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Managing Plastic Wastes

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12.1 Introduction

The petrochemical industry is a major field that upgrades about 10% of fossil hydrocarbons into about 350 Mt of polymers annually. The majority of them (40% in Europe) are used in packaging [1, 2]. However, polymers are also used in construction (20%), automotive (9%), electrical/electronic (6%), and many other applications. Eventually, polymers touch all facets of today's life, from housing to health, clothing, sport, transport, food, water, and many more. Often, however, the polymers eventually end up in the environment after use, being in the form of litter on land and in water or as CO_2, soot, and other gaseous contaminants when incinerated [3]. Beyond being unacceptable for our planet and all its living species, such (mis)management is also a waste of resources because spent plastics could in fact be used as valuable feedstock for new materials. This chapter discusses the issues of plastic waste and reviews the various options we have in hand to valorize end-of-life (EoL) polymers (Figure 12.1) in a circular economy. This chapter briefly addresses the challenges and opportunities in mechanical recycling, offers some in-depth details about the options for chemical recycling to polymer constituents or polymer feedstock, and finally addresses waste destruction in the form of energy valorization and biodegradation. Eventually, this chapter addresses life cycle analyses (LCAs) to compare the impact of various EoL options. Obviously, this chapter does not stand alone but establish earlier broad and insightful books and reviews [5–8].

12.2 Plastic Waste

To develop a circular economy, the petrochemical industry needs to complete the carbon cycle by collecting and recycling spent carbon. A minor fraction of spent

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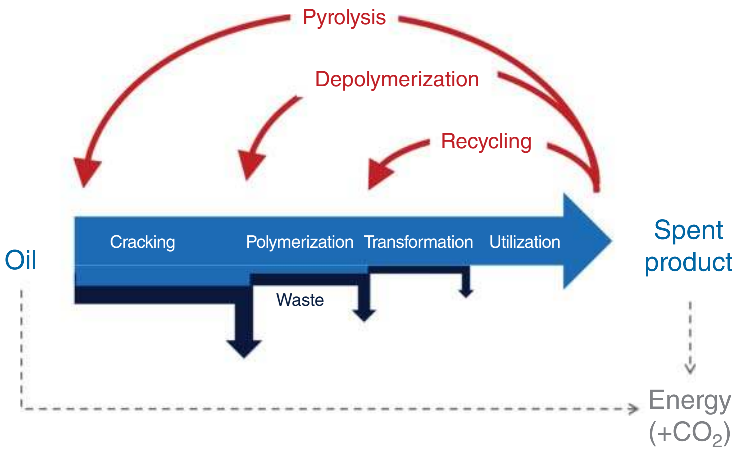

Figure 12.1 Options for recycling plastic waste for retransformation (mechanical recycling), repolymerization (chemical recycling to monomer), or recracking (chemical recycling to feedstock). Source: Adapted from Lange [4].

plastic is collected as a clean and well-sorted stream, e.g. post-industrial or car scrap wastes. However, the majority is collected in municipal solid waste (MSW), together with food scraps, yard trimmings, textile, paper, and other inorganic waste [9–11]. The world is producing about 1.1 Gt/yr MSW, with a production rate varying from <1 to >2 kg/capita/d, depending on the average income [12]. Approximately 10 wt% of plastic present in MSW mainly consists (~60 wt%) of polyolefins (i.e. high/low/linear-low density polyethylene HDPE, LDPE, LLDPE, and polypropylene (PP); the remaining fraction consists of polyethylene terephthalate (PET), polyvinyl chloride (PVC), polystyrene (PS), and other minor polymers [10, 11].

An efficient recycling of spent polymers not only ensures an efficient recycling of carbon but also aims at minimizing the consumption of energy and the production of waste over the life cycle of the product. This generally implies to operate through the shortest possible recycle loop. Depending on the quality and purity of waste, priority should therefore be given to reuse, reprocessing (mechanical recycling), depolymerization, conversion to hydrocarbon feedstock, and, as a last resort, energy recovery, as illustrated in Figure 12.1. This priority list is often presented as the priority pyramid in waste management.

Globally, about 12% of the spent plastic is recycled mechanically, while <1% is recycled back to its monomer [13]. The rest is either incinerated (25%) or ends up in the environment in landfill or unmanaged dumps.

With its ambitious “Green Deal,” the European Union (EU) aspires to become climate neutral by 2050, have developed a circular economy, have restored biodiversity, and have cut pollution [14]. Of specific interest for our discussion are the EU’s ambitions on circular economy [15] and, more specifically, on circular plastics, packaging, and textiles: the EU aims indeed at reducing waste, stimulating reuse (e.g. by banning single-use products whenever possible), and stimulating recycling. These ambitions further support the EU’s Bioeconomy Action Plan, which explicitly aims, among other things, at reducing its dependence on non-renewable, unsustainable resources, whether sourced domestically or abroad [16].

The circular economy is further supported by numerous brand owners such as Coca Cola, Unilever, Henkel, P&G, and many others that have pledged (i) to make their packaging reusable and/or recyclable, (ii) to reduce the use of virgin resin, and (iii) to stimulate the use of recycled resins and/or plant-based materials. Specific information on these pledges can be found on the individual brand owner's websites. In these advertisements, however, the brand owners remain silent about the additional costs of these pledges and the unpopular fact that the consumer will eventually get the bill.

12.3 Mechanical Recycling

So far, plastic recycling mainly includes mechanical recycling, with the focus on three dominant packaging polymers polyethylene (PE), PP, and PET. The recycling processes rely on cautious sorting of the cleanest and purest waste fraction, chipping the plastic into flakes, and washing them if necessary. The recycled flakes are then blended with a virgin polymer of the same family together with compatibilizers and additives to mitigate the shortcomings of the recycled material [6, 7, 17, 18]. Although very efficient and so far successful, mechanical recycling is bound to be limited to a few cycles using the minor fraction of the purest and cleanest waste stream. For instance, PET is generally the recycled once, from bottle to textile [19], while PP is claimed to technically support up to four recycles but is practically recycled once to textile and playground equipment [20]. In fact, mechanical recycling seems to mainly consist of downcycling. Hence, they need complementary recycling options, particularly chemical recycling. Therefore, let us review the limitations of mechanical recycling.

Firstly, the recycled materials, particularly post-consumer plastics, generally show lower performance than the virgin ones because of several reasons. Firstly, the sorted material may not come as a single-grade plastic but as the market-average grade. It may therefore not meet the requirement for high-end applications.

Secondly, plastic products may contain additives such as fillers, antioxidants, plasticizers, pigments, flame retardants, etc. Recycled materials will therefore contain the market average of these additives.

Thirdly, the sorted waste may not have the same purity as the virgin material. It may contain minor fractions of foreign polymers, for instance, traces of PET or PP in the sorted PE stream. As polymers are practically immiscible with one another, these polymer impurities tend to segregate into small foreign domains and, thereby, create weak spots into the recycled material. These shortcomings can be mitigated by the addition of small amounts of compatibilizers, e.g. short block copolymers with chain segments of the same nature as two polymers of the blend (e.g. PP–PE block compatibilizers) [6, 7, 17, 18]. Alternatively, the compatibilizers contain a main chain that resemble the target matrix and a reactive end group that can react with the functional group of the polymer impurity, e.g. one that can react with an alcohol group of PET or EVOH (ethylene-vinyl alcohol) polymers. The challenge of contamination may come in an even more difficult form, i.e. in multilayer films and in textiles, because these materials generally consist of multiple polymers that are interlayered or interwoven to reach the desired properties.

Fourth, the recycled polymer chains may be partly degraded, e.g. through oxidation or UV radiation upon use, or through thermal degradation upon repeated hot processing [6, 7, 17, 18]. Indeed, hydrocarbon polymers and PVC are reprocessed at 160–260 °C while performance polymers such as polyamide (PA) and PET are reprocessed at 220–320 °C [7]. As a result, the polymer may exhibit polar groups that need compatibilization. However, recycle polymers may also exhibit an increased M_w and higher viscosity. The resulting shortcomings can be mitigated by means of various additives [6, 7, 17, 18].

Fifth and final, some applications such as food packaging are forbidden to use materials that could be contaminated by traces of toxic impurities. Mechanical recycling to make plastics for food packaging is then not a viable option.

These shortcomings are particularly pronounced for post-consumer wastes. Some of them may be of lesser concern for well-defined post-industrial waste, which explains the pronounced interest of the recycling industry for these waste streams.

Obviously, the use of compatibilizers and additives is increasing the level of impurities in recycled materials. They will further increase upon multiple recycle loops to the point where it disqualifies the material for further mechanical recycling. More sophisticated recycling technologies are then required, e.g. dissolution/precipitation or chemical recycling, to be discussed in Sections (12.4 and 12.5).

Moreover, our discussion on mechanical recycling has so far assumed that the material to recycle is a thermoplastic: it can be melted and reshaped at will upon heating. This obviously excludes thermoset materials such as polyurethane mattresses, vulcanized rubber tires, and cross-linked unsaturated polyester composites to name but a few. For such materials, which represent about one-third of the polymeric materials [21], spent products can be chipped and “downcycled” as a filler for new products. This applies to rubber [22], epoxy blends [23], and polyurethane [24]. These materials are not prone to dissolution either. Hence, recycling is bound to proceed via deep deconstruction, i.e. via chemical recycling.

12.4 Dissolution/Precipitation

An approach to remove contaminants from spent polymers, being additives or foreign polymers, is dissolution/reprecipitation [8, 25]. Accordingly, the spent polymer is dissolved in an appropriate solvent, separated from insoluble impurities and additives and reprecipitated upon addition of an antisolvent. Obviously, the solvent and the antisolvent need to be separated for reuse at the dissolution or precipitation stage of the process. This step consumes much energy but maybe less than the alternatives: recovering the polymer by evaporating the solvent instead of precipitating it with the antisolvent. Dissolution processes have been developed for recycling PS [17, 26], PVC [24], PA [27], polymethylmetacrylate (PMMA) [24, 28], PE/PP [24], and multilayer films [24]. Most of these processes seem to be at pilot or demonstration stage [8], with the exception of APK's dissolution of multilayer films [29].

12.5 Chemical Recycling

Generally, the waste plastic stream does not meet the stringent quality requirements of mechanical recycling. For instance, the plastic has suffered minor, although significant, degradation upon use and/or reprocessing at elevated temperature (e.g. oxidation and/or minor depolymerization), or the sorted and cleaned plastic still contains traces of toxic components for use in food packaging. Chemical recycling is then necessary. Some polymers can and should be depolymerized back to their monomers. Other can only be converted back to a general feedstock. Still others cannot fit in either of these loops in an attractive manner. However, how to decide what is promising?

The basis for such a selection is illustrated in Figure 12.2 [4, 30]. The horizontal axis helps identifying the polymers that are easily depolymerized back to their monomer (heat of depolymerization dH < 70 kJ/mol of broken bonds, typically condensation polymers) and those that are only cracked to a general hydrocarbon through more severe pyrolysis (dH > 70 kJ/mol, typically addition polymers). The *y*-axis represents the cumulative amounts of resources that are wasted when producing the polymer. It, thereby, represents the "incentive" to recover the monomer rather than degrading it back to hydrocarbon. This simple mapping readily recommends cracking polyolefins back to general feedstocks (lower right quadrant) but depolymerizing PET and polyamides (PA) back to their monomers

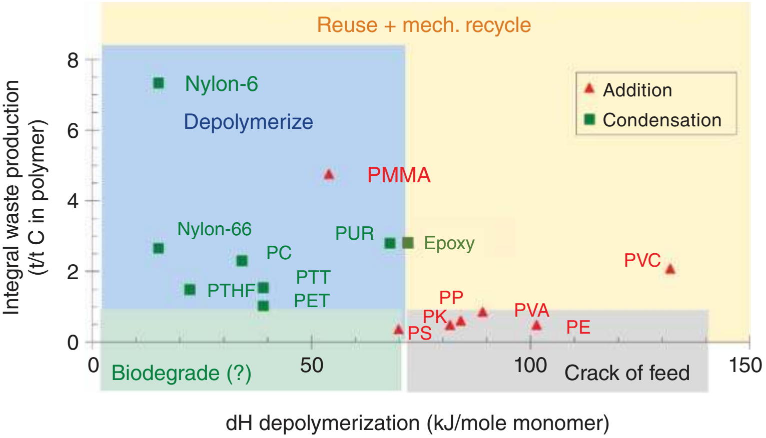

Figure 12.2 Options for plastic recycling (PC: polycarbonate, PTHF: polytetrahydrofuran, PTT: polytrimethylene terephthalate, PET: polyethylene terephthalate, PMMA: polymethylmetacrylate, PUR: polyurethane, PS: polystyrene, PP: polypropylene, PK: polyketone, PVA: polyvinylalcohol, PE: polyethylene, and PVC: polyvinylchloride). Source: Adapted from Lange [28].

(upper left quadrant). Polymers falling in the upper right quadrants (e.g. PVC) are demanding to make and are impossible to depolymerize back to the monomer. Society could consider abandoning them. Finally, although empty, the lower left quadrant would contain the ideal polymers that are easy to make and easy to depolymerize. These polymers would be promising candidates for biodegradation as they would consume only limited energy and chemistry invested in making them. Although not shown here, today's biodegradable plastics (e.g. polyhydroxyalkanoate (PHA) and polylactone) fall in the upper left quadrant as they are easily depolymerized but are fairly demanding to produce. However, let us now discuss how such depolymerization is carried out for the various polymers.

12.5.1 Depolymerization of Condensation Polymers

Condensation polymers are formed by nucleophilic substitution reactions that link the monomers through polar bridges, most commonly through ester linkage (–C(O)O–), amide linkage (–C(O)NH–), or urethane/carbamate linkage (–C(NH)O–). Most of them are prone to opening through hydrolysis, transesterification, or transamidation. Let us illustrate the approach for PET, PA, and polyurethane (PUR), which are well advanced [8, 17, 26].

The polyester PET is most commonly depolymerized by alcoholysis, i.e. methanolysis to dimethyl terephthalate of glycolysis (with ethylene glycol) to dihydroxyethyl terephthalate [31, 32]. The reaction is generally carried out at elevated temperature (~200 °C) in the presence of catalysts, traditionally a Lewis metal salt such as Zn acetate [33]. Methanolysis requires a complex product recovery and purification train, which becomes very challenging when depolymerizing copolymers, e.g. which contain some isophthalate (besides terephthalate) or some diethylene glycol (besides ethylene glycol). Deep solvent removal is indeed necessary since monoalcohols would terminate the growing chains during polycondensation polymerization. Glycolysis does not suffer these drawbacks and therefore holds more promises. It furthermore enables partial depolymerization to low-viscosity oligomers that can be fed back to the polymerization reactor. Many companies are piloting or demonstrating PET depolymerization processes with the aim of providing recycled materials for food packaging applications [34]. A depolymerization process scheme could look as presented in Figure 12.3.

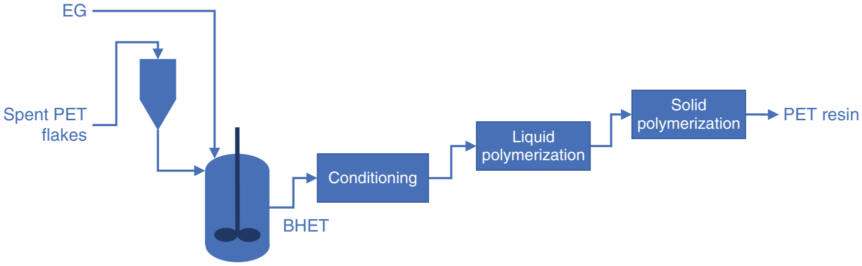

Figure 12.3 Process concept for PET chemical recycling (EG: ethylene glycol, BHET: bis-hydroxyethylene terephthalate). Source: Adapted from [35].

Polyamides (PA) are depolymerized in water at ~300 °C in the presence of inorganic acid [36]. However, this process seems limited to depolymerizing Nylon 6 to caprolactam for the depolymerization of Nylon 66 to adipic acid and hexamethylene diamine brings complications in product recovery and purification. Pyrolysis can also depolymerize Nylon 6 into caprolactam [37] but does not seem nearly as effective for nylon 66.

PUR can also be depolymerized by alcoholysis, glycolysis, and hydrolysis. However, it can also undergo aminolysis [38, 39]. In contrast to the previous cases, however, PUR depolymerization does not release the constituting monomers, i.e. propylene oxide and diisocyanates. Instead, it releases high-molecular weight products, namely, the oligomeric polyols and the aromatic, N-containing oligomers. The polyols can be recycled into new PUR, but the aromatic fraction is usually disposed of, as it cannot be properly upgraded to the original diisocyanates.

Although most elegant, selective depolymerization might still be economically challenging. The polymers that can be of interest typically represent a minor fraction of the total polymer waste. They are available in modest quantities and therefore require small-scale and costly logistics and reprocessing. This is surely the case when mixed with other plastic wastes. However, the small-scale logistics and reprocessing likely applies to well-sorted industrial waste as well.

Depolymerization of monomers will likely apply to the new and emerging bio-based polyesters such as polylactide (PLA), polyhydroxybutyrate (PHB), polybutylsuccinate (PBS), and polyethylenefuranoate (PEF). However, the small volume may challenge their recycling for a while.

12.5.2 Melt Pyrolysis of Polyolefins

Polyolefins cannot be depolymerized back to their monomeric constituents. Depolymerization requires harsh pyrolysis conditions and generally leads to a complex mixture of hydrocarbons, i.e. a general feedstock (lower right quadrant of Figure 12.2). Pyrolysis produces paraffinic/olefinic waxes under mild conditions, an aromatic product under more severe conditions, and gas and char at the highest severity [7, 26, 40, 41]. Such hydrocarbon products can be processed into a synthetic fuel. However, fractions of the aliphatic product produced under mild conditions can also be cracked into lower olefins, generally after removing the heaviest product and hydrotreating the desired distillate fraction. Steam cracking of plastic pyrolysis oil is expected to deliver olefins and aromatic base chemicals with ~65 wt% yield, with coproduction of ~10 wt% fuel gas, ~10 wt% of aromatic gasoline, and 15 wt% of aromatic fuel oil.

Pyrolysis is no new technology. Oil refineries are applying it at the large scale in various forms for decades for upgrading heavy oil fractions into gas and distillates. These technologies are then called thermal cracker, visbreaker, or coker [42]. Pyrolysis has also been explored for processing plastic waste by major chemical producers some 30 years. Although technically successful, these technologies were eventually abandoned because they could not compete with cheap crude oil. The rise in oil price in the early 2000 has encouraged small start-up companies to revisit plastic pyrolysis, which led to a plethora of technology providers today [17].

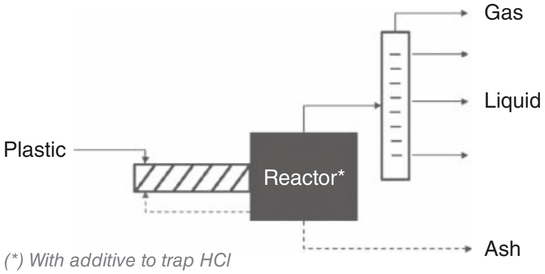

Figure 12.4 Process concept for melt pyrolysis of waste plastics.

The oil and chemical majors have also joined the effort, not so much with more pyrolysis technologies but rather with plans to process the resulting pyrolysis oil in their steam cracker. For instance, Shell announced in November 2019 to be processing a first truck of plastic pyrolysis oil in its cracker at Norco, USA, and announced its ambition to ramp up the volume of plastic recycling fed to the cracker to 1 Mt/yr by 2025 [43].

Polyolefins are generally pyrolyzed by the so-called melt-pyrolysis [35, 40]. A conceptual process scheme is provided in Figure 12.4. Accordingly, the plastic is fed and melted into an extruder before being fed to a large vessel that is heated to 450–500 °C and mechanically agitated. The cracked vapor is removed at the top of the vessel and, subsequently, condensed to liquid pyrolysis oil. The incondensable gases can be used for heating the reactor. The char is removed at the bottom of the vessel and disposed of. Tight temperature control and extensive agitation seem to be essential to minimize coke deposition and achieve high oil yields. These requirements seem to limit the scale of pyrolysis reactors at some 15–20 kt/yr, a scale that is very small when compared to the 3 Mt/yr liquid steam cracker that they are supposed to feed. The small scale is clearly harming the economic competitiveness of the process as it leads to high capital and operating costs. The pyrolysis technology is not fully omnivorous either. It is particularly suitable to process polyolefins, but it produces less oil and an oil that is more aromatic when the feed is contaminated with other polymers such as PS, PET, and PA. Small amounts of PVC in the feed are particularly nasty, as it liberates HCl that corrodes the equipment and make the oil unsuitable for further processing. One element of mitigation consists of heating the plastic waste in the feeding system and recovering the HCl-rich gas before feeding the plastic melt to the reactor. Another complementary approach is to feed caustic elements such as $CaCO_3$ to the reactor to trap and neutralize the remaining chloride. The resulting salt is then removed together with the coke.

12.5.3 Alternative Pyrolysis Processes

When run at the highest severity, the pyrolysis of polyolefins can deliver an olefin-rich gaseous stream as the main product. This could be considered as chemical recycling to monomers [35, 40]. However, the gaseous stream requires strict cryogenic fractionation to deliver polymer-grade ethylene, propylene, and butylenes, a purification that is uneconomical at the small scale of pyrolysis. The situation is more favorable when processing PS or PMMA waste, however. These addition polymers indeed crack back to their constituting monomer with reasonable selectivity upon moderate thermal treatment, as indicated by Figure 12.2. Moreover, the product can be condensed out of the gaseous by-products. Various processes are being developed and demonstrated for these streams [24, 26]. The small-scale pyrolysis might not be a critical limitation here since these waste streams are available in limited volume any way.

Beyond melt-pyrolysis, other technologies are also being developed to convert waste plastics into liquid hydrocarbons. For instance, the pyrolysis can be assisted by a catalyst, typically an acidic zeolite, to convert the pyrolysis vapors into cyclic and aromatic hydrocarbons [26]. Anellotech [44] and BioBTX [45] have developed such processes by modifying the process concept they developed earlier to upgrade lignocellulose to aromatic biofuels. The aromatic product holds promise for aromatic production and for fuel applications, but it is not suitable for cracking to olefins.

Hydrothermal liquefaction, as performed by Licella, is another process that has been developed for biomass and adapted for plastic waste [46]. Accordingly, the plastic waste is thermally degraded in near/super-critical water. This process is claimed to be more tolerant to the presence of engineering polymers in the feed. In fact, it can even digest the whole MSW, including its organic fraction, thereby producing an aromatic-rich oil that is partly of bio and plastic origin and could qualify as a low-carbon fuel (see Section 12.6).

Finally, the IH$^{2®}$ hydropyrolysis technology that has been developed by GTI and Shell runs the pyrolysis in the gas phase in the presence of hydrogen atmosphere and the hydrogenation catalyst (Figure 12.5) and is presently being demonstrated

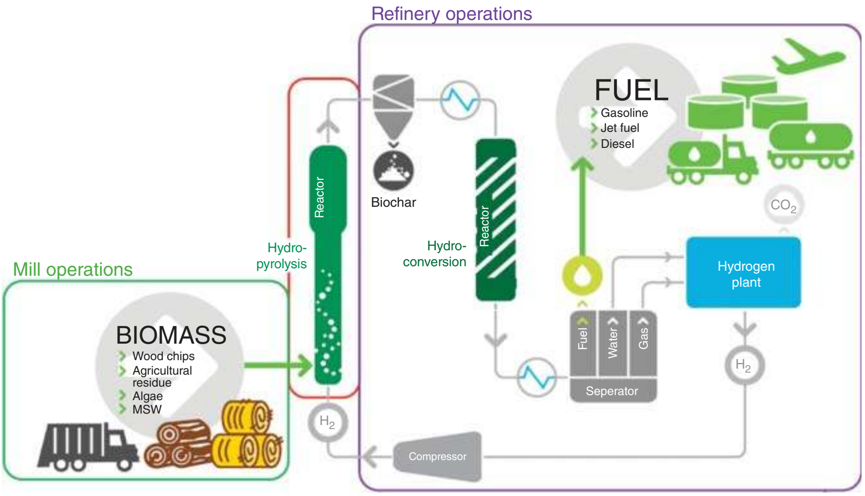

Figure 12.5 IH^2 Hydropyrolysis process, developed by GTI and Shell, converts MSW and RDF to hydrocarbon feedstock. Source: Based on Shell [47].

at the 2000 l/d scale [47]. It delivers a hydrocarbon stream that is rich in aromatics and free of heteroatoms. The technology is being developed for biomass but is compatible for biomass-rich waste fractions such as refuse-derived fuel (RDF) [48]. However, it remains unproven for pure waste plastic feedstock. Further discussion of this technology will therefore be moved to Section 12.6 that also considers gasification to valorize RDF.

Pyrolysis processes have also been explored for recycling thermoset resins such as PUR, rubber tires, or even epoxy composites [20–22]. While technically feasible, the product yield and quality does not appear very attractive so far.

12.6 Energy Recovery – Recycle Fuels and Incineration

The pyrolysis of plastic waste delivers a hydrocarbon fraction that can be made very suitable for transportation fuel. The crude pyrolysis oil may still need to undergo hydroprocessing to stabilize the fuel by hydrogenating the mono- and di-olefins and to remove residual oxygen and nitrogen. It may also need fractionation to select the desired boiling range and, possibly, dewaxing to avoid the gasoil-range product to crystallize at low temperature.

However, transportation fuels can also be produced from the more contaminated and cheaper stream such as the whole MSW or its sorting rejects, namely, the RDF or the solid-recovered fuel (SRF) than contains unsorted plastics still mixed with unsorted textile, paper/cardboard, and other organic fractions. These fractions can be upgraded to hydrocarbon fuels by means of gasification to synthesis gas (or syngas), a mixture of H_2 and CO, followed by syngas conditioning and conversion to fuel or chemicals [4]. For instance, Shell has partnered with other companies to help demonstrate Enerkem's gasification technology to convert MSW to syngas and, eventually, methanol [49].

Gasification technologies can, of course, be applied to mixed plastic waste or even well-sorted plastic waste. However, gasification technologies are expensive, thereby requiring large scale. They still deliver a low-value product, syngas, that needs further conditioning and conversion to get to hydrocarbons. It is therefore doubtful that it can compete with the much cheaper pyrolysis for processing well-sorted plastic waste.

Alternatively, the RDF fraction can be subjected to high-severity hydrotreating, e.g. using the IH^2 technology developed by GTI and Shell, as discussed above [46]. This technology produces an aromatic-rich distillate that is suitable as a component for gasoline and diesel fuels. Similarly, Licella's hydroliquefaction process (also discussed above) can convert the whole MSW to liquid hydrocarbons that are suitable for fuel applications [45].

Of course, the RDF or the whole MSW can also be burned to generate electricity while responsibly destroying the waste. Incineration plants should then be equipped with modern technologies such as gas cleaning technologies to free the exhausted gas from harmful components such as polyaromatic hydrocarbons, dioxins, NO_x, and SO_x before release to the atmosphere [50].

12.7 Waste Destruction – Biodegradation

Biodegradation, i.e. biological conversion to CO_2/H_2O/biomass, is truly wasting the energy and chemistry embedded in the polymer or is, at best, converted it to low-value compost. It is therefore not a recycle option but rather a waste destruction option. It can nevertheless be valuable in a few occasions. For instance, biodegradation is valuable for polymers that run a high risk to end up in the environment after use, e.g. for small-sized, single-use packaging. Biodegradation can also help not having to remove the polymer after use, as encountered in surgery, agricultural mulch films, or in plastic waste that is heavily spoiled with food rests (e.g. single-use food packaging and disposable cutlery).

Anaerobic biodigestion, i.e. biological conversion CO_2/CH_4/biomass, is more valuable when run in a well-controlled industrial setting as it delivers CH_4 as fuel. It thereby falls among the energy recovery options discussed above.

Both aerobic and anaerobic biodigestion processes are applicable to a limited set of polymers, those that are attacked by microorganisms. However, let us not dwell on this topic here as other chapters of this book will treat this topic in more detail. Chapter 2 (entitled "Fundamentals of Polymer Biodegradation Mechanisms").

12.8 Life Cycle Analyses

The literature and the web offer a wealth of LCAs that attempt to assess the environmental impact of plastics. Some aim at comparing plastics to other materials such as metal and glass; others aim at comparing bio-based to fossil-based plastics and still others aim at comparing various EoL scenarios such as landfill, incineration, conversion to fuel, or recycling to plastics. Some limit their analysis to the carbon footprint or green house gas (GHG) emissions, while others also consider other planetary boundaries such as land and water use, water and air pollution, biodiversity, etc. I personally find very delicate to draw solid conclusions from such studies because the overall conclusions heavily depend on too many factors, premises, boundaries, substitution scenarios, etc., which are often hidden in the small prints of the papers or in their supplementary information. I will nevertheless take the risk to extract a few important messages to be used in an indicative, at best semi-quantitative, manner. The reader is also referred to chapter 13 (chapter on LCA) for a deeper discussion.

Overall, the carbon intensity or GHG/CO_2 emissions of plastics seems to amount to 4–5 $t_{CO2}/t_{plastic}$ [51, 52], half of it being due to the production stage and the other half to the incineration at EoL [50]. This number is obviously an average over various plastics and is likely dominated by the most abundant plastics, i.e. the polyolefins. Indeed, the carbon footprint of the production stage varies largely with the type of polymers from 0.5 t_C/t_C (ton carbon wasted per ton carbon in the product) for polyolefins to 1—6 t_C/t_C for the major engineering plastics and likely more for high-performance polymers [28]. Recycling is generally seen as delivering significant GHG emission savings, when compared to incineration [51–54]. Obviously, the GHG savings vanish if one compares recycling with landfill, which could be

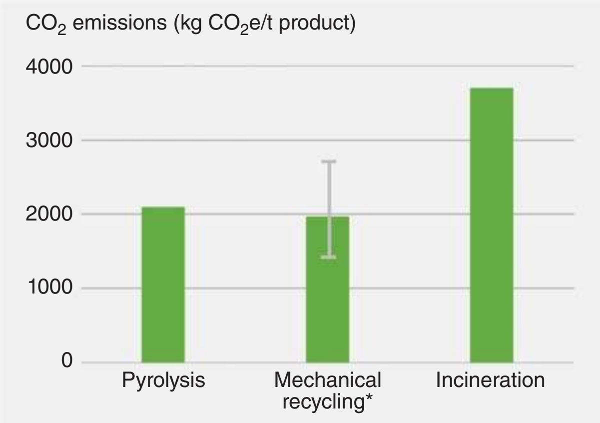

Figure 12.6 CO_2 emissions of various end-of-life scenarios for polyolefins [54] (The error bar reflects a different scenario of sorting quality and losses).

considered as a form of carbon sequestration if done responsibly, i.e. with long-term preservation of surrounding land, water, and air. However, numerous countries are discouraging landfill, and nine European countries have banned it [2, 11]. Considering the chemistry and energy requirement of the various recycling options, one is not surprised to see the CO_2 benefit decreasing in the order of mechanical recycling > chemical recycling by pyrolysis > chemical recycling by gasification > incineration for polyolefins [24]. According to BASF, the chemical recycling of polyolefin waste by pyrolysis would save 1 $t_{CO2}/t_{plastic}$, when compared to incineration of the waste, and does not underperform significantly over mechanical recycling, as illustrated in Figure 12.6 [55]. Vollmer et al. confirm the saving of 1 $t_{CO2}/t_{plastic}$ for pyrolysis of PE and report significant savings for chemical and mechanical recycling of acrylonitrile-butadiene-styrene (ABS), PA, and PET, when compared to incineration. They even find some savings when compared to landfill [8]. Intriguingly, they report the lowest C-footprint for the dissolution/precipitation approach.

Considering the topic of this book, a few words need to be devoted to the EoL by biodegradation. Qualitatively, we can expect biodegradation to deliver the highest C-footprint of all EoL options. Similar to incineration, biodegradation is converting the plastic to CO_2 and H_2O. Unlike incineration, however, it does not allow to recover the energy bound into the material and, thereby, does not save on other fuels. This conclusion is indeed confirmed by Posen et al. that report the CO_2 savings of PLA and PHB to decrease in the order of recycling > incineration > composting [56]. They also found CO_2 savings when substituting fossil polymers by PLA or PHB in the case the polymers are incinerated at EoL. No significant savings were found when the waste polymers were recycled.

12.9 Need for Fresh Carbon Input

However, recycle loops are inevitably accompanied with losses and will require to be replenished by a small fraction of fresh carbon. Fossil resources will keep supplying it for some decades ahead and the lost carbon will gradually need to be offset by CO_2 capture and sequestration, either artificially (CCS) or naturally by planting and preserving trees (nature-based solutions, NBS) to reduce the climate impact of the chemical industry. However, this will make the industry only partly circular. A fully circular economy will require fresh carbon input streams being fed by renewable carbon, i.e. by atmospheric CO_2.

Numerous research groups are exploring and developing technologies to capture CO_2 from the atmosphere and reduce it to fuels and chemicals with renewable electrons or renewable hydrogen [57]. Other groups are exploring biomass instead. Plants are indeed doing most of the work for us already; they capture the CO_2 from the atmosphere and reduce it from C(4+) carbon to C(0). Biomass appears indeed to be a much more attractive source of renewable carbon in the short to midterm. However, this will be discussed briefly in another Chapter 4 (on polymer tutorial).

12.10 Conclusion and Outlook

Over the years, the petrochemical industry has developed a plethora of polymers that are contributing to the comfort of modern societies. However, irresponsible disposal has also led to growing build-up of plastic litter, which is fouling the environment, harming wildlife, and wasting valuable resources. The industry has been struggling for a few decades to collect and (mechanically) recycle waste plastic. However, these efforts remain marginal in volume and are economically unsustainable. The litter problem has now become such that the society and industry have decided to join force to develop and deploy technologies to boost collection and recycling rate and to develop the regulation and financial schemes to support it. For instance, the chemical industry has partnered with industries along the whole plastic value chain from the manufacturer to the brand owners to waste processors and launched the *alliance to end plastic waste* to solve this problem through education, legislation, innovation, and environment cleaning [58].

Much work has already been accomplished in mechanical recycling of the highest quality materials. However, there are limits to the volume that is of suitable quality and to the number of times these streams can be recycled. Hence, the industry is developing or resuscitating complementary technologies that can recycle spent polymers of lesser quality, either to their monomers or to their general feedstock. The first technologies have now reached pilot or demonstration stage and offer the promise to recycle a much larger fraction than mechanically possible.

The largest potential is expected from the pyrolysis of polyolefins (PE and PP) because the technology is simple and robust, it can process the largest waste stream, it has modest purity requirements, and it delivers a synthetic hydrocarbon stream of reasonable value. Although well advanced, the pyrolysis technology still needs further improvements to reduce the cost and increase the value of the product. For instance, the technology should be made compatible for continuous operation, preferably in a fully automated manner and at the larger scale. When fed with mixed plastics, pyrolysis delivers an oil that is contaminated with aromatics as well as O- and N-containing components. These contaminants are not suitable for feeding to a steam cracker and need to be removed by post-treatment.

Gasification technologies are even more omnivorous than pyrolysis. However, they are also much more complex and costly. Moreover, they deliver a low-value product, i.e. synthesis gas that needs subsequent upgrading to deliver hydrocarbon streams. Hence, they will likely claim a role where no other recycling technologies can compete, e.g. for heavily heterogeneous and contaminated waste stream such as MSW or the RDF fraction left over after sorting the MSW.

Hydropyrolysis, e.g. IH^2, can also handle MSW and RDF. The production of higher value hydrocarbon might offset its lower overall yield and, thereby, deliver an advanced economy. Hence, we are looking forward to seeing it demonstrated and deployed.

Condensation polymers (PET, PUR, and PA) are minor components in the plastic waste and form, therefore, a less urgent issue. When properly sorted, these polymers should preferentially be recycled back to their constituting monomers and various technologies are being piloted for this purpose. However, the modest volume of these streams may eventually challenge the economics of sorting, logistic, and processing. The same will likely apply to the new and emerging bio-based polyesters such as PLA, PHB, PBS, and PEF. However, the small volume may challenge their recycling for a while.

LCA indicate significant CO_2 savings by recycling waste polymers instead of incinerating them. The savings seem to decrease in the following order:

$$\text{mechanical recycling} > \text{chemical recycling} > \text{incineration} > \text{biodegradation}$$

When combined, all these recycling technologies are promising to recycle a very large fraction of plastic waste. However, they will not be able to achieve full circularity because some waste stream will resist collections and all technologies will eventually deliver some reject stream that can, at best, end up as fuel or energy. These carbon losses will need to be compensated by virgin intake, initially from fossil resources with compensation by CCS/NBS, and at later stage from atmospheric CO_2 via artificial or natural photosynthesis. Bio-based plastics are very strong candidates to supply fresh carbon to the polymer cycles. The technology is ready for some polymers and in pilot stage for others. The conversion of atmospheric CO_2 and renewable electrons to polymers may come later, for the technology is in its infancy and threatens to remain prohibitive for many decades to come.

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