9 Chemical Recycling

9.1 Types of Chemical Recycling

Chemical (or tertiary) plastic recycling refers to processes by which at least one polymer of a plastic article is depolymerized to yield repolymerizable monomers and/or oligomers, which are recovered for producing new polymers. The chemical recycling of polymers aims mainly at saving the material resources and less at reducing the amount of waste generated by slowly degrading polymers. Chemical recycling can replace fossil fuel resources for chemical production of monomers and/or oligomers with recycled material from plastic waste.

Directive (EU) 2018/852 amending Directive 94/62/EC on packaging and packaging waste (see Chapter 10, Section 10.1) states that plastic waste can be considered as (chemically) recycled only if it is not subject to energy recovery and is processed into new materials that are not to be used as fuels (see Section 9.6) [1].

The main types of chemical recycling are solvolysis and thermolysis. A special type of chemical recycling is enzymatic depolymerization. The available processes for the depolymerization of rigid plastic packaging and nonpackaging films (e.g., agricultural films), fibers, foams, etc., can be equally applied to the depolymerization of flexible plastic packaging.

In principle, chemical recycling can enable the recovery of various polymers from multilayer flexible packaging reducing the need for the complex separation processes employed by mechanical recycling. Further, the mechanical recycling of plastics produces materials with inferior properties, and the recycling process, with the progressive degradation of the products, cannot be conducted endlessly. On the other hand, chemical recycling has not been applied so far to the depolymerization of polymers of flexible packaging because of economic considerations and other processing challenges. Chemical depolymerization has the highest product value; however, the feed for this process requires a pure plastic stream and, therefore, presorting. Chemical recycling processes are energy demanding requiring in general high temperature and/or pressure and/or the presence of catalysts.

There is no technology available for the depolymerization of polyolefins, namely polyethylenes, contained in flexible plastic packaging

Recycling of Flexible Plastic Packaging
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materials to monomers and/or oligomers with the purpose of obtaining new polymers. Most of the available technologies apply to the depolymerization of PET films and are borrowed from the chemical recycling of PET bottles.

Currently, chemical recycling represents only a marginal share of recycling (<0.5%) [2], due to its high cost [3]. Chemical recycling is still at early stages of development and is not expected to be fully operational before 2025 [3]. In the meantime, mechanical recycling will continue to play an important role in the circular economy. However, mechanical recycling has some limitations with regard to the physical and mechanical properties of the recycled product over repeated cycles and also in the food contact compliance area where certain end-use applications are temperature restricted [4]. Contaminants and additives could be accumulated in the material over several mechanical recycling cycles and might lead to poor performance or even health risks [5]. Chemical recycling addresses these issues, and when the technology is matured, it is expected to lead to the upcycling of plastic packaging waste to valuable new products. To bring it to an industrial scale, chemical recycling needs to establish a balance between economic viability, regulatory compliance, and environmental impact [5].

Chemical recycling is a promising option to recycle mixed, multilayer, or other complex plastics; it is complementary to mechanical recycling and can be a more sustainable alternative to incineration or landfill.

9.2 Solvolysis

Solvolysis refers to chemolytical processes including hydrolysis, alcoholysis, and aminolysis/ammoniolysis that break down polymers to monomers and/or oligomers, which are, then, used as feedstock for making new polymers. These chemical depolymerization processes require the addition of water or solvent (e.g., methanol or glycol) and catalyst(s) to the waste polymer followed by a purification step. Currently, solvolysis processes are mostly applicable to condensation polymers such as polyesters (e.g., PET) and polyamides. The total manufacturing costs of these recycling processes exceed that of manufacturing new polymer.

9.2.1 Hydrolysis

Hydrolysis is mainly applied to the chemical depolymerization of waste PET from packaging products including bottles and films. In hydrolysis, waste PET is reacted with water to depolymerize into terephthalic acid and ethylene glycol. The hydrolysis methods for terephthalic acid recovery are based on three mechanisms: acid hydrolysis, neutral hydrolysis, and alkaline hydrolysis.

Acid hydrolysis is carried out by making the PET react with a large excess of strong acid in solution, for example, concentrated sulfuric acid. The sulfuric acid acts in a very short period of time, say some minutes, at a temperature between room temperature and 95 °C, by dissolving the starting PET, with formation of terephthalic acid. The chemical method utilizing acid hydrolysis is scarcely applied in the industrial field, mainly due to the high corrosiveness of the reaction system and also due to the huge amount of salt solution produced for neutralizing the employed acid (2001, **EP1138663** A1, BROCCATELLI MASSIMO).

Neutral hydrolysis is conducted by treating the PET with water or steam, under pressure at a temperature between 200 and 300 °C, in the presence of appropriate catalysts. The main disadvantages of this technology are represented by high energy consumption and the difficulty of removing the impurities from the terephthalic acid obtained by precipitation, such as undissolved particulate matter and insoluble polymers originally present in the starting material (2001, **EP1138663** A1, BROCCATELLI MASSIMO).

Alkaline hydrolysis is carried out by use of alkaline hydroxides (sodium or potassium hydroxide). Use of these bases leads to formation of aqueous solutions of the terephthalate salts. These solutions can be cleared from mechanical impurities by filtering, flocculating, or settling processes. In addition, terephthalic acid is recovered from the aqueous solutions by precipitation in an acid medium, such as sulfuric acid. The main disadvantages of alkaline hydrolysis are connected with difficulties in manipulating the aggressive reagents used. In addition, there are problems connected with corrosion of these reagents, above all if they are used in solution. Further, it is impossible to obtain terephthalic acid free from undesirable yellow–pink colorations (2001, **EP1138663** A1, BROCCATELLI MASSIMO).

Although various processes are available for hydrolyzing PET waste, the purification of recovered terephthalic acid typically requires several process steps to remove impurities including inorganic compounds and salts. In addition, recrystallization and hydrogenation over noble metal catalysts are usually used to purify terephthalic acid (2007, **WO2007148353** A1 (2007, COBARR SPA; AL GHATTA HUSSAIN; HRONEC MILAN; RICHARDSON JAMES DAVID).

WO2007148353 A1 (2007, COBARR SPA; AL GHATTA HUSSAIN; HRONEC MILAN; RICHARDSON JAMES DAVID) discloses a process of recovering aromatic dicarboxylic acids from waste articles containing PET, such as films, by depolymerizing PET with water. It is possible to use waste articles containing PET and polyamide, for example, poly(m-xylylene adipamide) (nylon-MXD6) or other polymers, particularly those in the form of multilayer films. The hydrolytic depolymerization of PET waste proceeds usually in one step at temperatures between 230 and 300 °C, preferably at 260−275 °C and at a pressure sufficient to maintain liquid phase. The depolymerization reaction occurs in the presence of at least one amine such as ammonia, aliphatic amines, aliphatic aromatic amines, or aromatic amines. The amine is present at 0.05−1 wt% to PET. The depolymerization proceeds in the presence of 1−8 wt% of activated charcoal calculated to PET. The reaction mixture is passed through a fixed-bed adsorber filled with activated charcoal at 50 °C below the depolymerization temperature of PET with water. The aromatic dicarboxylic acid is separated from the reaction mixture cooled to the temperature in the range from 180 to 90 °C.

9.2.2 Aminolysis/Ammoniolysis

The reactivity of the amine group in aminolysis or ammoniolysis is higher than the hydroxyl group in alcohols or glycols used in alcoholysis or glycolysis. Further, drawbacks of hydrolysis and alcoholysis (e.g., methanolysis) such as high temperature and high pressure conditions can be avoided by aminolysis [6].

US6723873 B1 (2004, EASTMAN CHEM CO) discloses a process for recovering terephthalic acid from waste PET by ammoniolysis. In this process, PET is reacted with ammonium hydroxide to form diammonium terephthalate, which is then converted to terephthalic acid by heating at a temperature from 225 to 300 °C. Although the predominant source is discarded PET bottles, scrap PET film is also a major source of waste PET.

9.2.3 Alcoholysis

Alcoholysis processes use methanol or ethanol for the depolymerization of waste PET. In methanolysis, waste PET is reacted with methanol to produce dimethyl terephthalate and ethylene glycol. In ethanolysis, waste PET is reacted with ethanol to produce diethyl terephthalate and ethylene glycol. These reaction products may be readily purified and used thereafter to produce virgin polyester.[1]

Alcoholysis processes are also carried out under supercritical conditions for the depolymerization of waste PET. Kulkarni et al. (2011) [7] used sub- and supercritical water for the decomposition of polymer components and recovery of aluminum (Al) from waste multilayer packaging of the type PET/PA6/CPP and PET/PE/Al/PE/low-density polyethylene (LDPE), where CPP is cast polypropylene, PE is polyethylene, and PA6 is nylon 6. PET and PA6 were relatively easily depolymerized to their monomers in subcritical water, whereas polyethylene and polypropylene were depolymerized to monomers at relatively higher temperatures and reaction times.

Favaro et al. (2013) [8] used acetone for the delamination of a multilayer food packaging film of the type Al/PET/PU adhesive/(linear low-density polyethylene [LLDPE] and LDPE) and ethanol in supercritical conditions for the depolymerization of the delaminated PET. The obtained products were diethyl terephthalate and ethylene glycol. The diethyl terephthalate was obtained through precipitation in water and was of high purity and yield (80%). The ethylene glycol was purified from ethanol and water by distillation. Also, metallic aluminum was obtained by the PET-depolymerizing process. The optimal reaction time was 120 min. The polyethylene obtained during the delamination process could be easily recycled by extrusion.

9.2.4 Glycolysis

In glycolysis, waste PET is reacted with glycol such as ethylene glycol producing the monomer, bis(2-hydroxyethyl) terephthalate, and other oligomers. This process has significant advantages over methanolysis or hydrolysis primarily because the bis(2-hydroxyethyl) terephthalate may be used as a raw material in either a dimethyl terephthalate or terephthalic acid polyester production process without significant major modification of the production facility.

JP2009120766 A (2009, TEIJIN FIBERS LTD) discloses a method for recovering dimethyl terephthalate and ethylene glycol from a multilayer product such as film including at least a PET layer and a gas barrier layer made of polyamide, such as (nylon-MXD6). The method comprises the following steps: (1) shredding the film into a particle size of 1−10 mm; (2) separating the polyamide by selectively dissolving it in ethylene glycol at 110 °C or less; (3) subjecting the undissolved PET to depolymerization by

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[1] The methanolysis reactions can be viewed as the mirror images of PET synthesis reactions.

adding it into ethylene glycol comprising a depolymerization catalyst (e.g., sodium carbonate) at 210 °C or less to obtain bis(hydroxyethyl) terephthalate; and (4) subjecting the bis(2-hydroxyethyl)terephthalate to transesterification by adding it into methanol comprising a transesterification catalyst (e.g., sodium carbonate) to obtain a transesterification liquid containing dimethyl terephthalate and ethylene glycol, which are separated and recovered.

9.3 Oxidative and Catalytic Depolymerization

Depolymerization of plastics to monomers require the development of catalysts that are selective and efficient, yet preserve the functional groups in monomers, while meeting requisite cost and energy metrics [9]. The following technologies use selective catalysts for the depolymerization of polyethylene films. The obtained chemical compounds are used for making chemicals, fuels and polymers (e.g. polyamides and polyurethanes).

Recently, there have been attempts to depolymerize polyethylene into chemical compounds such as dicarboxylic acids by oxidative depolymerization. BioCellection, a social impact for-profit start-up, has developed a technology that is suitable for the treatment of polyethylene, with a current focus on plastic films including LDPE bubble packaging films, plastic bags, plastic wrap, and combinations thereof [10] (2019, **US2019322834** A1, BIOCELLECTION INC). BioCellection's process, termed Accelerated Thermal Oxidative Depolymerization (ATOD), accelerates the depolymerization of post-industrial and post-consumer polyethylene waste into oxygenated monomers. The process uses an oxidant-based technology operating at less than 200 °C to selectively oxidize polyethylene chains into chemical compounds with less than 50 carbon atoms. An example of oxidizing agent is nitric acid, optionally in combination with a catalyst (e.g., zeolite). The oxidant is then recaptured and recycled back into the system (see Fig. 9.1). The final product is a mixture of dicarboxylic acids that can be synthesized into higher value products via synthetic chemistry or used as biological substrates for synthetic biology [11].

A microwave-assisted oxidation process was developed for the recycling of LDPE waste using nitric acid as the oxidizing agent. LDPE freezer bags were used as model LDPE. After only 3 h of microwave-assisted recycling in 0.1 g/mL nitric acid solution, the freezer bags were converted mainly into dicarboxylic acids with a yield of 71%, and the carbon efficiency of the process was 37%. Because of its favorable transition state, succinic acid was the main degradation product. By adjusting the recycling

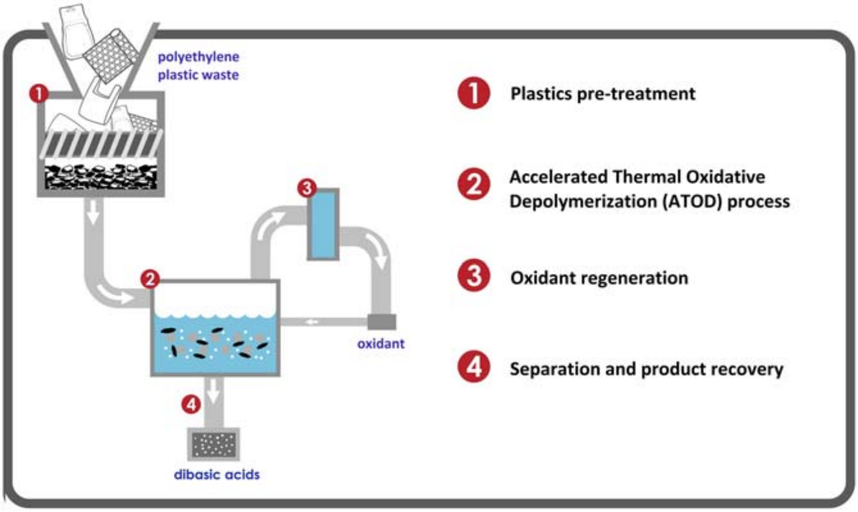

Figure 9.1 Selective oxidation for the conversion of polyethylene to chemical compounds (image provided by BioCellection).

time and nitric acid concentration, the length of the dicarboxylic acids could be tuned to some extent. Microwave-assisted recycling of polyethylene waste is a promising technique for retaining the intrinsic material value of the polymer via chemical recycling to functional chemicals [12].

EP2407528 A (2012, GREENMANTRA RECYCLING TECHNOLOGIES LTD) discloses a process and an apparatus shown in Fig. 9.2 for converting mixed polyethylene waste to make waxes and grease base stock through catalytic depolymerization, comprising the following steps: (1) preheating the mixed polyethylene waste, preferably in an extruder attached to a high pressure reactor, to form a molten mixed polyethylene waste; (2) starting depolymerization reaction of the molten mixed polyethylene waste using a catalyst in a high-pressure reactor at a desired temperature of about 300 to 600 °C using heaters in the high-pressure reactor and wherein the catalyst is disposed on a stirring blade; (3) allowing progression of the depolymerization reaction of the molten mixed polyethylene waste to continue until a pressure in the high-pressure reactor reaches a desired value; and (4) turning off the heaters and stopping the depolymerization reaction of the molten mixed polyethylene waste on the pressure in the reactor reaching the desired value and wherein the mixed polyethylene waste is converted to wax or a grease base stock. The catalyst used is $(Fe{-}Cu{-}Mo{-}P)/Al_2O_3$. The catalyst is prepared by binding

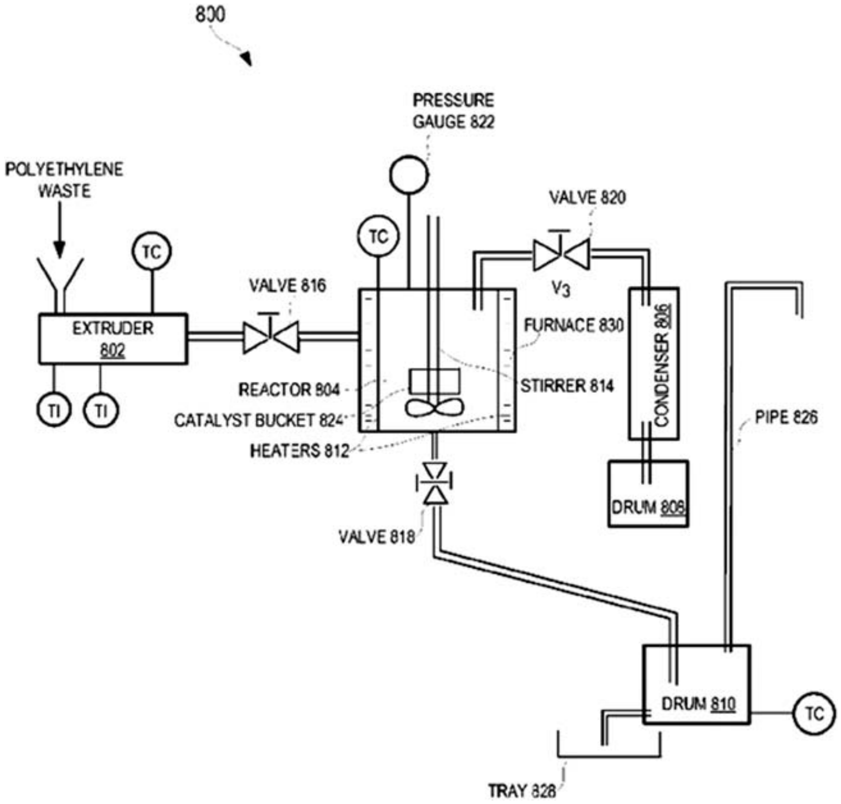

Figure 9.2 Block diagram of the apparatus (800) for producing waxes and grease base stocks through catalytic depolymerization of waste plastics (2012, **EP2407528** A, GREENMANTRA RECYCLING TECHNOLOGIES LTD).

a ferrous-copper complex to an alumina support and reacting it with a heteropolyacid to obtain the final catalyst. The mixed polyethylene waste includes LDPE, LLDPE and HDPE. The polyethylene waste may be available as shopping bags, grocery bags as sacks of HDPE or milk pouches of LDPE.

9.4 Chemical Pyrolysis

Chemical pyrolysis is a process of thermal and chemical depolymerization of waste plastics in an oxygen-depleted environment with the goal of recovering monomers and/or oligomers (see also Section 9.6.3).

WO2018018153 A1 (2018, PYROWAVE INC) discloses a microwave-assisted pyrolysis process for the depolymerization of waste plastics for the production of monomers, waxes, and heavy oils comprising the steps of: (1) steam purge of the plastic and a catalyst (preferably, 0.5−2.5% w/w in a container); (2) pyrolysis of the plastic and the catalyst in the container with a microwave for a time sufficient to allow generation of heat providing a thermal treatment between 300 and 650 °C through absorption of microwaves (915−2450 MHz) by the catalyst; (3) condensing the waxes in a first condenser having an operating temperature sufficient to maintain the waxes liquid, and the monomers and heavy oils in a vapor form, to provide a condensed waxes fraction; and (4) condensing the monomers and heavy oils in a second condenser having an operating temperature lower than the first condenser and sufficient to maintain the monomers and heavy oils liquid and provide a condensed monomers and heavy oils fraction, or a combination thereof. The catalyst comprises a compound having a high dielectric loss to absorb microwaves, transfer heat to the plastic, and initiate a pyrolysis reaction. The catalyst may be the carbonaceous residue (char) from a previously performed pyrolysis reaction. The waste plastics include LDPE, HDPE, PVC, PET, and polystyrene and can originate from packaging. The plastic may be shredded before the steam purge.

BASF developed the so-called ChemCycling technology, which involves using mixed plastic waste to produce virgin polymers through thermochemical processes [13]. BASF started its ChemCycling project in 2018 in partnership with Recenso GmbH (formerly Alphakat Engineering GmbH), which has developed a process to convert mixed plastic fractions into processing oil [14] (2014, **DE102012022710** A1, ALPHAKAT GMBH). Recenso's catalytic tribochemical conversion process is a single-step catalytic liquefaction process using a combination of thermal, catalytic, and physical forces for cracking hydrocarbon (1995, **WO9503375** A1; 1996, **EP0713906** A1 BASF AG). The primary outputs of the process are ethylene and propylene. These chemicals are converted into basic plastic granulate (polyethylene and polypropylene) that can be used to produce packaging films, etc. The technology can be applied to the recycling of multilayer plastics structures, which are difficult to handle by existing recycling processes because they combine various types of plastic [15].

BASF acknowledges that technological and regulatory conditions must be met before the project is market-ready—the existing technologies to recycle plastic waste into raw materials such as pyrolysis oil or syngas must be further developed and adapted so that consistently high quality is assured; regional regulatory frameworks will considerably influence to what extent this approach can be established in each market.

9.5 Enzymatic Depolymerization

Enzymatic depolymerization is a new promising recycling technique. This technique is distinguished from the disposal by the fact that the main aim is to reuse the products generated after the enzymatic degradation. Currently, there are no effective enzymes for the depolymerization of nonbiodegradable polymers on an industrial scale.

WO2015173265 A1 (2015, CARBIOS) discloses a process for recycling at least one mixed PET plastic article, the method comprising depolymerizing at least PET of the mixed PET plastic article to monomers and/or oligomers using an enzyme, preferably a cutinase, and recovering the resulting monomers and/or oligomers. The process of the invention may be advantageously applied to mixed PET plastic articles coming directly from plastic waste collection and/or postindustrial waste. The content of PET in the mixed PET plastic article may vary from 10 to less than 95 wt%, preferably from 10 to 95 wt%. For instance, in flexible food packaging such as pouches, the PET content is from 14 to about 65 wt%, PET being associated with PVC, oriented polystyrene, LDPE, oriented polypropylene, oriented PET, aluminum, polypropylene, etc. The claimed process can be used for the recycling of pouches used for food packaging comprising PET laminated with aluminum layer or foil.

Example: A food packaging pouch made of PET and aluminum foil ("Elle et Vire Crème légère épaisse") was hydrolyzed for terephthalic acid recovery. The proportion of aluminum was estimated to 10% w/w. PET was semicrystalline. The PET—aluminum powder was hydrolyzed by the cutinase Thc Cutl from *Thermobifida cellulosilytica* DSM 44535 and about 88 μM of terephthalic acid was recovered in 24 h, whereas no terephthalic acid was detected in controls. In the same way, about 51 μM of mono(2-hydroxyethyl) terephthalate was recovered in 24 h.

In another embodiment, the process of the invention may be used for recycling a flexible food packaging composed of a PET film coated with nanocrystalline cellulose. The process of the invention can also be used for the recycling of flexible packaging such as the one used for pharmaceutical packaging comprising several layers including PET, paper, and aluminum.

9.6 Recovery Options

Recovery options include processes that convert flexible plastic packaging materials into energy (quaternary recycling), chemicals, and compost/soil amendments (for biodegradable polymers) as opposed to recycling options that include processes that recover polymers from flexible plastic packaging materials or convert them to repolymerizable monomers or oligomers. Recovery options are the last resort for flexible plastic packaging that would not be recycled for technical or economic reasons.

Although the recovery processes are outside the scope of the book, for the shake of completeness, a short presentation is given in the following of the available recovery technologies for the conversion of flexible plastic packaging.

9.6.1 Incineration

Incineration can be used for the disposal of metal foil containing packaging films and the recovery of the aluminum contained therein. During incineration, only a part of this aluminum is oxidized into energy. The remaining aluminum melts and can be recovered from the incinerator "bottom ashes" at the exit of the incinerator using eddy current technology (see Chapter 6; Section 6.8) [16].

ES2242544 A1 (2005, HERNANDEZ I MONTON ENRIC; VERNET FOLCH FRANCESC) discloses a method for the recovery of aluminum from aluminum/polyethylene laminates used for food packaging with the apparatus of Fig. 9.3. The aluminum-polyethylene laminate is placed into a cylindrical rotating furnace (3) that is positioned with an adequate incline and sufficient rotational velocity, the laminate being pulled along by the fluid flow formed by combustion air (in an oxygen-deficient atmosphere) on entering the furnace; in the area surrounding the combustion zone, because of the high temperature, the polymer gasifies, and it detaches from the aluminum foil and undergoes combustion, providing the necessary thermal energy for the process. The gases produced by the combustion are subjected to a rotation of 180 degrees, and this makes the aluminum foils, which are suspended within these gas currents, precipitate at the far end of the cylinder, from where they are extracted by the adequate means.

JP2006118777 A (2006, GIKO KK; KO SODO) discloses an incineration apparatus, shown in Fig. 9.4, for treating a flexible packaging film

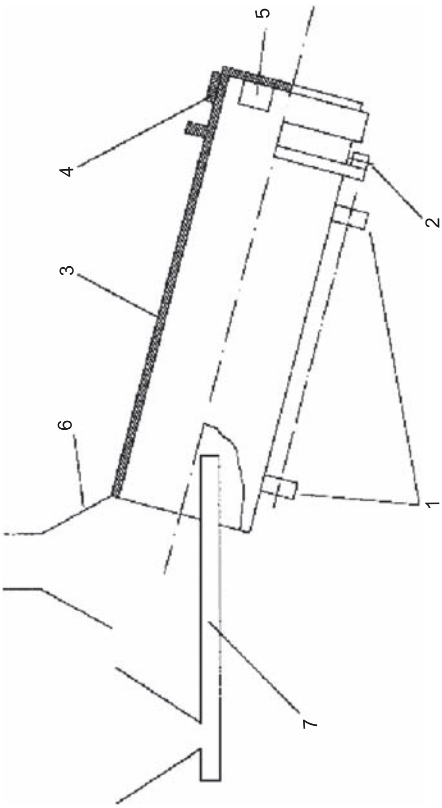

Figure 9.3 2005, **ES2242544** A1, HERNANDEZ I MONTON ENRIC; VERNET FOLCH FRANCESC. 1, Gears of displacement and traction; 2, Gear of axial displacement; 3, Cylindrical furnace lined with refractory material drum; 4, Ring sealing of the discharge port; 5, Discharge port; 6, Gas collection hood; and 7, Material feed screw.

obtained by laminating an aluminum foil on a film of polyethylene, polypropylene, polyamide, polyester, or a film obtained by vapor-depositing aluminum. The incineration apparatus comprises two furnaces, a furnace (20) for thermally fusing, decomposing, and gasifying the plastic film and a furnace (30) for combusting the generated gas containing gasified hydrocarbon with a heavy oil burner (B2). The two furnaces are interconnected via a control valve. A screw feeder is disposed in the gasifying furnace (20), and the packaging film is conveyed. In

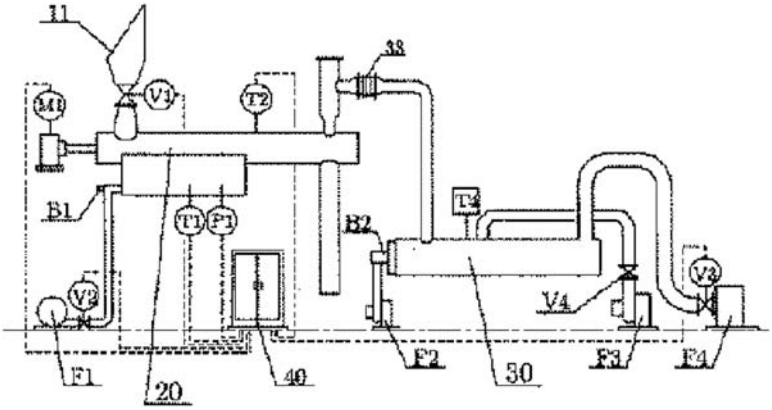

Figure 9.4 Schematic view of the incineration apparatus (2006, **JP2006118777** A, GIKO KK; KO SODO). 11, Hopper; 15, Air supply pipe; 17, Screw feeder; 20, Gasification furnace; 30, Combustion furnace; 33, Expansion joint; B1, LPG burner; P1, Pressure sensor; B2, Heavy oil burner T1, Temperature sensor, melt decomposition detection; F1, Blower; T2, Temperature sensor (for gasification detection); F2, Blower; T4, Thermometer; F3, Blower; V1, Rotary valve; F4, Suction fan; V2, Valve (for air control for gasification); M1, Motor; V3, Control valve; V4, Valve.

a steady operation state of the gasifying furnace (20), the exhaust gas is set to 700 °C or lower to prevent aluminization by controlling the conveyance speed of the treated film, the air supply for gasification fed into the furnace, and the amount of the exhaust gas. In the combustion furnace (30), the fed gas is combusted at 900 °C or lower to prevent generation of dioxins. The incineration of the flexible packaging film is adopted for the disposal of the film and the recovery of the aluminum.

9.6.2 Waste-to-Energy

Some types of flexible plastic packaging such as multilayer and/or metalized or metal foil containing films are difficult to recycle in a technically feasible and economically profitable manner. When recycling is not an option, the energy embodied in flexible plastic packaging can be recovered in a waste-to-energy incineration facility to produce electricity and heat.

9.6.3 Pyrolysis

Pyrolysis, also known as thermolysis or thermal decomposition, is another energy recovery option for waste packaging. Pyrolysis consists of heating the feed material at a high temperature (300−600°C) in a vessel in the absence of oxygen. The predominant decomposition products are syngas (a mixture of hydrogen and carbon monoxide), pyrolysis oil, water, methane, and CO_2. The composition of the resultant fuels is determined by a combination of the initial mixture of feedstock constituents, temperature, and time within the reactor.

Pyrolysis allows the processing of mixed waste, including flexible packaging, meaning the inputs do not need to be sorted before being used in the process. The output gas of pyrolysis has an energy value of between 22 and 30 MJ/m^3. Natural gas, for instance, has an energy value of about 38 MJ/m^3. Flexible packaging waste, which is largely made of polyethylene and polypropylene, is considered a favorable input for the pyrolysis process. The products of pyrolysis can be used to create electricity or as fuels or as a chemical feedstock to create new products. One of the challenges with pyrolysis is that the input of the feedstock (waste) can vary daily. This is unlike most fossil fuel−based plants that use coal or natural gas as feedstocks, which are relatively stable [17].

DE4437881 A1 (1996, DÜRBUSCH REINHARD) discloses a method for recovering the starting materials from PET film waste by thermal decomposition of the film. Waste film was shredded in a Condux®-type mill and transported by means of a ceramic screw under wetting with low molecular weight hydrocarbons through a high frequency field of 2.45 GHz, wherein the polyester is converted to starting materials or raw compounds.

Pyrolysis technologies have been unable to convert the full range of plastics in the waste stream, which then requires that some level of sorting be performed in preparation of the feedstock, thus reducing the economic viability. In addition, because of changes in the plastic waste stream, many pyrolysis technologies have not been able to produce a consistent end product capable of being upgraded to petroleum products that can consistently meet required industry specifications. Such out-of-spec products require further processing that consumes great amounts of energy, thus further reducing the economic viability (2017, **WO2017173006** A2, RES POLYFLOW LLC).

WO2017173006 A2 (2017, RES POLYFLOW LLC) discloses a process and an apparatus for pyrolysis of mixed plastic feedstock producing petroleum products. In an example, a plastic feedstock of films, multilayer films, sheets, foams, and moldings is charged into a reactor apparatus. Heat energy is applied to the feedstock while advancing the feedstock through the reactor apparatus in an anaerobic operation. The energy input to the reactor apparatus is controlled by controlling a temperature gradient within the reactor vessel to produce petroleum gas product. The process involves in situ chemical reactions comprising cracking and recombination reactions that are controlled to convert solid hydrocarbonaceous portion of the feedstock to molten fluids and gases inside the reactor vessel and to produce gaseous petroleum products that exit the reactor vessel. The separated solid residue from the pyrolysis process is also removed from the reactions vessel.

Currently, pyrolysis appears to be a viable option of flexible plastic multilayer packaging [18]:

- In pilots conducted by the Flexible Packaging Association (FPA) on postconsumer flexible packaging waste, oil yield from pyrolysis was 70%−80%.
- Processing can be done on-site by the MRF or off-site by the processor.
- Location is critical because transportation costs can determine the cost viability of the processing technology.
- Volume continues to be a challenge for processing multilayer packaging. It is estimated that it would take a community of 6 million people, at a 20% collection rate, to fill a small commercial-size pyrolysis unit exclusively with multilayer packaging.

Enval, a UK spin-off company, developed a process, known as microwave-induced pyrolysis, for the recovery of aluminum, hydrocarbons, and gases from industrial and postconsumer multilayer plastic packaging such as pouches, sachets, or squeezed tubes that have aluminum foil layers. Microwave-induced pyrolysis involves the pyrolysis of the packaging waste in a stirred bed of particulate carbon that is heated by microwave radiation. As opposed to incineration, pyrolysis takes place without the combustion of the material, avoiding the production of greenhouse gases or toxic emissions [19].

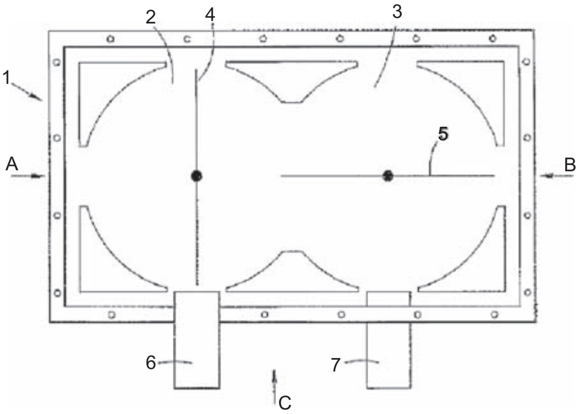

Figure 9.5 Schematic view of the interior of the microwave induced pyrolysis reactor (2005, **WO2005061098** A1, UNIV CAMBRIDGE TECH). A, B, and C, Sides of view; 1, Reactor; 2, First cylindrical chamber; 3, Second cylindrical chamber; 4, 5, Stirrers; 6, Inlet; and 7, Exit.

The Enval technology is disclosed in patent: **WO2005061098** A1 (2005, UNIV CAMBRIDGE TECH). The patent describes a continuous method for recycling multilayer packaging waste comprising a metal, such as aluminum, laminated with a plastic film using the microwave induced pyrolysis reactor shown in Fig. 9.5. The reactor (1) comprises a first chamber (2) having a first rotary stirrer (4) and a second chamber (3) having a second rotary stirrer (5), each chamber (2, 3) containing a bed of particulate microwave–absorbing material, preferably carbon black and activated carbon powder. The multilayer packaging waste and additional particulate microwave–absorbing material are introduced into the first chamber (2) via an inlet (6); stirring the mixture of particulate microwave–absorbing material and multilayer packaging waste in the first chamber (2) using the first rotary stirrer (3) under a reducing or inert atmosphere, and applying microwave energy in the first chamber (2) to heat the particulate microwave–absorbing material to a temperature sufficient to pyrolyze the multilayer packaging waste; transferring a portion of the mixture in the first chamber (2) to the second chamber (3);

stirring the mixture in the second chamber (3) using the second rotary stirrer (5) and applying microwave energy in the second chamber (3) to heat the particulate microwave−absorbing material to a temperature sufficient to pyrolyze the plastic material remaining in the laminate, whereby laminated or delaminated metal migrates toward and floats on the upper surface of the mixture in the second chamber (3), said second rotary stirrer (5) rotating in a horizontal plane and being so configured as to fluidize the mixture such that the upper surface of the fluidized mixture has a radial profile that biases laminate or delaminated metal floating on the fluidized mixture to migrate radially outwards; transferring a portion of the mixture in the second chamber (3) to an exit (7) from the reactor (1); and recovering metal from the exit (7).

According to RSE, Enval's technology is best suited for processing preconsumer pouch multilayer pouches sorted out from other films and pouches. RSE makes this assessment because pouches made with aluminum foil are estimated to contain less than 5% polypropylene and multilayer pouches sold, and detecting and sorting out such a small fraction is not believed to be cost-effective [20].

9.6.4 Gasification

Gasification (also known as partial oxidation) of waste plastics is carried out at high temperatures (600−900 °C) in an air-lean or oxygen-deficient environment. The process essentially oxidizes the plastics and converts them into a mixture composed mainly of syngas, with minor amounts of gaseous hydrocarbons. The syngas produced by gasification can be turned into higher value commercial products such as fuels, chemicals, and fertilizers or used as substitute natural gas that can be used to generate electricity.

Gasification is considered more energy efficient than pyrolysis overall as it does not require an additional energy source. The facilities can also operate with a mixed feedstock, other than plastics. The gasification process, however, tends to require large-scale facilities and may be more costly than pyrolysis facilities [17]. The commercialization of this technology is in the early stages.

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						neutral annealing coal with mixed turbines."
DE4437881 A1	19960425		DE19944437881 19941022	DÜRBUSCH REINHARD	DÜRBUSCH REINHARD	Verfahren zur Gewinnung von Rohstoffen aus Polyester-Folienabfällen. "Recovering the raw materials from polyester film waste."
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EP1138663 A1	20011004	AT226187 T 20021115; AT229932 T 20030115; BR0100830 A 20011030; BR0100830 B1 20110517; CA2337597 A1 20010829; CA2337597 C 20100406; DE60000606 T2 20030814; DE60001047 T2 20031009;	EP20000830145 20000229	BROCCATELLI MASSIMO	BROCCATELLI MASSIMO	Method for recovery of terephthalic acid from a material containing poly(ethylene terephthalates).

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US6723873 B1	20040420		US20000651161 20000830	MURDOCH WILLIAM SPEIGHT	EASTMAN CHEM CO	Production of terephthalic acid and ethylene glycol from polyethlene terephthalate by ammoniolysis.

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