nearly all conventional fuels are organic molecules. The heat content of an organic molecule depends upon number of carbon atoms in the molecular chain and the complexity of the molecular structure (linear, branched, cyclic, etc.). Thus, when any polymer decomposes or the polymer structure gets fragmented randomly, each fragment, depending upon number of carbon atoms, can be classified into various types of fuels. Hence, pyrolysis of polymers such as PE, PP and PS yield valuable hydrocarbons.

A few polymers such as polyvinyl chloride, ABS, and PET are associated with heteroatoms such as Cl, N, and O apart from carbon and hydrogen. During pyrolysis these heteroatoms get converted into compounds such as HCl, N_2, H_2O etc.

3 PYROLYSIS: MODE OF OPERATION AND APPARATUS

3.1 BATCH PYROLYSIS

The batch-type reactor used for the catalytic pyrolysis of waste plastic is shown in Figure 27.1. As shown in the figure, the mechanical agitator is installed in the batch-type reactor wrapped around with an electric heater, to control the pyrolysis temperature of the waste plastic. The organic vapor generated from waste plastics, is then passed through the catalytic cracker bed. After that, the vapor is discharged through condensers I and II, which are maintained at different temperatures for product oil conversion.

The reclaimed oil can be utilized for various applications. In addition, the oil can be fed into refinery plants as a global recycle system.

3.1.1 Pyrolysis Reactor Configuration

The thermal treatment device for pyrolysis should be properly designed and operated in order to be more economical in terms of a cost-effective and energy-efficient operation. The primary driving force for this process is the intraparticle heat conduction. The principles of a pyrolyzer design should take the heat transfer and contact mode into account. Different reactors are used to carry out pyrolysis of the waste plastics. Among them, three

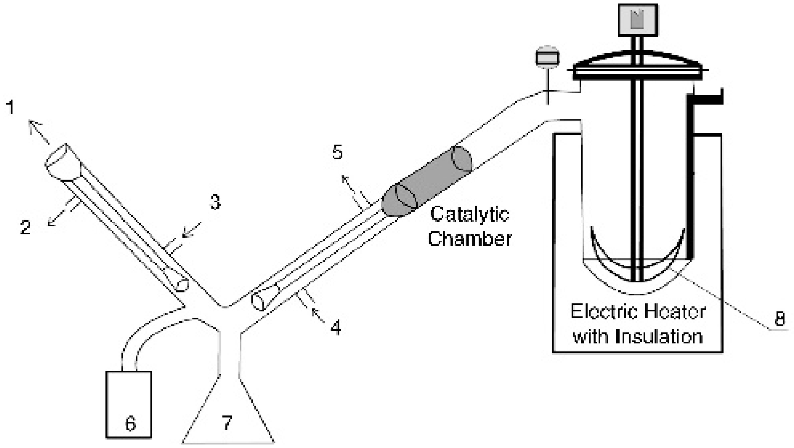

Figure 27.1 Batch-type reactor for pyrolysis of waste plastic [1]. 1 uncondensed gas; 2 water outlet for condenser; 3 water inlet for condenser; 4 thermal fluid inlet for condenser; 5 thermal fluid outlet for condenser; 6 lighter liquid hydrocarbons; 7 liquid hydrocarbons; 8 agitator

main kinds of reactor: fluidized-bed; rotary kiln; and screw pyrolyzers, are used. A brief description of these reactors is given below.

3.2 TYPES OF PYROLYZERS

3.2.1 Fluidized-bed Pyrolyzer

The gas fluidized-bed reactor is the most efficient approach to pyrolysis. In this reactor the waste plastic is suspended around the heating medium and subjected to pyrolysis by means of immersed heating tubes and gas–solid convective heat transfer. At present the only difficulty with this reactor is the problem of its structure. Fluidized-bed pyrolyzers have been designed for pyrolysis of waste tyre rubber in Taiwan and in Hangzou. A schematic apparatus of a fluidized-bed pyrolyzer is shown in Figure 27.2.

The reactor is constructed with a cylindrical column and an expanded freeboard. The distributor is a perforated plate. An inert gas matrix composed primary of crystal sand, is used as the bed material. The blower supplies the inert gas for fluidization or the amount of air for partial combustion. A cyclone is used to collect fine particles. Scrubbers serve to quench the off-gases and remove condensables that were withdrawn from reactors.

3.2.2 Rotary Kiln Pyrolyzer

The main advantage of rotary kiln pyrolyzers is that the rotation of the pyrolyzing chamber guarantees the permanent turning and mixing of the waste plastic, so that the mixture is continuously homogenized and blended with inert pyrolysis gas. A rotary kiln pyrolyzer is shown in Figure 27.3.

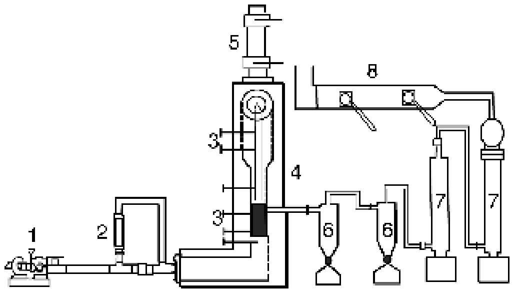

Figure 27.2 Fluidized-bed pyrolyzer [2]. 1 blower; 2 air flowmeter; 3 thermocouples; 4 fluidized-bed reactor; 5 two-stage feeder; 6 cyclone; 7 scrubber; 8 after-burner

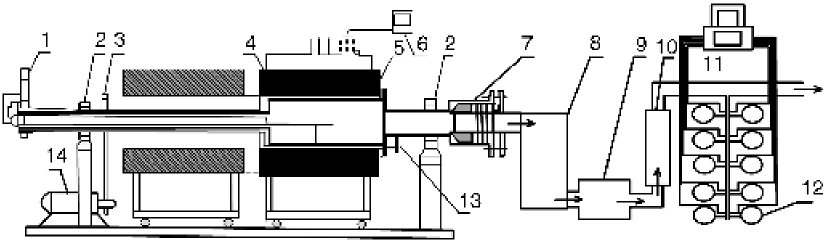

Figure 27.3 Rotary kiln pyrolyzer [2]. 1 thermometer; 2 bearing; 3 gear transmission; 4 electric furnace; 5 rotary kiln; 6 temperature controller; 7 seal; 8 two-step condenser; 9 filter; 10 total flowmeter; 11 computer; 12 gas sampler; 13 feed and discharge opening; 14 adjustable-speed motor. (Adapted from Shah, N., Rockwell, J. and Huffman, G.P., Conversion of Waste Plastic to Oil: Direct Liquefaction versus Pyrolysis and Hydroprocessing, *Energy & Fuels*, **13**, 832–838 (1999))

The furnace has an adjustable rotation rate of 0.5–10 rpm. The kiln is heated externally. The sealing of rotary kilns is a difficult task, especially for a pyrolyzer. The internal pressure of the kiln is higher than atmospheric pressure. A special friction-type seal is required for a pyrolyzer operating at high temperature. Solid waste with different shapes, sizes, and heating values can be fed into rotary kilns in batches or continuously.

3.2.3 Screw Pyrolyzer

The screw pyrolyzer, with its lower cost of construction and operation, has great prospects in the future. A screw pyrolysis conveyer is provided with internal and external heating modes. It has a special configuration for the removal of the coke formed during the process, which is a threat to heat transfer, and continuous operation. Figure 27.4 shows a screw pyrolyzer.

4 PYROLYSIS: THERMAL CRACKING/NONCATALYTIC CRACKING

4.1 OPERATION

The thermal cracking of waste plastic involves breaking of polymeric bonds by the effect of heat alone. The waste stream may comprise PP, PVC, PET, thermosetting plastic,

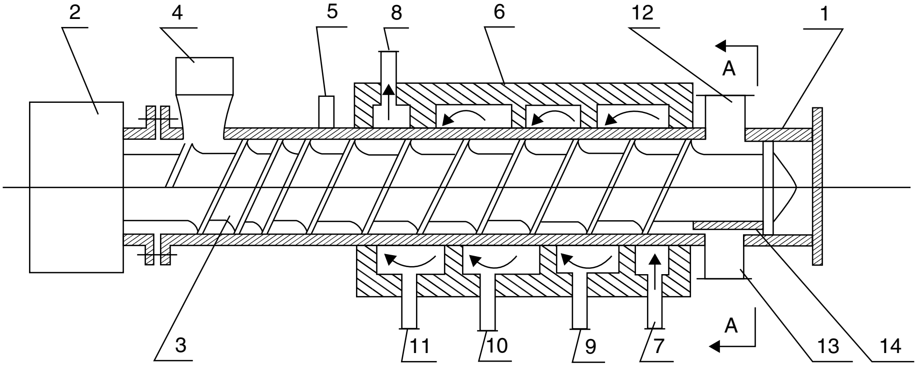

Figure 27.4 Screw pyrolyzer [2]. 1 horizontal vessel; 2 gearbox; 3 screw shaft; 4 hopper; 5 mouth for balance; 6 jacket heating; 7 inlet of heating gas; 8 outlet of heating gas; 9–11 drain pipes; 12 outlet of volatile gas; 13 char discharge; 14 baffle

paper, garbage, metals, etc. The heating medium can be sand, thermal fluid or any other suitable media. The waste plastic is first crushed to 200 mm size and sent to a kiln, which is maintained at 250–350°C. At this temperature, chlorine from the waste is discharged and the gaseous product is sent to an HCl absorber. The substantially dechlorinated waste is sent to a mechanically agitated reactor at 350–550°C, where pyrolysis occurs. A reflux tower, which is installed above the thermal cracking reactors, makes it possible to collect the light oil selectively. The heavy oil fraction, produced by thermal cracking, is condensed and returned to the thermal cracking reactor for recracking. This enables reduction of the wax fraction yield.

4.2 PROCESS MECHANISM

All matter has energy stored in its molecular structure and molecules are joined by bonds with a specific energy that holds them together. If this energy is surpassed it disintegrates into smaller fragments. Thus, in the pyrolysis process when the heat supplied exceeds different bond dissociation energies, cleavage of the bonds takes place.

4.3 DEGRADATION OF POLYMERS

When polymers are subjected to elevated temperature in an inert atmosphere they degrade by different mechanisms, which are described as follows.

4.3.1 Random Depolymerization

This kind of scission is typical of polyethylene (PE). The backbone of the polymer is broken randomly as all C–C bonds are of the same strength (Figure 27.5). Hence, the hydrocarbon chain breaks randomly and the resulting products are of the form of alkanes, alkenes and alkadienes of smaller size. This is a free radical mechanism. The covalent bond between two carbon atoms is cleaved homolytically to form fragments carrying one

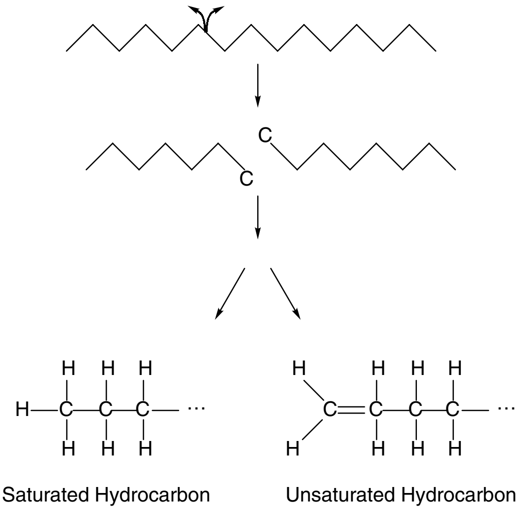

Figure 27.5 Random depolymerization

electron each. These fragments with odd electrons are called as free radicals. Random depolymerization also involves formation of free radicals at some point on polymer backbone, producing small fragments of varying chain length.

The structure of polypropylene is similar to PE, except that it possesses branched methyl groups along its backbone, making every other carbon atom in the chain tertiary as it holds a methyl group. This leads to scission of the carbon chain, predominantly between secondary and tertiary carbon atoms.

4.3.2 Side Group Elimination

This involves elimination of side groups attached to the backbone of the polymer, resulting in the backbone becoming polyunsaturated. In the pyrolysis of polyvinyl chloride, after elimination of chlorine, a conjugated double bond backbone is obtained (Figure 27.6). The conjugated chain breaks randomly at the C–C bond, leading to formation of aromatic compounds such as benzene, toluene, styrene, etc. The degradation of PVC is initiated at about 250°C with elimination of HCl. Polymers having similar structure, such as polyvinyl acetate, undergo this type of scission, resulting in formation of a conjugated double bond backbone.

4.3.3 Chain End Depolymerization

This leads to the formation of monomer. This is a free radical mechanism in which polymer is degraded to the monomer that makes up the polymer (Figure 27.7). Formation of a free radical on the backbone of polymer causes the polymer to undergo scission to form a saturated small molecule and propagate the free radical on the polymer backbone.

In PMMA there are different kinds of bonds since C–H and C=O possess high values of bond dissociation energy, whereas the bond dissociation energies of C–O and C–C

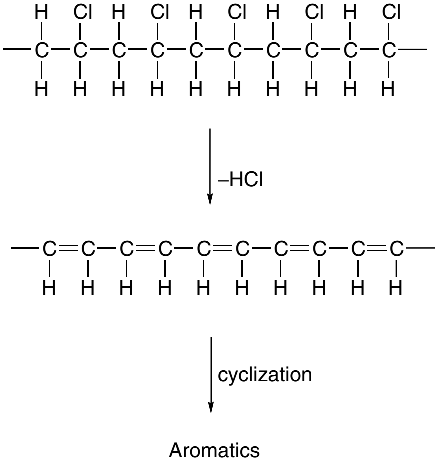

Figure 27.6 Side group elimination

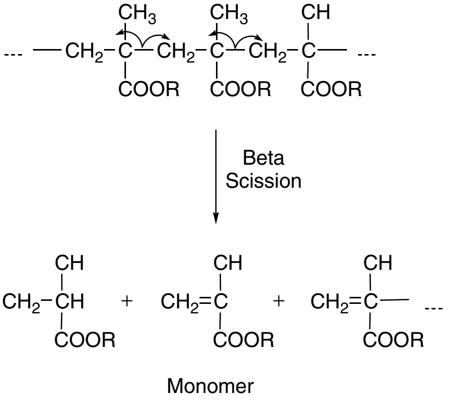

Figure 27.7 Chain end depolymerization of polymethylmethacrylate PMMA ($R = CH_3$)

are comparable so the C–C bond at the quaternary carbon cleaves first, resulting in the formation of monomer.

Apart from these three degradation mechanisms, rearrangements of the fractions formed may take place. A polymer does not undergo only one pyrolysis route always, but multiple routes may be taken simultaneously. The type of reaction is totally governed by the strength of bonds in the molecules. The lowest energy path will be favored.

5 PYROLYSIS CATALYST

5.1 ROLE AND EFFECT OF CATALYST

The catalyst plays a vital role in a pyrolysis process. Pyrolysis in the presence of catalyst requires less energy than a noncatalytic process and results in formation of more branched

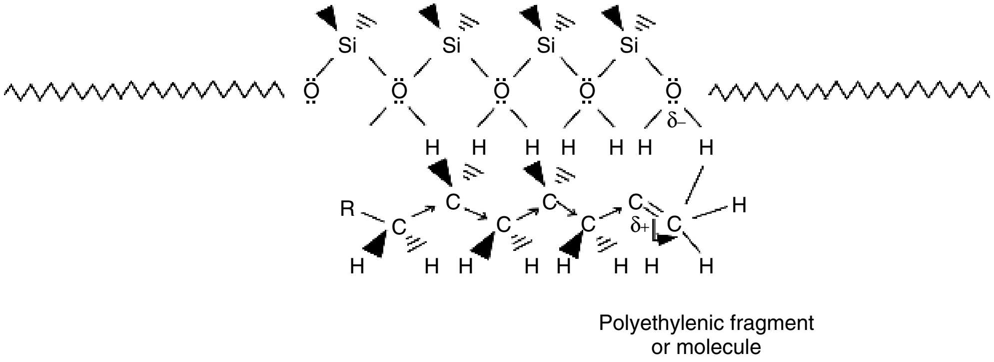

Figure 27.8 Mode of fragmentation

hydrocarbons (Figure 27.8). The use of an acid catalyst allows the pyrolysis temperature to be reduced. A catalyst reduces the pyrolysis initiation reaction time, and improves output quality and quantity of the product. The catalysts employed are silica–alumina, synthetic or natural zeolite, synthesized fly ash catalyst (treated with NaOH), which may be impregnated with NiO, HZSH-5, $FeCl_2$, etc.

A typical catalyst comprises 20–25% zeolite, 30–35% clay and matrix bound by about 20–30% silica or alumina binder.

Among all varieties of zeolites, the zeolites with 10-membered oxygen rings in their structure and medium pore size, ZSM-5 and ZSM-11 are remarkably stable as acidic catalysts.

In the presence of the silica formation of a carbanion ion takes place easily, thus enhancing the fragmentation reaction at lower temperature.

5.2 PROPERTIES OF CATALYST

The catalyst is an important factor in the pyrolysis process. Various properties of catalysts also govern the output product in pyrolysis.

5.2.1 Chemical Properties

- *Micro activity test (MAT).* This test was developed and standardized by ASTM (ASTM-D-3907). In the MAT test, a sample of cracking catalyst is contacted with gas oil in a fixed-bed reactor. Gas chromatographic analysis on gas and liquid products is used to determine the yield structure. Recently, the MAT conditions have been adapted to simulate commercial units more accurately in terms of contact times. A higher catalyst activity results in improved conversion and higher regenerator temperature.
- *Hydrogen factor.* This is a relative number proportional to the specific hydrogen yield, defined as specific $H_2 = H_2$ yield (100-conversion)/conversion. The hydrogen factor depends on the catalyst quality and is affected by nickel deposited on an equilibrium

catalyst. The trend of the hydrogen factor is of importance and this can be correlated with the H_2/CH_4 ratio in the unit.

- *Zeolite* are porous sodium aluminosilicates. Among them only Y zeolites are used in catalytic cracking. They are preferred because of appropriate pore size (6.5–13.5 Å), high thermal and hydrothermal stability and good acidity. They can be further tailored into ultrastable Y (USY) zeolites by varying the SiO_2/Al_2O_3 ratio and rare earth content.
- *Alumina (Al_2O_3).* Alumina is present in several components of the catalyst such as zeolite, clay (kaolin) and active matrices. The alumina content of catalyst can often be used to calculate the degree of exchange when switching to a different catalyst.
- *Rare earth RE_2O_3 wt%.* The rare earth content of a zeolite indicates the hydrogen transfer activity. Higher rare earth content results in more hydrogen transfer and consequently reduces the product olefinity and research octane level liquid fuel. Hydrogen transfer terminates the cracking reaction. Thus, reducing cracking from gasoline to LPG. The specific activity increases in general with rare earth content.
- *Sodium.* Sodium acts as a catalyst poison, it neutralizes acid cites. High sodium level in a catalyst destroys the zeolite. Such catalyst is more sensitive to high temperature due to increased rates of sintering and surface area destruction; eventually plugging of cyclone diplegs may occur due to formation of low-melting eutectics.Cyclone diplegs are the means used to return catalyst collected in cyclones to the reactor. Large additions of fresh catalyst are required to cope with sodium poisoning.
- *Nickel.* Nickel is introduced with feed and deposited on the equilibrium catalyst. Nickel enhances nonselective cracking reactions, particularly those producing more hydrogen.

5.2.2 Physical Properties

- *Surface Area (SA, m^2/g).* The surface area is the measure of the catalyst activity (as long as the same catalyst types are compared) and has a strong effect on the performance of an Fluidized Catalytic Cracking Unit (FCCU). High surface area also results in increased adsorption of hydrocarbons, and a higher steam rate in the stripper may be required. The zeolite and matrix surface areas of a catalyst can be analysed separately. Matrix pores provide access of the hydrocarbons to the active zeolite sites and matrix surface area often correlates with the bottoms conversion activity of the catalyst or the Light Cycle Oil (LCO) yield at constant conversion.
- *Apparent bulk density (ABD, g/ml).* ABD is determined by measuring the mass as a known volume of catalyst settles freely under its own weight. A higher ABD improves cyclone efficiency, in general. Its effect on catalyst circulation depends on the unit design and operation, as well as the particle size distribution.
- *Particle size distribution (PSD).* The PSD is an indicator of the fluidization properties of the catalyst. In general, fluidization improves as the fraction of 0–40 μm particles is increased. However, a higher percentage of 0–40 μm particles will also result in

greater catalyst losses. The catalyst manufacturers control the PSD of the fresh catalyst, mainly through the spray drying cycle. In the spray dryer, the catalyst slurry must be effectively atomized to achieve proper distribution from the particle size distribution; the average particle size (APS) is calculated. It is not actually the average size of the catalyst particles, but rather the median value.

- *Pore size.* The pore size distribution of the catalyst matrix plays a key role in the catalytic performance of the catalyst. An optimum pore size distribution usually helps in a balanced distribution of smaller and larger pores, and depends on feedstock type and cracking conditions. The pore size distribution of the matrix changes when another component is added; e.g. by adding 35–40% kaolin to a silica–alumina gel, a pore structure with a significant amount of micropores can be obtained. Figure 27.9
- *Pore volume.* Pore volume is an indication of the quantity of voids in the catalyst particles and can be a clue in detecting the type of catalyst deactivation that takes place in a commercial unit. Hydrothermal deactivation has very little effect on pore volume, whereas thermal deactivation decreases pore volume.
- *X-ray crystallinity.* This characteristic is generally indicative of the zeolite content of the catalyst. It is determined by measuring the area of one or several peaks in the X-ray diffraction pattern of the catalyst and expressing it as a percentage of the corresponding area of a reference material (usually a well–crystallized Na Y Zeolite). X-ray crystallinity measurements are often used by refiners to monitor the quantity of fresh and equilibrium catalysts.
- *Loss on ignition (LOI, wt%).* LOI is determined by measuring the loss of weight (mostly water) upon ignition at 815°C for an hour. The measurement is required because catalysts are paid for on a dry basis. LOI has no effect on catalyst performance. This test is performed only on the fresh catalyst.
- *Attrition index (AI, wt%).* A fresh catalyst sample is subjected to high-velocity fluidization for a long time. In this process, wear on the particles occurs as they are

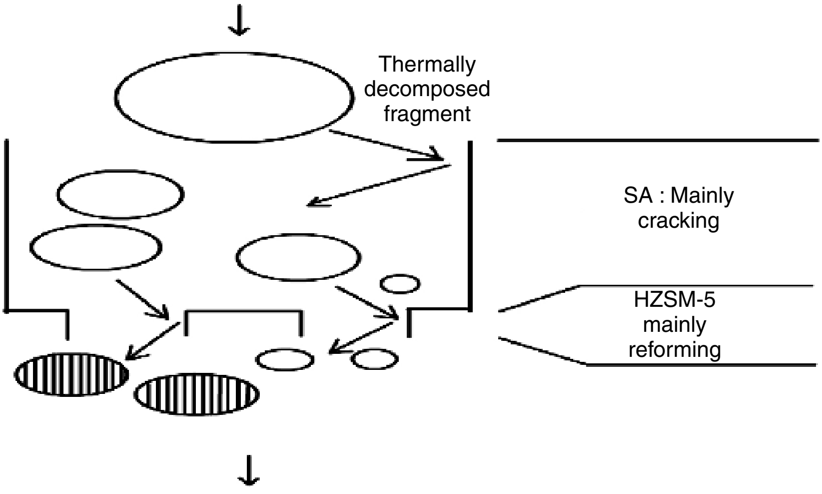

Figure 27.9 Role of zeolite in pyrolysis

blown against each other and against the wall with a high velocity. The fines formed are then weighed. The attrition index is defined as the weight % of fines generated during the fluidization, with respect to the weight of fresh catalyst, excluding fines, before fluidization. A high AI implies high resistance to attrition. AI levels up to 10 yield low catalyst losses in fines.

6 PYROLYSIS: OUTPUT CHARACTERISTICS

6.1 EFFECT OF TEMPERATURE ON PYROLYSIS PRODUCTS

Polymers are formed by a –C–C–bond skeleton. When a polymer is subjected to pyrolysis, the heat supplied is utilized for breaking this skeleton and thus the process is endothermic. At higher reaction temperature conversion of polymer to lower hydrocarbons increases with temperature and the presence of catalyst A higher ratio of thermal to catalytic cracking suppresses hydrogen transfer in the C_2–C_6 range and enhances the olefinity, but decreases the degree of branching. Thus diene concentration of LPG and gasoline increases markedly with temperature. The quality and quantity of output product also depends upon the rate at which the temperature is raised.

If the contact time is very short it limits the secondary reaction, which contributes to gas and coke. This results in a reduction of quantity and quality of gas and coke.

The cracking mechanism of polymers follows first-order kinetics.

6.2 BY-PRODUCTS OF PYROLYSIS

Pyrolysis is the process of thermal degradation of hydrocarbons in an oxygen-starved environment in the presence or absence of catalyst at temperature about 500–700°C for plastic. This process is utilized for the degradation of plastic to lower hydrocarbons. The physical state of products depends upon the size of hydrocarbon fraction. Broadly, these products are classified as solid, liquid and gases. The total output product by weight is equivalent to total input of feedstock; hence if the percentage of solids or gases decreases; there is a corresponding increase in the percentage of the liquid fraction and vice versa.

Gaseous products include LPG range gases; liquid products include liquid hydrocarbons; solids include coke/residue. The average composition and properties of the output products depend upon the following factors.

- properties of catalyst (as discussed earlier);
- operating conditions;
- pressure.

Operating condition can have a great impact on the properties of liquid output, its composition as well as the overall percentage output of solid, liquid and gaseous product. When the temperature is increased, rate of reaction increases. Approximately for every 40°C rise in temperature, the decomposition rate doubles.

When the reactor pressure is high, then the residence time also increases which results in more unsaturation in the product and hence lower octane number of the gasoline is obtained. When the reaction is carried out at atmospheric pressure, shorter contact time reduce the chances of secondary cracking and hydrogen transfer reactions, thereby increasing the olefinity in the liquid product.

When pyrolysis is performed under vacuum, the spectrum and quality of products obtained is distinct from other pyrolysis processes (atmospheric). The advantage of reduced pressure is that the secondary decomposition reactions of gaseous hydrocarbons are limited.

7 PYROLYSIS OF HETEROATOM POLYMERS

During the pyrolysis of mixed waste plastic, one of the main problems associated with the feedstock recycling is the presence of plastic containing hetroatoms, e.g. PVC, ABS, PVDC, etc. Efforts are made to remove the heteroatoms before pyrolysis. Chlorine can be removed either by thermal degradation or by using a catalyst. The HCl generated in the process can be used as industrial hydrochloric acid.

7.1 PYROLYSIS OF PVC

PVC degrades around 250–300°C, giving HCl. The mechanism of PVC degradation is highly complex in nature; the free radical path seems to play a major role. The probable mechanism is that a free radical $R^\bullet$, produced either by impurity or by reaching a desired temperature, attaches to a methylene group and subtracts H with simultaneous transfer of the free radical site onto the chain. The labile chlorine atom which is at a β-position with respect to the free radical chlorine atom is now released as a free radical and stabilizes the structure.

PVC is basically colorless and turns deep yellow-orange, brown or black, depending upon concentration of conjugated double bonds, which in turn depends on the degree of degradation. The role of HCl in this reaction is catalytic since the degradation is accelerated as soon as HCl is evolved. Thus, chlorine is removed from PVC in inorganic form. Sometimes if chlorine is not removed effectively, then during pyrolysis Chloro-organic fuels will be obtained. Chloro-organic compounds containing waste-plastic-derived oil is not useful, as it causes corrosion of equipment.

Azaruddin *et al.* [3] carried out dechlorination for removal of organic chlorine composite catalyst system without using hydrogen in the dechlorination reaction. The catalyst was stable in the presence of HCl. The catalyst deactivated with time due to the adsorption of HCl produced during the reaction on the catalyst surface.

In their study of decomposition of PVC, they reported that metal oxides with a large enough metal ion radius such as iron oxide are able to dechlorinate the PVC by attracting chlorine and weakening of C–Cl bonds in PVC and Chloro-organic compounds. Iron oxide initially acts as catalyst and under the reaction conditions it is converted to iron chloride by reacting with HCl. The iron chloride phase is also active for dechlorination of chloroorganic compounds.

Alternatively, HCl formed in the process can be collected separately and utilized for various industrial purposes.

Moriyama and Yoshioka [4] carried out dechlorination of plastic by extracting with a 50% NaOH solution at 250–300°C. The chlorine content was removed quantitatively and reduced to 0.012%. A mixture of NaOH, water and a sample of waste plastic were heated in an autoclave inserted in a Ni tube fitted with a stirrer to 250–300°C for 3 h under N_2. The degree of dechlorination was calculated by chloride ion concentration in NaOH solutions using an ion chromatograph. The chlorine content in the product dropped only to 120 ppm at 300°C for 2 h, but increased gradually on lowering the temperature to 270 ppm at 275°C.

Yamada *et al.* [5] developed a PVC recycling system with an integrated dechlorination pyrolysis process in which PVC waste plastics are crushed to optimum size in order to remove the chain from PVC. The dechlorination is carried out in a rotary kiln furnace; coarse coke is supplied to prevent an agglomeration of PVC particle and adhesion to the inner wall of the kiln.

Shiraga and Uddin [6] carried out thermal and catalytic degradation of mixed plastic containing PVC. The solid acid catalyst employed in this study is silica–alumina with a chlorine sorbent such as goethite hydrated Iron Oxide FeO (OH). The dechlorination ability effects of contact mode, liquid phase contact, (LP) or vapor phase contact (VP) were studied. Dechlorination results show that the vapor phase contact was more effective for chlorine removal.

Zadgaonkar in India developed a dechlorination method by heating PVC with coal where the chlorine from PVC is removed quantitatively. The waste plastic and coal with additive AZ_5 is heated to a temperature of 200–225°C. The HCl gas evolved is absorbed over distilled water. In this process coal acts as a hydrogen supplier and thus the unsaturation of dechlorinated polymer backbone decreases. The Zadgaonkar process has proved to be economically viable.

7.2 PYROLYSIS OF ABS

ABS containing brominated flame retardant is widely used for computer casings. ABS with or without flame retardant also contains nitrogen as heteroatom. The majority of nitrogen concentrates in the liquid product. If nitrogen remains as organic compounds during the Pyrolysis it can produce toxic hydrogen cyanide (HCN). Thermal degradation of ABS gives oil with high a content of benzene derivatives and also contains organic nitrogen as aliphatic and aromatic nitriles or nitrogen-containing heterocyclic compounds. This can be avoided by removing nitrogen before pyrolysis. Brominated flame retardants in ABS give organic bromine compounds in oil. Liquid hydrocarbon products from ABS-Br degradation are distributed in the range C_5–C_{23} with a majority of C_6, C_9 and C_{16} hydrocarbons. The majority of bromine is present in wax products. Removal of bromine before pyrolysis is a better option to avoid bromine contamination in output products.

8 REFINEMENT OF PYROLYSIS OUTPUT PRODUCTS

8.1 REMOVAL OF UNSATURATION AND OLEFINIC PRODUCTS

The major products in the pyrolysis of plastic are liquid hydrocarbons (50–80%), which on fractional distillation separate into gasoline, kerosene, diesel and LCO. As discussed earlier the operating conditions and type of catalyst largely affect the properties of the liquid hydrocarbons. For a given type of zeolite catalyst, lowering the rare earth level will result in a lower rate of hydrogen transfer relative to cracking; consequently the gasoline fraction will contain more olefins. An increase in gasoline olefinicity initially causes a boost in Research Octane Number (RON) and a less sharp increase in Motor Octane Number (MON). At still higher olefinicity, the RON response levels off and the MON gain vanishes. Further improvement requires a zeolite type with high carbonium ion cracking to enhance isomerization and cyclization reactions.

There are two methods for upgrading the fuel obtained in pyrolysis of plastic

a) upgrading the catalyst;
b) upgrading the liquid hydrocarbon obtained in the process.

Besides feed properties and operational variables, the type of catalyst has a profound effect on final olefins level in the gasoline product. Catalysis with better metal tolerance, especially to nickel and vanadium, are most suitable for olefin reduction. Catalyst capacity to saturate olefins and to form corresponding paraffins depend upon the hydrogen transfer index (HTI).

$$\text{Hydrogen transfer index} = \text{Isobutane(wt\%)/total } C_4 \text{ wt\%}$$

A shape-selective catalyst such as ZSM-5 cracks midrange C_7-C_{10} gasoline olefins to smaller olefins C_2-C_6 in the light gasoline range. Thus, boosting the octane number is due to formation of branched paraffins. This can be achieved by maintaining a high silica: alumina ratio (Y-zeolite). Another method to reduce olefins is cracking in the presence of hydrogen. This is also called destructive hydrogenation and leads to the formation of saturated compounds of lower molecular weight.

$$C_8H_{18} + H_2 \xrightarrow{\text{Hydrocracking}} \begin{array}{c} C_3H_8 + C_5H_{12} \\ \text{(Propane + pentane)} \end{array}$$

Hydrocracking leads to high conversion to gasoline and also produces high-quality diesel fuels.

8.2 VARIOUS EXAMPLES OF PYROLYSIS

Lingaiah *et al.* [7] carried out catalytic dehydrochlorination of PVC-containing waste plastics-derived fuel oils over $FeCl_2/SiO_2$ catalyst. This catalyst selectively dechlorinates the chloroalkanes with high activity, except for an initial deactivation due to formation HCl. The $FeCl_2/SiO_2$ catalyst was prepared by an impregnation method using the required amount of aqueous iron (II) chloride solution. The dechlorination of the fuel oil was carried out over 6 wt% $FeCl_2/SiO_2$ catalyst at 350°C. It is noteworthy that the carbon number distribution of the fuel oil does not change significantly during dehydrochlorination.

Miskokzi *et al.* [8] studied the cracking characteristics of low-density PE in the presence of different zeolite catalysts (Figure 27.10); H-ZSM-5, FCC catalysts and clinoptilolite

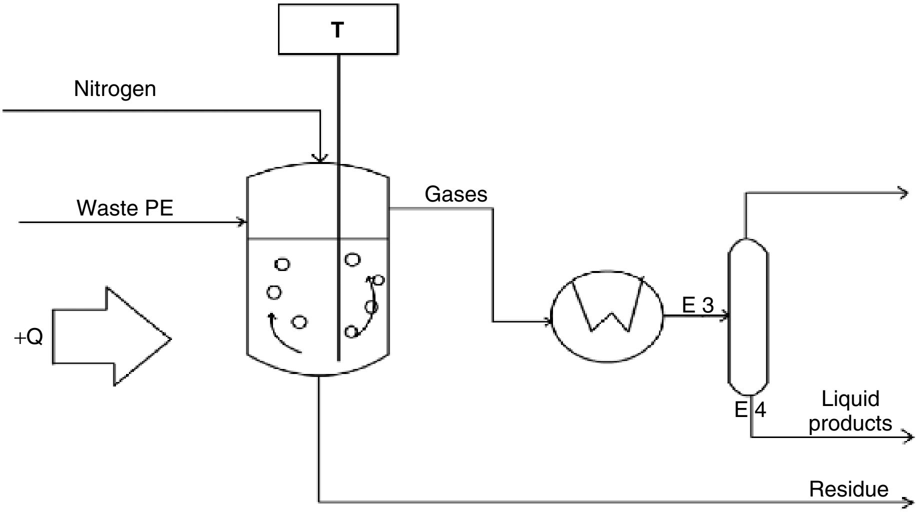

Figure 27.10 Pyrolysis of LDPE (Miskolczi)

containing rhyolite tuff (CRT) were used. The catalyst affected the yield of volatile products most significantly, whereas the composition of the gas remains unaffected.

Further, each catalyst had a significant effect on the position of double bonds and olefinic content. The catalyst also affects the other properties of liquid fraction such as density. A decrease in density of the liquid indicates low average molecular weight. They also observed that the pour points were lower with ZSM-5 and FCC catalyst than with CRT. Maximum distillation temperatures of liquid products were lower after catalytic cracking than for thermal cracking.

Uemichi *et al.* [9], carried out chemical recycling of polyethylene by catalytic degradation into aromatic hydrocarbons using H-Ga silicate. This exhibits excellent catalytic activity towards the formation of aromatic hydrocarbons, mainly benzene, toluene and xylene. This catalyst is less acidic than H-ZSM-5, but the acid sites are significantly stronger than those on silica–alumina which exhibit low cracking activity. H-Ga silicate is highly effective as a catalyst for the production of aromatic hydrocarbons such as benzene, toluene and xylenes; important raw material accounted for most of the aromatic products.

Huffman *et al.* [10], studied the effect of different catalyst on liquefaction of plastic and coprocessing of coal with plastic. The various catalyst used were HZSM-5, ZrO_2–WO_2, $TiCl_3$–SiO_2, Al_2O_3, and TiO_2–SiO_2; of these HZSM-5 gave the best oil yield and total liquid yield. Although other catalysts tested have little effect on the quantity of oil produced at temperatures greater than 430°C, they improve the oil quantity.

It is also reported that thermal pyrolysis gave a gasoline fraction of about 27% while the HZSM-5 oil product exhibited a gasoline fraction of 42%; other catalysts gave intermediate gasoline fractions ranging from 28 to 38%

Roy *et al.* [11] carried out vacuum pyrolysis of used tyres, with a bench-scale reactor and with cross-ply tyres as feedstock. When the pyrolysis of rubber is carried out under vacuum the spectrum of quality products obtained is distinct from the usual atmospheric pressure pyrolysis process. The vacuum pyrolysis enables the recovery of commercially useful products such as pyrolytic oil containing *d*,*l*-limonene. The naphtha fraction (IBP $<160°C$) used as a high octane number component for gasoline middle distillate shows lubricating properties like heavy oil used as feedstock for production of needle coke (aka "acicular coke") is a highly crystalline petroleum coke used in the production of electrodes for the steel and aluminium industries.

8.3 COMPARISON OF PYROLYSIS OF PE AND PP

Different types of polymer degrade into liquid products at different temperature and form hydrocarbons with structural differences according to the structure of the parent polymer. The liquid hydrocarbons obtained by pyrolysis of PE are widely distributed from C_3 to C_{25} and are composed of linear olefins and paraffins. The liquid hydrocarbons obtained from pyrolysis of PP are also distributed in the range C_3–C_{25}, but the gasoline fraction obtained in PP pyrolysis has a higher octane number compared with gasoline obtained from PE pyrolysis.

Both these polymers are linear polymers made up of a C–C backbone, with the only difference that in PP one of the hydrogens in ethylene is replaced by a methyl group. Hence the carbon atom which holds the methyl group becomes tertiary and scission occurs mainly between secondary and tertiary carbon atoms, whereas in PE, all carbon atoms on the polymer backbone are the same, and scission can occur randomly between any two carbon atoms.

9 RECENTLY DEVELOPED INNOVATIVE TECHNOLOGIES

9.1 THERMOFUEL OF WASTE PLASTIC BY OZMOTECH

Ozmotech have developed a Thermofuel process whereby waste plastic is converted into diesel by thermal degradation in the absence of oxygen. In this process the plastic waste is first melted and then cracked in a stainless steel chamber at a temperature of 350–425°C under inert gas (nitrogen). The catalytic reaction tower is designed in such a way that hot pyrolytic gases take a spiral or zigzag path to maximize contact area and time with the metal catalyst. The metal catalyst cracks hydrocarbon chains longer than C_{25} and reforms chains shorter than C_6. This leads to the formation of saturated alkanes.

The catalyst is not consumed or poisoned, unlike zeolite catalysts. The catalyst metal plate needs periodic cleaning and polishing.

Polymers containing heteroatoms other than carbon and hydrogen, such as chlorine, oxygen, nitrogen, etc. (polyurethane, Nylon, PVC, ABS, PET) are not suitable for the process as they may cause problems such as plant corrosion and poor fuel quality.

9.2 CONVERSION OF WASTE PLASTICS TO FUELS: ZADGAONKAR'S PROCESS

The author has developed a process (see Figure 27.11) for depolymerization of waste plastic which results in the formation of lighter hydrocarbons. The products obtained can be classified into three categories: (a) solid–coke 5–7%; (b) liquid–fuels 75–80%; and (c) gases (LPG range) 15–20%. Laboratory-scale and bench-scale processes operate in batch mode and consist of the following steps:

1. Depolymerization,
2. Fractional distillation.

9.2.1 Process Description of Commercial Plant

The *feed system* consists of sizing equipment for sizing hard, thick flexible and thin flexible materials, which normally constitute the municipal waste stream. The system essentially consists of sorters and sizing equipment such as a crusher, a cutter and a shredder. The various sizes and shapes of the material are sorted into categories suitable for crushing, cutting and shredding. The sorted material is crushed, cut or shredded and graded to uniform size for ease of handling and melting. The unwanted organic waste, mud, metal, etc. are also separated in the process of sizing and grading. The graded material is passed through cyclone filters to separate fine dust, clay and other impurities from the graded waste plastic pieces. This process of sizing, grading and cleaning the waste is semiautomatic. The cleaned feed is stored in a surge hopper before feeding to the process by a conveyor feeder.

The graded and cleaned particles of waste plastic are then introduced into a *melting/preheating system* with an extruder feeder. The hard metal, clay and sand, glass, etc. are separated here by sedimentation, and then the waste plastic is charged in the dechlorination section. The solid metal, glass, etc. is removed from the melting/preheating section periodically.

The *dechlorination section* of the plant consists of components which together effect release of chlorine from plastics such as PVC in the presence of coal and additives. The hot viscous waste plastic is fed from the upper end of the vessel and allowed to heat up at 220–250°C. The coal acts as a source of hydrogen required for the reaction. The released gaseous hydrochloride travels upwards through the vessel and is discharged to gaseous product recovery.

This is a reaction involving polymer degradation by breaking the substituent groups, but not the main chain. Although the mechanism of PVC degradation is highly complex in nature, the free radical path seems to play a major role. The labile chlorine atom, which is at a β-position with respect to the free radical carbon atom, is now released as a free radical so as to stabilize the structure by substituting hydrogen. The chlorine-free radicals attack free hydrogen released from coal.

The *reactor section* of the plant consists of the reactor, which together with other equipment carries out a continuous conversion of waste plastic to fuels. The molten waste plastic, free of chlorine, nitrogen and other organic impurities, is fed in to the reactor at the top end and allowed to flow over a heated surface at 350°C in the presence of the coal and patented additives. Upon contact with the hot surface and the mixture of coal and additives, the viscous waste plastic converts to gaseous form.

The breaking of chemical bonds under the influence of heat is the result of overcoming bond dissociation energies. Organic substances such as polymers are highly heat sensitive due to the limited strength of the covalent bonds that make up their structures. Scission can occur either randomly or by a chain-end process, often referred to as an unzipping reaction.

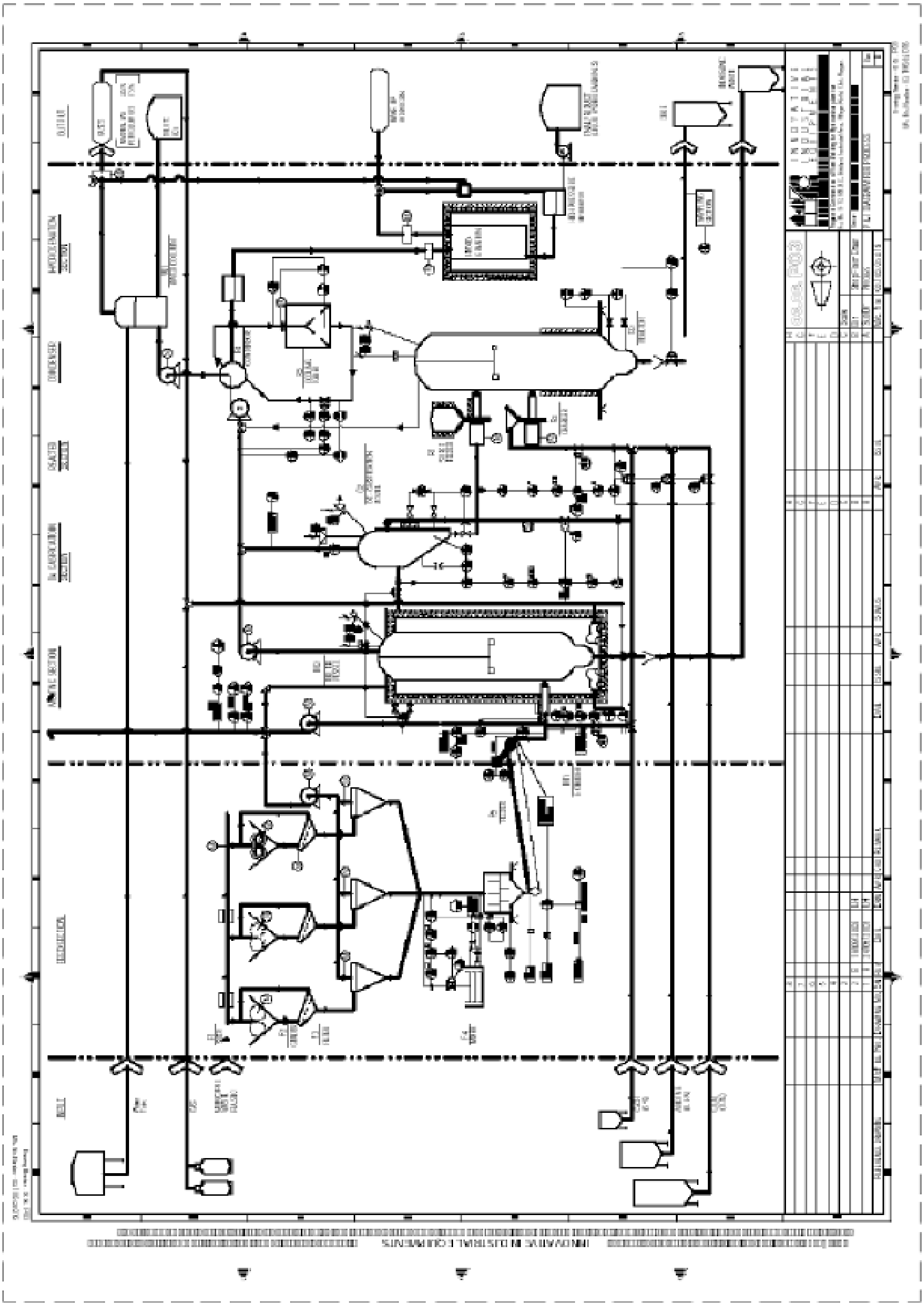

Figure 27.11 Schematic for Zadgaonkar's process for conversion of waste plastics to fuels

The reaction breaks complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable products and decrease the amount of residuals. This process rearranges the molecular structure of hydrocarbon compounds to convert heavy hydrocarbon feedstock into lighter fractions such as diesel, kerosene, gasoline, LPG, heating oil, and petrochemical feedstock.

The reaction results in the formation of gases such as methane, ethane, ethylene, propane, propylene, iso-butane, *n*-butane, hydrogen gaseous petrol, kerosene, diesel, heavy oil (CLO). The gases are subsequently allowed to pass through a condenser.

The process includes a *condenser* for continuous separation of the mixture of gases and the mixture of liquid fuels. The condensed heavier fractions are collected in the accumulator and the uncondensed gases are collected and stored separately through the vent gas stream consisting of noncondensable with gases up to C_4. The liquid hydrocarbons are subjected to fractional distillation.

The *analytical section* houses the components and instrumentation necessary for analysis and sample collection of slipstreams of gas. The gases are analysed for residual toxic gases such as furans and dioxins, as well as total organic carbon, total carbon and suspended particles.

The analytical section also houses the instruments for analyzing the process products for the quality of CNG and LPG range gases, hydrogen, gaseous hydrogen of chloride, and distilled products such as petroleum ether, gasoline-I, gasoline-II, kerosene, diesel and lubricating oil (CLO).

9.2.2 Unique Features of Zadgaonkars' Process

A) The process is 100% eco friendly.
B) This process is not only a solution to the waste plastic problem, but can change the global economic scenario by saving millions of dollars in imports of crude oil.
C) This is a unique process through which 100% of waste is converted into value-added products.
D) Percentage composition of output can be altered by changing/adjusting reaction conditions.
E) Liquid fuel obtained in the first stage i.e. Depolymerisation, can be directly utilized as fuel for DG sets, thereby generating electricity through a nonconventional waste plastic source, for applications such as agricultural pumps, as well as producing, boiler fuels, marine fuel, fuel oil and input feed for petroleum refineries. Gaseous fuel can be utilized as domestic or industrial fuel.
   Solid fuel (coke) can be utilized in thermal power plants and metallurgical industries. (*Note:* The utilization of solid, liquid and gaseous fuels is certified by the Indian Oil Corporation, Government of India.)
F) Any type of waste plastic (i.e. Polypropylene, Polyethylene, PET, PVC, ABS, etc.) in isolation or in combination can be converted into value-added fuel.

A full fledged commercial plant based on continuous mode is operating successfully since February 2005, at K-13, Butibori Industrial Area, Nagpur, India, which is now under expansion.

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28

Converting Waste Plastics into Liquid Fuel by Pyrolysis: Developments in China

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1 PROGRESS IN CONVERTING WASTE PLASTICS INTO LIQUID FUEL BY PYROLYSIS

Since the 1970s, shortage of energy and environmental pollution have become more and more serious. As a way to ease this problem, the pyrolysis of waste plastics for recovery of liquid fuel has been paid more and more attention, and various pyrolysis technologies have been developed. The thermal cracking technology for waste plastics was investigated in the early 1970s [1]. It was found that under high temperature, the carbon chains can be broken up and various monomers, active molecular groups and some small molecules will be formed. As a result, liquid products with relatively high H/C ratio can be obtained. The process and mechanism of thermal cracking have been studied extensively [2–4], and a series of thermal cracking processes such as the United Carbon process [5], the Hamburg University process [6] and the BP process [7] were developed and industrialized.

The thermal cracking process is characterized by low costs and simple operation, but the high energy consumption and the low conversion efficiency and yield have seriously hampered its development. To improve the quality and yield of liquid fuel, great efforts have been made by many researchers and a large number of experimental studies have been carried out by introducing suitable catalysts [8–30], as listed in Table 28.1. The use of catalysts can not only lower the activation energy, reduce the energy consumption and increase the treatment efficiency, but can also improve the selectivity and quality of products significantly. Some plastic pyrolysis processes have been developed and commercialized, such as the Veba process [31], the USS process [32] and the Mazda process [33]. The Veba process has been shut down recently. Further improvement of the quality and

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Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels Edited by J. Scheirs and W. Kaminsky © 2006 John Wiley & Sons, Ltd ISBN: 0-470-02152-7

Table 28.1 Laboratory experiments on catalytic plastics cracking

Investigator	Reactor	Plastics species	Catalysts
Uemichi *et al.* [8–11]	Flow reactor	PE, PP	Silica–alumina, CaX zeolite, activated carbon, metal supported on silica–alumina or activated carbon
Ishihara *et al.* [12–16]	Batch flow reactor	PE, PP, PS	Active charcoal, silica–alumina, NaY zeolite
Mordi *et al.* [17, 18]	Sealed reactor	LDPE, PP	HZSM-5, H-mordenite, H-theta-1 zeolite
Beltrame *et al.* [19, 20]	Flow reactor	PE, PS	Silica gel, alumina, silica–alumina, rare earths, Y and H-Y zeolites
Vasile *et al.* [21–23]	Flow reactor	LDPE, HDPE, PP	Silica–alumina, ZSM-5 zeolite, dealkylation catalyst
Ueno *et al.* [24, 25]	Flow reactor	PE, PS	Silica–alumina, HZSM-5 zeolite, active carbon, metal oxides
Sakata *et al.* [26–28]	Flow reactor	LDPE, HDPE, PP, PET, PVC	Silica–alumina
Gongzhao Liu *et al.* [29]	Continuous agitator reactor	PE, PP, PS	Silica–alumina, aluminate
Zhiyuan Yao *et al.* [30]	Flow reactor	PE, PP, PS, PVC, PET	Reformed ZSM-5 zeolite

yield of liquid fuel products can be achieved by cracking–catalytic reforming [34–36], which is also called the ‘two-step’ process. This kind of process has been widely applied in industry with good results. Currently, processes using this technology include the Fuji recycling process [37, 38], the BASF process [39], the Likun process [40], the Hunan University process [41, 42] and so on.

2 THEORY OF PLASTICS PYROLYSIS

2.1 MASS BALANCE FOR THE PYROLYSIS PROCESS

Waste plastic may be converted into gasoline-range hydrocarbons by pyrolysis [43]. The thermal cracking of waste plastics proceeds by typical random decomposition, with products being mainly alkanes, alkenes as well as high-boiling-point hydrocarbon products (carbon number > 24). The products of catalytic cracking are, however, composed of more iso-alkanes and aromatics, which are highly desirable gasoline-range hydrocarbons. Reforming catalysts have the highest selectivity to aromatics, and the products after catalytic reforming are mainly aromatics.

All the plastics have their own activation energy when cracked. The corresponding reaction temperatures required are different. At appropriate temperature, pressure and with a suitable catalyst applied, high yield of high-commercial-value products such as gasoline and diesel can be achieved. PE and PP will be degraded under high temperature (>350°C) and the yields of light fractions will keep growing with the increase of temperature: at low temperature, the products will be mainly composed of high-boiling-point hydrocarbon and polymers; At moderate temperature (400–500°C), gas will account for 20–40% of the products, liquid 35–70% and residue 10–30% [45]. At high temperature (≃800°C), the main products will be ethylene, propylene and methane [46]. When LDPE is pyrolyzed for 2 h at 420°C, the products will be mainly composed of olefins (60%), terminal olefinic bond hydrocarbons (35%) and non-terminal olefinic bond hydrocarbons (5%). High yield of oil products (94.5%), mainly C_{10}–C_{30}, hydrocarbons will be achieved by pyrolysis of HDPE at 400–450°C, and the gas fraction, which is mainly hydrogen gas and hydrocarbon (C_1–C_5), will account for only 5.5% of the products. At 400°C, a conversion rate of 95% is achieved. The oil products mainly consist of C_9 hydrocarbons (mainly composed of 2,4-dimethylheptene) and C_6, C_{11} and C_{14} hydrocarbons. When PP is pyrolyzed in a fluid-bed reactor at 450–640°C, a conversion rate of 50–85% can be achieved. And if catalyst is introduced, oil products with a research octane number (RON) of 83 can easily be obtained by hydrogenation of PP in a high-pressure reactor. The liquid fuel obtained is absolutely qualified for gasoline use. If water is added, the RON can even reach as high as 86, and 40% of the oil products will be alkenes.

The components of products from thermal and catalytic cracking of HDPE, LDPE, LP, PP, PS were analyzed [48], and the results are shown in Table 28.2 and Table 28.3. The products from thermal cracking of HDPE, LDPE and LP (linear polyethylene) are mainly wax-like substances at normal temperature. The fraction under 200°C recovered from HDPE accounts for 16% of the total cracking products, while that from LP accounts for 23%. Compared with the products of PE, PP produces less solid residue, but more liquid components, and PS produces the highest proportion of liquid fraction, which is 99.17% by thermal cracking and 99.56% by catalytic cracking.

In another experiment conducted by Sakata [49], the degradation of PE produced liquid products which consisted of C_5–C_{25} hydrocarbons with a yield of 70 wt%. In contrast, the degradation of PVC produced only 4.7 wt% liquid products which consisted of C_5–C_{20} hydrocarbons while the degradation of PET surprisingly produced no liquid products. The addition of either PVC or PET to PE decreased the overall liquid product yield, however, it promoted the degradation of PE into low-molecular liquid hydrocarbon products.

Table 28.2 Mass balance on thermal cracking of polyolefins

Feedstock	HDPE	LDPE	LP	PP	PS
Liquid yield (%)	91.30	91.71	93.80	91.05	99.02
State of liquid products at normal temperature	Milk white Wax	Milk white Wax	Milk white Wax	Yellow Solid and liquid mixture	Rufous Liquid
Gas yield (wt%)	7.61	7.42	5.60	7.60	
Coke yield (%)	0.14	0.15	0.14	0.14	0.15
Total (%)	99.05	99.28	99.54	98.79	99.17

Rufous = reddish-brown

Table 28.3 Mass balance on catalytic cracking of polyolefins

Feedstock	HDPE	LDPE	LP	PP	PS
Liquid yield (%)	76.81	77.40	85.20	87.20	86.20
State of liquid products at normal temperature	Solid and liquid mixture	Solid and liquid mixture	Light yellow liquid	Light yellow liquid	Rufous liquid
Gas yield (wt%)	14.04	14.08	8.15	9.34	0.34
Coke yield (%)	8.30	8.04	6.52	3.35	13.02
Total (%)	99.15	99.79	99.87	99.89	99.56

2.2 ENERGY BALANCE FOR THE PYROLYSIS PROCESS

The temperature required in the process of catalytic cracking of waste plastics is much lower than that of thermal cracking, and further heat supply is unnecessary when the catalytic bed is preheated to some extent, because the energy carried by the gas products from the reactor is enough to sustain the required reaction temperature. Therefore, only the energy balance on the thermal cracking part is discussed here for simplification. Take PE for example, after degradation and condensation, PE is converted into liquid fuel (a mixture of gasoline and diesel oil) and gas fuel. To simplify the calculation, the average molecular weight of PE is taken as 8.75×10^4, and the average degree of polymerization is considered to be 3125. The components of fuel gas, gasoline, diesel oil and residual oil are represented by C_3H_8, C_8H_{18}, $C_{16}H_{34}$, $C_{30}H_{62}$ respectively.

2.2.1 Energy Balance Calculation

The mass flow of thermal degradation of PE is shown in Figure 28.1. For the thermal degradation of 1 kg PE feedstock, the overall energy needed [51] is calculated by:

$$Q = \sum_{\text{out}} n_i H_i - \sum_{\text{in}} n_i H_i \tag{28.1}$$

where Q is the overall energy required in the thermal cracking process (kJ), n_i is the molar number of component i (mol), H_i is the enthalpy of component i (kJ mol^{-1}).

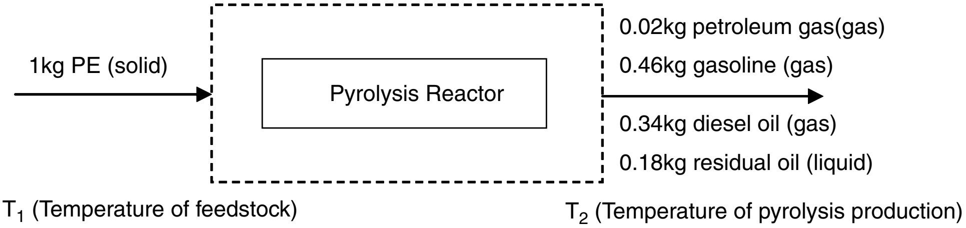

Figure 28.1 Mass Flow of PE pyrolysis

According to Equations (28.2–28.4), the enthalpy of formation of C_3H_8, C_8H_{18} and $C_{16}H_{34}$ (all gases) at temperature of T_2 can be calculated respectively [52]:

$$\Delta H_f(C_3H_8, g, T_2) = -59.94 \text{ kJ mol}^{-1},\ \Delta H_f(C_8H_{18}, g, T_2) = -92.88 \text{ kJ mol}^{-1}$$

$$\Delta H_f(C_{16}H_{34}, g, T_2) = -156.08 \text{ kJ mol}^{-1}$$

$$C_nH_{2n+2}(g, T_1) \xrightarrow{\Delta H} C_nH_{2n+2}(g, T_2) \tag{2}$$

$$\Delta H_f(C_nH_{2n+2}, g, T_2) = \Delta H_f(C_nH_{2n+2}, g, T_1) + \Delta H \tag{3}$$

in which,

$$\Delta H = \int_{T_1}^{T_2} cp(C_nH_{2n+2}, g, T)\mathrm{d}T \tag{4}$$

According to Equations (28.5–28.8), the enthalpy of formation of $C_{30}H_{62}$ (liquid) at T_2 is obtained: $\Delta H_f(C_{30}H_{62}, l, T_2) = -384.69 \text{ kJ mol}^{-1}$

$$C_{30}H_{62}(g, T_1) \xrightarrow{\Delta H_1} C_{30}H_{62}(g, T_b) \xrightarrow{-\Delta H_V} C_{30}H_{62}(l, T_b) \xrightarrow{\Delta H_2} C_{30}H_{62}(l, T_2) \tag{5}$$

$$\Delta H_f(C_{30}H_{62}, g, T_2) = \Delta H_f(C_{30}H_{62}, g, T_1) + \Delta H_1 - \Delta H_V + \Delta H_2 \tag{6}$$

$$\Delta H_1 = \int_{T_1}^{T_b} c_p(g, T)\mathrm{d}T \tag{7}$$

$$\Delta H_2 = \int_{T_b}^{T_2} c_p(l, T)\mathrm{d}T \tag{8}$$

in which T_b and ΔH_v are the boiling point and the heat of evaporation under normal pressure.

Based on the amount of mass flow of products and the enthalpy of formation calculated, the overall output enthalpy is obtained, which is -808.6 kJ kg^{-1}. Under the conditions of 101–203 MPa, 200–300°C, the overall output enthalpy can be obtained as -2124.7 kJ kg^{-1} according to Equation (28.9):

$$\begin{aligned} &n(CH_2 = CH_2)(g, T_1, 0.1\text{MPa}) \longrightarrow n(CH_2 = CH_2)(g, T_r, 0.1\text{MPa}) \longrightarrow \\ &n(CH_2 = CH_2)(g, T_r, 150\text{MPa}) \longrightarrow (\text{-}CH_2 = CH_2\text{-})_n(s, T_r, 150\text{MPa}) \longrightarrow \\ &(\text{-}CH_2 = CH_2\text{-})_n(s, T_1, 0.1\text{MPa}) \longrightarrow (\text{-}CH_2 = CH_2\text{-})_n(s, T_r, 0.1\text{MPa}) \end{aligned} \tag{9}$$

in which T_r is the reaction temperature.

According to Equation (28.1), the total energy needed for the thermal degradation of PE can be obtained as 1316.1 kJ kg^{-1}.

2.2.2 Estimation of Energy Profit

Supposing PE is converted to gasoline, diesel oil, residual oil and fuel gas, the net energy profit can be obtained by:

$$Q_j = \sum w_i Q_i - Q \tag{10}$$

Table 28.4 The components and yield of thermal degradation products of PE

	Gasoline	Diesel oil	Residual oil	Petroleum gas
Percentage (%)	43–49	31–37	17–19	1–3
Yield/(mol kg^{-1})	3.77–4.30	1.37–1.64	0.40–0.45	0.23–0.68

Table 28.5 The heat values and net energy profit of various products (10^4 kJ kg^{-1})

	Gasoline	Diesel oil	Residual oil	Petroleum gas	Net energy profit
Theoretical heat value	4.320	4.290	4.180	4.620	4.170
Experimental heat value	4.462	5.263	6.571		4.900

in which w_i and Q_i are the weight percentage (shown in Table 28.4) and the heat value (kJ kg^{-1}) of component i, respectively.

The theoretical [53] and experimental heat values of various products and net energy profit are shown in Table 28.5.

Taking the heat value of standard coal (29260 kJ kg^{-1}) as the basis, the theoretical and experimental values of net energy profit for the thermal degradation of 1 kg PE will be approximated to the calorific value of 1.43 and 1.67 kg standard coal, respectively.

2.3 MECHANISM OF PLASTICS PYROLYSIS

Thermal degradation of plastics can be classified as depolymerization, random decomposition and mid chain degradation [54, 55]. In the process of depolymerization, the conjunction bonds between monomers are broken up, which leads to the forming of monomers. Depolymerization type plastics mainly include α-polymethyl styrene, polymethyl methacrylate and polytetrachloroethylene. In the random decomposition process, scission of carbon chains occurs randomly, and low-molecular hydrocarbons are produced. Random-decomposition-type plastics include PP, PVC and so on. In most cases, both decompositions take place. To be more specific, the degradation of polyolefins can be classified as the following three types:

(a) polymers are degraded to monomers;
(b) the chains break up randomly and low-molecular polymers are generated (random chain scission happens in the pyrolysis of most polyolefins);
(c) the substituent groups or functional groups are removed and low molecular polymers are produced, accompanied by the formation of unsaturated hydrocarbons and cross-linking, even coking.

A comprehensive treatment of the mechanism of plastics pyrolysis has been presented by Cullis and Hirschler [56]. Four types of mechanisms of plastics pyrolysis have been proposed:

(a) End-chain scission or depolymerization: the polymer is broken up from the end groups, successively yielding the corresponding monomers; this is also considered the main manner of polymer pyrolysis by Prakash *et al.* [57] and Songip *et al.* [58].

(b) Random-chain scission: the polymer chain is broken up randomly into fragments of uneven length.
(c) Chain-stripping: elimination of reactive substitutes or side groups on the polymer chain, leading to the evolution of a cracking product on one hand, and a charring polymer chain on the other.
(d) Cross-linking: formation of a chain network, which often occurs for thermosetting polymers when heated.

These different mechanisms and product distributions, to some extent, are related to the bond dissociation energies, the chain defects of the polymers, and the degree of aromaticity, as well as the presence of halogen and other heteroatoms in the polymer chains. Large amount of styrene monomers can be obtained by pyrolysis of PS, while a wide range of hydrocarbons are produced by random degradation of PE and PP [3, 59, 60].

Thermal degradations are carried out by a free radical mechanism, while catalytic degradation are realized by carbonium ions, which consist of hydrocarbon ions carrying a single positive charge.

A mechanisms of catalytic pyrolysis of waste plastics was proposed by Buekens [61], using PE as an example, in which FCC catalyst is adopted and the main content include:

1. *Initiation* may occur on some defect sites of the polymer chains. For instance, an olefinic linkage could be converted into an on-chain carbonium ion by proton addition. Then the polymer chain may be broken up through β-scission. Initiation may also take place through random hydride ion abstraction by low-molecular-weight carbonium ions (R^+), The newly formed on-chain carbonium ion then undergoes β-scission.
2. *Depropagation*: the molecular weight of the main polymer chains may be reduced through successive attacks by acidic sites or other carbonium ions and chain cleavage, yielding an oligomer fraction (approximately C_{30}–C_{80}). Further cleavage of the oligomer fraction probably by direct β-scission of chain-end carbonium ions leads to gas formation on the one hand, and a liquid fraction (approximately C_{10}–C_{25}) on the other.
3. *Isomerization*: the carbonium ion intermediates can undergo rearrangement by hydrogen or carbon atom shifts, leading to, e.g. a double-bond isomerization of an olefin. Other important isomerization reactions are methyl group shift and isomerization of saturated hydrocarbons.
4. *Aromatization*: some carbonium ion intermediates can undergo cyclization reactions. An example is when hydride ion abstraction first takes place on an olefin at a position several carbons removed from the double bond, the result being the formation of an olefinic carbonium ion. This carbonium ion could undergo intramolecular attack on the double bond, which provides a route to cyclization and formation of aromatics.

2.4 METHODS FOR PLASTICS PYROLYSIS

There are mainly three methods for pyrolysis of plastics, namely: thermal cracking, catalytic cracking, and cracking–catalytic reforming [62]. Each has its own suitable process, as shown in Figure 28.2. Other methods for plastics pyrolysis include hydrogenation

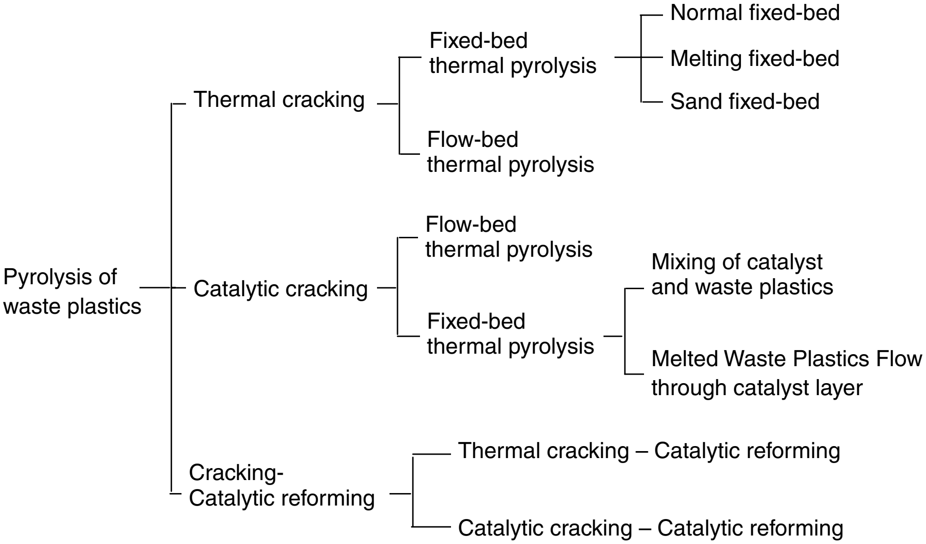

Figure 28.2 Main methods for waste plastics pyrolysis and their relative processes

[63, 64], gasification [65, 66], pyrolysis in supercritical water [67, 68], coliquefaction with coal [69–71], and so on.

2.4.1 Thermal Cracking

Thermal cracking is the simplest form of waste plastics pyrolysis. In the process of thermal cracking, plastics are degraded simply by heat, which overcomes the required activation energy [72]. The process is simple, but quite rough at the same time, and hydrocarbons with a wide range of boiling points are produced; furthermore, the yields of oil products (mainly gasoline and diesel oil) are low. The gasoline obtained contains large amounts of olefins and has a very low RON value. The diesel oil produced is high in freezing point and low in cetane value. Most products of PE by pyrolysis are straight-chain alkanes and α-alkenes [48].

2.4.2 Catalytic Cracking

In the process of catalytic cracking, characteristic reactions such as chain scission, hydrogen transfer and condensation take place under certain temperature and pressure conditions and when an appropriate catalyst is utilized, products with certain range of molecular weights and structures are obtained. Catalysts with surface acid sites and with the ability of hydrogen ion donation such as silica–alumina and molecular sieve catalyst have been already widely utilized. These catalysts can also enhance the isomerization of products and increase the yield of isomeric hydrocarbons. However, large amounts of coke will deposit on the surface of catalysts and consequently lead to their deactivation. Therefore, the recycling of catalysts is difficult to achieve.

With thermal cracking and catalytic cracking taking place at the same time, the process can achieve very high reaction rates. Large amounts of isomers and aromatics can be produced in a short period of time. The catalyst is usually mixed, however, with sand contained in the plastics and the coke produced, which will result in difficult recycling. To solve this problem, various processes have been developed such as precleaning the waste plastics and making the melted plastics flow through a bed of catalyst [73–75].

2.4.3 Cracking–Catalytic Reforming

In cracking–catalytic reforming (also called the two-step process, as distinct from the one-step process described above), plastics are first cracked under high temperature and then undergo catalytic reforming; oil products with relatively high quality are finally obtained the end. The liquid fuel products of thermal cracking consist mainly of hydrocarbons with a wide range of boiling points, among which the yields of light fraction such as gasoline and diesel oil are low, and the quality is poor. In order to improve the RON, the content of isomers, cycloparaffins and aromatics must be improved, which can be achieved by catalytic reforming. To further raise the reaction rate, catalysts can also be added during thermal cracking. High yields of liquid fuel with good quality can be obtained by the cracking–catalytic reforming process; moreover, the operation is flexible. This method is also suitable for the treatment of mixed waste plastics, and most important of all, the catalysts can be recycled. All these have greatly contributed to the fast development of this technology and made it the most widely applied process in industry.

2.4.4 Other Methods

Hydrogenation [63, 64] or hydrocracking involves the pyrolysis of plastics under a hydrogen atmosphere at a pressure of approximately 10 MPa, in three steps: depolymerization; hydrogenation of the liquid phase; and hydrogenation of the products. Owing to the presence of hydrogen, saturated hydrocarbons are produced in the reaction process. Moreover, plastics containing heteroatoms (e.g. Cl, N, O, S) can be easily treated by hydrogenation.

Gasification [65, 66] is the partial oxidation and pyrolysis of plastics under high temperature, with steam and oxygen as gasification agents. This process produces products which consist mainly of H_2, CO, CO_2 and CH_4. No pretreatment is needed here, and mixtures of various plastics, even mixtures of plastics and municipal solid waste, can be easily degraded. And most of all, this technology can effectively prevent coking.

Pyrolysis in supercritical water [67, 68]: owing to the many special characteristics of supercritical water, waste plastics can be degraded efficiently in supercritical water, which has recently received great attention has been studied comprehensively. This technology can not only realize the recovery of valuable products from waste plastics, but also provide a solution to the ever-growing energy crisis and environmental pollution. No catalysts or reaction agents are needed here, so the cost is very low.

Coliquefaction with coal [69–71]: in the process of coal and waste plastics coliquefaction, the hydrogen atoms contained in plastics transfer from plastics to coal, leading to partial or even total liquefaction of coal. On the one hand, as hydrogen donors, plastics can reduce the hydrogen consumption for coal coliquefaction dramatically. On the other hand, the existence of coal as catalyst can also greatly promote the pyrolysis of plastics. This technology has not only provided a solution for the ‘white pollution’ problem, but also reduced the cost of coal coliquefaction.

3 PROCESS OF PLASTICS PYROLYSIS

A series of industry-scale processes for recovery of liquid fuel from waste plastics have been developed and applied in countries such as the United States, Japan, Germany and England. Some of the processes, such as the Veba process, the BP process, the Fuji process and the Hunan University process have been applied widely and successfully in industry. Some typical pyrolysis processes are listed in Table 28.6.

3.1 VEBA PROCESS

In the Veba process [31], a mixture of vacuum residue, lignite and waste plastics is pyrolyzed under conditions similar to the case of crude oil hydrogenation. The main products include gaseous hydrocarbons, alkanes, cyclanes and aromatics.

The main difference between Veba process and other processes lies in that hydrogenation technology is used in this process, which improves the quality of products. At the same time, waste plastics are stirred and fully mixed by hydrogen. This whole apparatus is capable of disposing of 40 000 tons of waste plastics per year, but is relatively complicated and expensive.

3.2 BP PROCESS

The BP process [7] is based on a sand fluidized-bed pyrolysis reactor. The cracking temperature is kept at 400–600°C. Low-molecular hydrocarbons can be obtained. The process mainly involves converting waste plastics into normal linear hydrocarbons, the average molecular weight of which is 300–500. Most plastics can be treated by this process. Polyolefins are decomposed into small molecules with the same linear structure. PS is converted into styrene monomers and PET into mixture of hydrocarbons, carbon monoxide and carbon dioxide. A maximum of 2% PVC is allowed in this process, and the content of chlorine in the products is lower than 5 ppm. The distribution of alkene products in this process is like that in petroleum pyrolysis. The BP process was industrialized in 1997.

The biggest difference between this process and the others lies in the reactor, which was originally a fixed-bed reactor. A sand fluidized-bed reactor has been adopted for the BP process, which can guarantee a uniform temperature in the reactor due to the uniform particle size and fluidized nature of sand. In traditional processes, because of the poor heat transfer properties of plastics, a uniform temperature is difficult to achieve in the plastics feedstocks so a long reaction time was always required. On the other hand, after waste plastics are heated and melted, they usually adhere to the surface of reactors owing to their poor flow characteristics. The BP process has successfully solved all these problems, and a continuous production of liquid oil is achieved.

Table 28.6 Typical pyrolysis process of waste plastics

Developer	Scale	Feedstock	Reactor	Temperature (°C)	Catalyst	Main products	Yield of products (%)
United Carbon Company	35–70 kg/d	PE, PP, PS, PVC, PA, PET	Extruder	420–600		Wax	
Japanese Carbon Company		PE, PP, PS	Extruder	500–600		Monomers	
Fuji Recycle Company	5000 t/a	PE, PP, PS (industrial waste)	Melting furnace	390	ZSM-5	Gasoline	80–90
Fuji Recycle Company	4000 t/a	PE, PP, PS, PET (PC<15%)	Melting furnace	310	ZSM-5	Light oil, kerosene	80–90
USS	250 kg/h	PE, PP, PS, PET, FRP	Batch agitator reactor	400	Al,Ni,Cu	C_9 fuel oil	80–90
Mitsubishi Heavy Industry	170 kg/h	PP	Melting furnace	550		Light oil	95
Sanyo Engine Company	128 kg/h	PE, PP, PS	Melting furnace	510–560			68
Mitsu Ship Company	24∼30 t/d	PE, polymers with low molecular weight	Agitator tank	420∼455		Fuel oil	85
Veba Company	40000 t/a	polyolefins	Hydrogenation reactor		Lignite	Fuel oil	
BP Company	20 kg/h	PS, PET	Sand flow-bed reactor	400–600		Petrochemicals	
Japan Physics and Chemistry Research Institution	300 t/d	Thermoplastic polymers	Melting furnace	First phase: 200–250 Second phase: 360–450	Al,Ni,Cu,etc.	Gasoline, kerosene	

(*continued overleaf*)

Table 28.6 (*continued*)

Developer	Scale	Feedstock	Reactor	Temperature (°C)	Catalyst	Main products	Yield of products (%)
BASF Company		PVC < 5%	Melting furnace	400–500		Fuel oil, fuel gas, α-olefins	90
Mazda Company	2 kg/batch	PE, PP, PS, PU, ABS	Electric furnace	400–500	$AlCl_3$, $ZrCl_4$, etc.	Gasoline, kerosene	60
Hamburg University	80–240 kg/d	PE, PS, PVC	Flow-bed reactor	640–840		Aromatics	
Hamburg University		PE, PS, PVC	Molten salt reactor	600–800		Aromatics	
Hunan University	1 t/h	Waste plastics, heavy oil	Flow-bed reactor	430–450	YNN, silica–alumina/ PPA zeolite	Gasoline, kerosene	75–80
Amoco Company		PE, PP, PS	Melting furnace			Hydrocarbons	
China Likun Company		PE, PP, PS				Gasoline, kerosene	

3.3 FUJI PROCESS

The Fuji process [37, 38] is a typical two-step process, as shown in Figure 28.3. Waste plastics are converted into gasoline, kerosene and diesel oil by pyrolysis and reforming over ZSM-5 catalyst. After being crushed, the waste plastics enter the molten bath through an extruder and are mixed with the part of uncracked plastics which was returned from the thermal cracking reactor. Then the mixture is heated to 280–300°C in the molten bath and then enter the thermal cracking reactor and are pyrolyzed at a temperature of 350–400°C. The products of thermal cracking enter the catalytic reforming reactor and are converted into gasoline, kerosene and diesel oil, with a yield of 80–90%. This process has the following characteristics: first, a centrifugal blender is used, which can greatly accelerate the heat transfer process and stir the melted material by cycling them from the thermal cracking reactor to the molten bath. Furthermore, it can avoid the accumulation of residue in the molten bath. Second, recycling instead of mechanical stirring of plastics is adopted in this process, which is a big difference between this process and others. Finally, the process makes full use of the low decomposition temperature of PVC, with HCl being removed before the pyrolysis of mixed plastics takes place.

3.4 BASF PROCESS

The BASF process [39] has some resemblance to the Fuji process; it is also a two-step process, and a PVC content lower than 5% is required in the feedstocks. The waste plastics are melted at 250–380°C and volume reduction and better uniformity are achieved. In this process, relatively cheap alkaline solid substances such as calcium oxide, sodium carbonate or other alkalis in solution are used to remove HCl by absorption. Depending on the different plastics processed, oil product yields ranging from 20 to 70% can be achieved. This process is suitable for the treatment of mixed plastics containing heteroatom contaminants.

3.5 HAMBURG UNIVERSITY PROCESS

Hamburg University [6] developed a fluid-bed reactor cracking process. In the process, plastics are fed into the reactor by a screw and cracked. The cracked gases are preheated

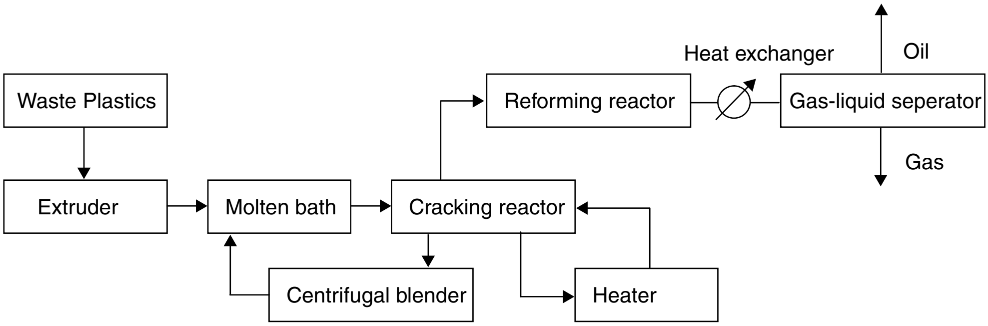

Figure 28.3 Flow chart of the Fuji process

to 400°C, passed through a heat exchanger and then separated from the solid residue and dust in a cyclone separator. A high yield of alkenes can be achieved. One advantage of this process is that the type of fluid gas is changeable, so various products can be obtained. For instance, if steam instead of hot hydrocarbon gases is adopted as the fluidizing agent, more ethylene can be recovered from PE by this process. An experimental factory which applies this technology has been built in Ebenhousen, German. The production capacity of the factory is 5000 t/a.

3.6 HUNAN UNIVERSITY PROCESS

A new fluid-bed reactor cracking process was developed by Hunan University [41, 42] and the Hunan Waste Resources Recycling Company to treat waste plastics. The process is shown in Figure 28.4. After cleaning and granulating, the waste plastics are fed to the fluidized-bed reactor by a double screw feeder, at the same time, catalysts are added while a stirrer keeps running at a velocity of 2 rpm. Waste plastics get fully cracked and the solid residue, mainly coke, sand and catalyst, is transferred to the reactivation reactor. After reactivation, the catalyst enters a cyclone separator with gas flow, be collected and finally returned to the fluid-bed reactor again. The cracked gas enters the cyclone separator, where the heavy fractions drop to the bottom and go to the reforming reactor while the light fractions escape from the top. The reformed fractions then enter a fractionating rectifying tower and are cooled. In the end, oil products such as gasoline, diesel oil and heavy oil are obtained and the residual gases are compressed and burned. Currently, a demonstration project using this process has already been put into operation in Changsha, China. It can treat 30 000 t waste plastics per year.

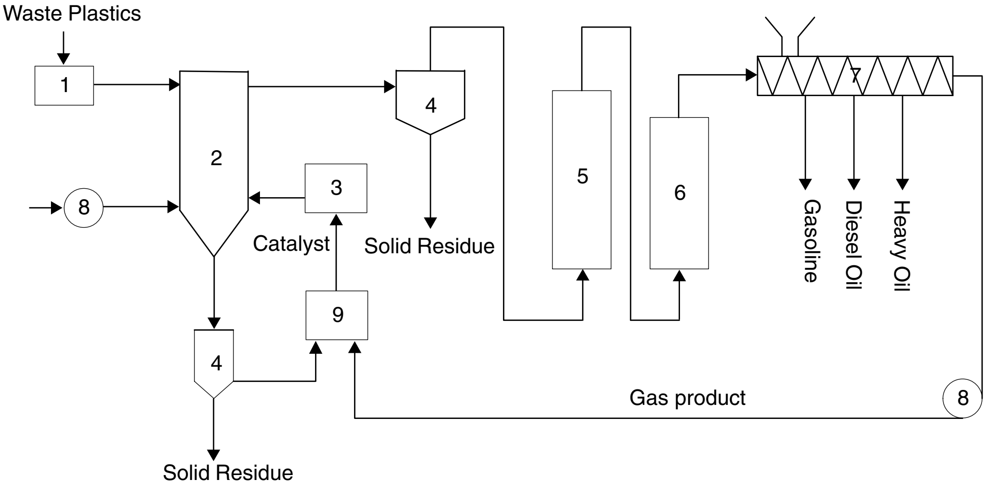

Figure 28.4 Flow chart of the Hunan University process. 1 twin screw feeder; 2 fluidized-bed reactor; 3 catalyst feeder; 4 cyclone separator; 5 catalytic reforming column; 6 rectifying tower; 7 condenser; 8 compressor; 9 reactivation reactor

3.7 UNITED CARBON PROCESS

The United Carbon plastics cracking system [5] includes four main parts: electrically-heated extruder, thermal cracking reactor, heat exchanger, and product-collecting facilities. The extruder is mainly used for compressing, melting plastics polymers and transferring them to the cracking reactor. The cracking reactor is a pipe structure which makes it easier for plastics to achieve a uniform temperature quickly. The products are cooled down in the heat exchanger before finally entering the collecting facilities. This process is suitable for all types of plastics. The reaction temperature is 420–600°C. No catalyst is added in the process, and the main product is wax. The flow chart of the United Carbon process is shown in Figure 28.5.

3.8 LIKUN PROCESS

The Likun process [40] is another two-step cracking process operated under normal pressure. The process is shown in Figure 28.6. Waste PE, PP and PS are used as raw materials for oil recovery. In the first phase, the plastics are pyrolyzed at 350–400°C. In the second phase, the cracked gases undergo catalytic reforming over zeolite at 300–380°C. The

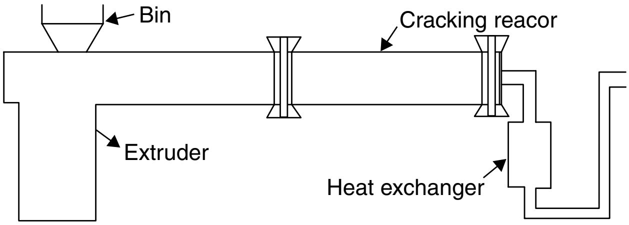

Figure 28.5 Flow chart of the United Carbon Process

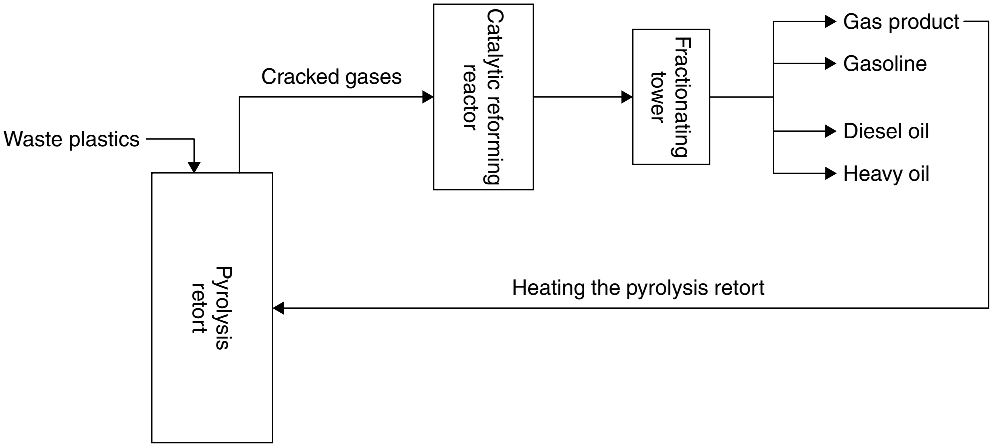

Figure 28.6 Flow chart of the Likun process

main products are gasoline and diesel oil. A conversion rate of 75% can be achieved. This process has the following advantages: (1) the process is simple, conducted under normal pressure and can achieve continuous production, and (2) high energy efficiency is achieved, so investment and operation cost are relatively low. In this process 700–750 kg gasoline and diesel oil products can be recovered from 1 tonne of waste plastics.

3.9 OTHER PROCESSES

The USS process [32] adopts a single reactor cracking system with stirrer. The upper part of the reactor acts as a catalytic reaction tower and the bottom part as the thermal cracking reactor. Although its structure is complicated, this process can reduce the total process flow path and thereby reduce the equipment and capital needed. The process can be applied in treating PE, PP and PS, but is not suitable for PVC pyrolysis.

The Kurata process [76] is a two-step process which uses thermoplastic resins as raw material and adds catalysts that consist of five metallic elements such as Ni, Cu, Al and so on. The temperatures of the two phases are 200–250°C and 360–450°C, respectively. During the cracking reaction, the polymer molecules are rearranged. Equipment for HCl neutralizing is positioned at the end of the process, so there is no clear limitation on the content of PVC in feedstocks. HCl can be easily removed at a rate of 99.91%, even when the content of PVC is as high as 20%, and the concentration of chlorine in the products is lower than 100 ppm. An important difference between this process and the others is that its products are mainly composed of kerosene.

A high-capacity oil recovery equipment was developed by Libond Industry [77] and the Macromolecule Cracking Research Institution of Japan, which is capable of treating 100 kg waste plastics per hour. The yield of coke can be controlled at less than 1%, and a high conversion rate (97%) and oil quality can be achieved. There is a screw pump and a screw roller in the center of the reactor. Plastics are fed into the reactor after being granulated, cracked under high temperature and then collected. Part of the uncracked plastics are pumped back to the reactor by the screw pump and cracked again. The solid residue is discharged from the bottom of the reactor by the screw auger. The temperature is kept at around 450°C. The plastics are rolled along the wall of the reactor throughout the whole process, so the heat loss is very small and the cracking efficiency is greatly improved. By this process, the yield of coke can be controlled at less than 1%, and a high conversion rate (97%) and good oil quality can be achieved.

4 MAIN FACTORS IN PLASTICS PYROLYSIS

4.1 TEMPERATURE

Temperature is one of the most important factors that affect the process of plastics pyrolysis. The required temperature varies with different types of plastics and the desired composition of products. At a temperature above 600°C, the products are mainly composed of mixed fuel gases such as H_2, CH_4 and light hydrocarbons; At 400–600°C, wax and liquid fuel are produced. The liquid fuel products consist mainly of naphtha, heavy oil, gasoline, diesel oil and kerosene. PE and PP are converted mainly to fuel oil and gas by pyrolysis, while PS produces more styrene monomers and light hydrocarbons. If appropriate catalysts are added, the cracking temperature can drop to 200–300°C while the yield of liquid products is increased.

4.1.1 Effects of Temperature on Thermal Cracking

With increase of temperature, the yield of gas products and light hydrocarbons(C_3–C_4)increase, while that of high carbon number products (C_{21}–C_{30}) decreases [78]. In the thermal cracking process, the proportions of the gasoline and diesel fractions in the liquid products increase with temperature, while that of heavy oil fraction decreases. The maximum carbon number of the heavy oil fraction at the end boiling point also increases with the reaction temperature. Furthermore, owing to the acceleration of dehydrogenation under high temperature, the yield of coke increases, too.

Prakash *et al.* [79] reported that the reaction time required to achieve the highest conversion rate from plastics to oil decreased with increase of temperature, and the conversion rate of plastics increased, but the selectivity of liquid fuel products decreased dramatically.

Karaduman [80] investigated the effects of temperature on the yields in flash pyrolysis of PE. The gas yield continued to increase with temperature. The yield of liquid products and the total conversion rate also kept increasing up to a certain temperature, but after this point, began to fall slowly due to partial decomposition of the expected products. The yield of solid residue decreased with the increase of temperature.

4.1.2 Effects of Temperature on Catalytic Cracking

The introduction of catalysts can lower the activation energy for plastics cracking, which can greatly lower the reaction temperature needed. But temperature is still a very important factor that can greatly affect the pyrolysis process.

High temperature can accelerate the scission of carbon chains, and as a result, gasoline yield and the conversion rate from plastics into heavy oil are improved significantly. The effects of temperature on catalytic cracking of various plastics have been investigated by Huang *et al.* [81]. With the increase of temperature, the conversion rate increases initially, but then gradually slows down and ultimately levels off. But the gasoline yield began to drop after certain temperature point, and large amounts of gas and coke are produced. It was found that the optimum temperature varies with different types of plastics. Generally, the larger substituent in the side chain, the easier the plastic can be degraded. Therefore, the order of required temperature for pyrolysis of PS, PP and PVC is: PS<PP<PVC. The main conditions and products of PE, PP, and PVC are listed in Table 28.7.

The effects of temperature on catalytic cracking of various plastics over FZ-W catalyst have been investigated [84] and are shown in Table 28.8. In the temperature range 300–350°C, the highest yield of oil products was achieved. When the temperature is below 300°C, yields of residue and noncondensed gases are low, large amount of feedstocks were left uncracked; Above 350°C, the yields of residue and noncondensed gas increased, and the amount of oil products obtained decreased relatively.

Table 28.7 Main pyrolysis conditions and products of PE, PP and PVC [82, 83]

Species	Temperature range(°C)	Catalyst	Product
PE	120–140	O_2	Olefin oxide
	350–500	H_2, $ZnCl_2$	Gasoline with high RON
	350–450	$Al_2O_3 \cdot SiO_2$	Fuel oil
	400–650	Silica–alumina	Isobutene
PP	320–380	Y-molecular sieve	Gasoline and diesel oil
	200	Cu	Ethylene chloride
PVC	350	Phosphoric acid, sodium silicate	Aromatics
	400–500	$AlCl_3$, $ZrCl_4$, etc.	Gasoline and diesel oil
PS	400–450	Solid acid, solid base, transition metal oxide	Styrene monomers

Table 28.8 Effects of temperature on yield of oil products [84]

Reaction temperature (°C)	200	250	280	300	330	350	400	450	500
Oil products yield (wt%)	60.5	61.2	63.8	70.8	75.5	71.6	68.7	64.3	60.2

4.2 CATALYST

Two sorts of catalyst have been widely applied in plastics pyrolysis [85], namely: molecular sieve catalyst or reformed molecular sieve catalyst, such as Y-zeolite and REY zeolite; metal oxide catalyst, such as silica–alumina, Al_2O_3, CuO, ZnO, Fe_2O_3, cerium oxide and Co–Mo oxide.

4.2.1 Molecular Sieve Catalyst

Molecular sieve catalyst is composed of silica oxide and alumina, with a special structure. Since its first introduction in pyrolysis of heavy oil by America Mobil Co. in the 1960s, molecular sieve catalysts have been widely used in the petrochemical industry. The quality and yield of gasoline as well as the oil production scale have been greatly improved. Similarly, a large number of investigations on the function of molecular sieve catalysts in plastic pyrolysis have been carried out, and it has been proven that molecular sieve catalyst can also greatly promote the pyrolysis of plastics and improve the quality and yield of oil products.

Catalysts tend to be deactivated in the process of plastics pyrolysis because of coke deposition on their surface. The deactivation of HZSM-5, HY, H-zeolite and silica–alumina was compared by Uemichi *et al.* [86]. In the case of PE pyrolysis and HZSM-5 added as catalyst, no deactivation occurred due to the low coke deposit, and high yields of light hydrocarbons (mainly branched hydrocarbons and aromatics) were achieved. In the case of PS, however, coke production increased dramatically, so HZSM-5 was deactivated very quickly. Silica–alumina catalyst was deactivated gradually and slowly with the increase of cracking gas, while HY- and H-zeolite molecule sieve catalysts were deactivated very quickly. Walendziewski *et al.* [87] studied the catalytic cracking of waste plastics over platinum catalyst, and more than 90% yield of gas and liquid fractions was attained at a temperature of 390°C.

4.2.2 Metal Oxide Catalyst

Metal oxide catalysts have also been widely used in the pyrolysis of waste plastics. It is reported that PET can be successively decomposed over FeO(OH) [88], a transition metal oxide catalyst with high activity. The yield of sublimate substances such as terephthalic acid or benzoic acid were greatly decreased, which effectively avoid the blockage of pipes. FeO(OH) is transformed to porous Fe_2O_3 after steam treatment above 600°C so the number of active sites on the surface increased greatly. Other metal oxide catalysts, such as ZnO and TiO_2 have also been applied [89]. Compared with the noncatalyst condition, the yields of coke and gas products decreased while the yield of liquid oil increased. ZnO can promote the forming of 2,4-dimethyl-1-heptene, but has almost no effects on other fractions. TiO_2 can restrain the formation of volatile fractions and has little influence on others.

5 PYROLYSIS OF PVC

In the decomposition process of heteroatom-containing plastics such as PVC, EVA and ABS, heteroatom contaminants are produced which may cause corrosion of equipment and deteriorate the quality of the fuel products. Therefore, these types of plastics should be treated by special process. Taking PVC as a example, it is one of the most thermally unstable polymers, 58.5 wt% of which is chlorine. HCl is generated when PVC is heated to about 300°C. Because HCl may corrode equipment, deactivate catalysts and deteriorate the quality of products it needs to be removed. Generally, HCl can be removed in three ways: before degradation, during degradation and after degradation [90].

After preliminary removal of HCl, PVC products can be further degraded at higher temperature, and linear and cyclic light hydrocarbons are produced. However, HCl can be only partially removed by the above methods, and the conversion rate of PVC to oil products is relatively low. Therefore, PVC is generally not degraded separately, but mixed with other plastics such as PE, PP, PS and PET in a certain ratio before degradation.

There are all kinds of processes and reactors for pyrolysis of PVC-containing mixed plastics which can be basically divided into three classes: thermal cracking, catalytic cracking and hydrogenation. The main products are gasoline, diesel oil, fuel gas and HCl.

In the *thermal cracking* process, reactors such as a molten bath reactor or a fluidized bed reactor are usually adopted. A special thermal cracking process for the degradation of mixed plastics containing PVC was developed by Mitsubishi Heavy Industry [91]. After being granulated to certain dimensions, the mixed plastics were transferred to the screw extruder through a nonreturn valve. Before entering the cracking reactor, the mixed plastics are heated and melted in the extruder. The molten plastics are pyrolyzed at a temperature of 400–450°C in the reactor. A condensor is installed on the top of cracking reactor, and the temperature is kept at 200–300°C. High-boiling-point substances (i.e. ‘heavies’) in the cracked gas are condensed and returned to the reactor for further cracking. The noncondensed gases are cooled to normal temperature by a cooler, and the liquid products enter the oil collector. The HCl generated in the process and other noncondensed gases pass into the absorption tower. Hydrochloric acid is obtained by mixing with water and then separated by a decanter. The other gases enter the neutralizing tank, where the residual hydrochloric acid is removed, before collection in the gas holder. A conversion rate of 55.7% was achieved in this process.

Good results were also achieved by *catalytic cracking* in the Fuji and BASF [92] processes, in which mixed plastics containing PVC were pyrolyzed over ZHSM-5 [93].

After granulation and removal of metal and glass, plastics can be mixed with oil and then cracked and removed of HCl in *a hydrogenation* reactor at 500°C and 40 MPa pressure in hydrogen atmosphere [91, 95]. A high yield of gas and oil products can be achieved by hydrogenation.

Among other methods, the recovering of fuel oil from mixtures of residual oil, lignite and plastic waste under high pressure and in hydrogen atmosphere was successfully realized by Veba [94]. Lignite acts as both feedstock and catalyst here. Na_2CO_3 and CaO are added to neutralize the HCl generated in the reaction process. Gaseous C_1-C_4, hydrocarbons alkanes, cycloalkanes and aromatics were obtained. However, the high pressure and the hydrogen atmosphere greatly increased the cost.

Another cracking technology was developed by the Toshiba company [95]. After being crushed into pieces, mixed plastics containing PVC entered the cracking reactor and were heated; highly concentrated alkali liquor is added to neutralize the HCl. After chlorine is removed, the other fractions continued to be heated and cracked in the reactor. High-quality gasoline and diesel oil products were achieved by this process.

The pyrolysis of mixed plastics containing PVC in supercritical water has also been demonstrated [96]. The temperature in the reactor increases from 200°C at the top to 1200°C at the bottom. HCl is generated in the first reaction zone. In the second zone, HCl continues to react with alkali metal and is removed, and residue and fuel gas which mainly consists of H_2 and CH_4 are produced by reaction of plastic waste and supercritical water. In the third reaction zone, part of the residue produced was oxidized and CO and fuel gases were generated.

A gasification process for mixed plastics containing PVC without special dechlorination equipment was developed by Borgianni [97]. Experimental results showed that addition of Na_2CO_3 can effectively remove the chlorine generated, the concentration of pollutants in gas products is pretty low and the fuel gas obtained can be used directly for power generation or for heating.

6 CATALYTIC REFORMING OF CRACKED GAS

The RON of gasoline obtained by thermal cracking or catalytic cracking is generally just about 80, and the flash point of diesel oil product is also very low. By isomerization and aromatization, catalytic reforming of cracked gas can greatly improve the quality of liquid fuel products.

The results of catalytic reforming of cracked gas over three isomerization catalysts (JD-01, JD-02, BJ-01, which have been developed by the oil refining industry in China) are listed in Table 28.9 [98].

It is shown that after catalytic reformation, the quality of liquid fuel produced is improved greatly. RON of gasoline reached more than 90 and the flash point of diesel oil also increased.

It has been reported [34] that normal catalysts such as silica–alumina (SA) and HZSM-5 zeolite have little effects on the reforming of waste-plastics-derived heavy oil, but good

Table 28.9 Experimental results of catalytic reforming

Catalyst	Overall yield of oil products (%)	Yield of gasoline (%)	Yield of diesel oil (%)	RON
JD-01	82.0	53.0	29.0	93.66
JD-02	80.3	52.6	27.7	91.00
BJ-01	82.4	53.9	28.9	90.28
No isomerization				83.03

results can be achieved by the application of HY and REY zeolite because they have larger hole dimensions. Under the REY condition, the gasoline yield reached 48% with a RON of 67. By comparison, under of SA and HZSM-5, the gasoline yield and RON are only 18% and 23 respectively.

The results of ZrO_2 in cracked gas reforming was compared with FCC catalyst [36]. When ZrO_2 is applied, the yield of both gasoline and diesel oil reached a very high level, and high-quality gasoline is obtained. In the case of FCC catalysts, however, both the yield and quality of liquid products are just a little better than the nonreforming case. Therefore, it is obvious that ZrO_2 is a better catalyst for cracked gas reforming.

In the Fuji process, molecular sieve catalyst is used for catalytic reforming, and the results are shown in Table 28.10.

When no reforming process is carried out in the pyrolysis of PP, 90.50% of the gasoline fraction in the products is olefin, and the yield fractions of isomerized paraffins, cycloalkanes and aromatics are very low. The gasoline has a RON of no more than 80 and is very unstable [99]. However, after reforming and fractionation [100], the results improved significantly, as shown in Table 28.11. Two kinds of molecular sieve catalysts were adopted for the process.

Table 28.10 Components and yield of products by the Fuji process [37]

Plastics	Components (%)			Yield (%)			Density g/cc
	Paraffin	Olefin	Aromatics	Fuel oil	Cracked gas	Residue	
PE+PP	48.2	13.0	38.8	80	15	5	0.8036
PS	4.8	3.7	91.5	90	5	5	0.8880

Table 28.11 The composition and properties of gasoline fraction

	Thermal pyrolysis	Thermal pyrolysis–Catalytic reforming		Catalytic pyrolysis (440°C)	
Temperature (°C) and catalyst applied	440	A(380)	B(340)	A(440)	B(440)
Paraffin	9.07	5.45	3.34	2.55	2.31
Isomerized paraffin	5.09	23.69	18.69	30.92	28.53
Olefin	81.43	53.80	61.13	48.66	52.73
Cycloalkane	3.38	6.05`	6.37	11.87	9.69
Aromatics	1.03	11.01	10.20	6.00	7.11
RON	80.0	87.3	90.8	86.6	88.6
Stability	Bad	Good	Good	Good	Good

A, B are two kinds of molecular sieve catalysts

Table 28.12 Properties of diesel oil fraction

	Thermal pyrolysis	Thermal pyrolysis–catalytic reformation		Catalytic pyrolysis (440°C)	
Temperature (°C) and catalyst applied	440	A(380)	B(340)		440
ρ_{20}(g/cm^3)	0.8568	0.8617	0.8567	0.8687	0.8674
T_{50}/°C	280	280	270	298	300
Cetane number	45.35	42.72	42.42	44.06	45.30
Stability	Bad	Good	Good	Good	Good

The characteristics of the diesel fraction by pyrolysis of PP at 440°C are shown in Table 28.12.

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