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Perspective

Managing Plastic Waste—Sorting, Recycling, Disposal, and Product Redesign

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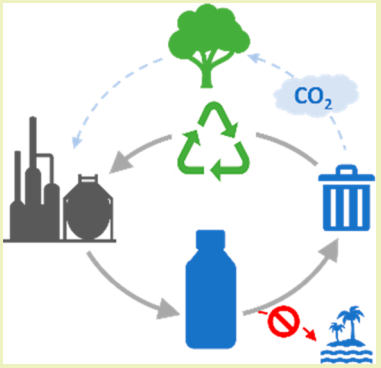
ABSTRACT: Over the years, the petrochemical industry has developed a plethora of polymers that are contributing to the well-being of humanity. Irresponsible disposal of used plastics has, however, led to the buildup of litter, which is fouling the environment, harming wildlife, and wasting valuable resources. This paper critically reviews the challenge and opportunities in converting plastic waste into a feedstock for the industry. It discusses (a) the amount, quality, and sorting of plastic waste; (b) mechanical recycling and extraction or dissolution/precipitation; (c) chemical recycling to monomers and to feedstock and other chemicals; and (d) waste disposal by incineration, biodegradation, landfill, and microplastics. It will, finally, broaden the circularity discussion with life-cycle analyses (LCA), design for recycling, and the future role of renewable carbon as a feedstock.



KEYWORDS: *plastic, sorting, recycling, energy, biodegradation, design for recycling*

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INTRODUCTION

The petrochemical industry is a global industry that yearly upgrades some 10% of fossil hydrocarbons into valuable polymers at a scale of about 350 Mt per annum. The majority of them (40% in Europe) are used in packaging.[1,2] But polymers are also used in construction (20%), automotive (9%), electrical/electronic (6%), and many others applications. Eventually, polymers touch all facets of today's life, from housing to health, clothing, sport, transport, food, water, and many more.

Too often, however, the polymers end up in the environment after use. They are found as litter on land and in water or as CO_2, soot, and other air contaminants in the air, e.g., upon incineration.[3] This is inacceptable for our planet and all its living species. But this is also a waste of resources, for spent plastics are in fact valuable feedstock for new materials.

This Review paper will sketch the problem of plastic waste and will review the various options that we have to valorize end-of-life polymers in a circular approach. It will thereby focus on the last 2R's of the waste hierarchy of *Reduce*−*Reuse*−*Recycle*−*Refuse*, namely, the Recycle and Refuse. To this end, this paper will briefly discuss the amount and quality of plastic waste and the technologies that are available to sort it in refined plastic streams. It will then address challenges and opportunities in mechanical recycling, including the recovery and purification by extraction and dissolution/precipitation. It will discuss chemical recycling to monomers and to feedstock, provide guidelines to choose between them and dive into archetype technologies for chemical recycling. It will then address the disposal option for residual waste, i.e., incineration, biodegradation, and landfill, and briefly discuss microplastics. Finally, it will broaden the circularity discussion by discussing life-cycle analyses (LCA), design for recycling, and the need to eventually switch to renewable carbon as a feedstock, i.e., to atmospheric CO_2 and biomass.

Obviously, this Review does not stand alone but builds on broad and insightful books and reviews that are worth reading.[4−7] It tries to complement them by broadening the scope to cover all aspects of plastic waste, as summarized above, and by critically analyzing the technological achievements and emerging developments through an industrial and economic lens.

PLASTIC WASTE

The world is producing around 1.1 Gt/a of consumer waste (municipal solid waste or MSW), with production varying from <1 kg/capita per day for low-income countries to >2 kg/capita per day for high income ones.[8] MSW typically contains 10 wt % plastics, amid food scraps, yard trimmings, textiles, paper, and other inorganic waste.[9−11] The ∼10 wt % of plastics

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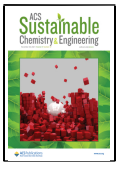

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consists mainly (~60 wt %) of the polyolefins HDPE, LDPE, LLDPE, and PP, the remaining fraction being PET, PVC, PS, and other minor polymers.[10,11] A much smaller fraction of plastic waste comes as postindustrial or car scrap wastes, generally as a clean and well-sorted stream. Globally, about 12% of the spent plastic is recycled.[12] A larger fraction is incinerated (25%), but the bulk (~60%) ends up in the environment, in landfills, in unmanaged dumps, or as litter on land or in rivers and oceans.

With its ambitious "Green Deal", the EU aspires by 2050 to become climate neutral, to have developed a circular economy, to have restored biodiversity, and to have cut pollution.[13] Of specific interest for our discussion are the EU's ambitions on circular economy[14] 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 nonrenewable, unsustainable resources, whether sourced domestically or abroad.[15]

The emergence of a circular economy is further supported by numerous brand owners such as Coca Cola, Unilever, Henkel, P&G, and many others that have pledged (a) to make their packaging reusable and/or recyclable, (b) to reduce the use of virgin/fossil plastics, and (c) to stimulate the use of recycled resins and/or plant-based materials. Specific information on these pledges can be found on the Web sites of the individual brand owners. Notice, however, the brand owners remain silent about additional costs of these pledges and the fact that they will eventually be billed to the consumer.

Recycling—Options and Drivers. An efficient recycling of spent polymers should not only ensure an efficient recycling of the carbon. It should also aim 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 smallest recycle loop possible. Depending on the quality and purity of the waste, the priority should therefore be given to reuse, then reprocessing (mechanical recycling), then depolymerization to the monomer, then conversion to a hydrocarbon feedstock and, as last resort, energy recovery (see Figure 1). This priority list, often referred to as the waste hierarchy, aims at (1) maximizing the value of the product of recycling and (2) minimizing the waste of energy and material along the full cycle (illustrated by the waste arrows in Figure 1[16]).

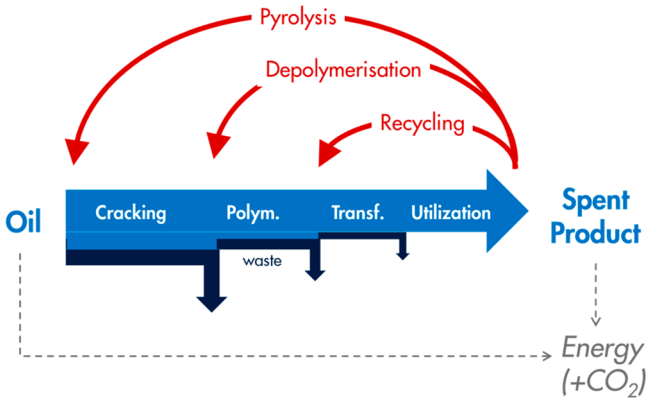

Figure 1. Options for recycling plastic waste for retransformation (mechanical recycling), repolymerization (chemical recycling to monomer), or recracking (chemical recycling to feedstock). Adapted with permission from ref 16. Copyright 2002 Royal Society of Chemistry.

Waste Quality. Postconsumer plastic is intrinsically heterogeneous and, thereby, of undefined quality. It consists of a variety of plastic items that are made of a variety of polymers (e.g., mainly PE, PP, and PET) and often contain minor amounts of foreign materials (e.g., foreign polymers, additives, and other contaminants). For instance, postconsumer plastic bottles, trays, and films have been shown to consist of 75 to 90 wt % dominant polymer (PE, PP, PET, or PS), 5−15 wt % foreign polymers and paper, and 5−15 wt % residue.[17] The foreign material and residue were mainly encountered in the cap/lid and labels.[17] The material heterogeneity is even larger for multilayered films, as the main polymer was found to account for only 55 wt % of the film.[17]

The nature and purpose of the various additives has been summarized in the literature.[32,45] The literature provides also valuable information on barrier additives for food packaging, namely polymeric, metallic or metal oxide films and additives.[18]

Waste Sorting. Plastic waste is usually sorted through a sequence of sorting steps.[6,19] These comprise a sorting on size, either manually or by means of sieves, an elimination of foreign materials (e.g., metal and glass), a sorting on plastic materials and, finally, sizing and granulation into plastic recyclate.

Foreign materials can be removed by using gravity in air flow (air classifier) or water stream (sink-float) as illustrated in Figure 2a-b. But metals can also be removed by exploiting their magnetic properties, i.e. by magnetic attraction of ferrous metal or by induced magnetic repulsion of nonferrous metals (Figure 2c).[19]

Gravity can also be used to sort some plastics among themselves, e.g., to separate the polyolefins (density of ~0.9 g/mL) from PET or PVC (density of ~1.4 g/mL). The gravity sorting can further be sharpened with the assistance of electrostatic or magnetic fields, though the result seems to be very sensitive to eventual contamination of the waste.[19]

More common, however, is to sort the various plastics by spreading them on a conveyor belt, identifying the plastic to sort using an infrared detector (e.g., near or short wave infrared NIR or SWIR) and sorting it with an actuator or air jet (Figure 2d).[19] The standard IR detector can be replaced or complemented by hyperspectral imaging spectroscopy (HIS) to recognize a full-shape product or by an X-ray fluorescence detector to recognize heavy elements such as Cl and Br. These advances are reported to allow challenging sorting, e.g., HDPE/LDPE, PET/PLA, or black products that cannot be identified with conventional NIR detectors.[19]

Such sorting results in fractions rich in films, PP, PET, HDPE, and mixed plastic (PE, PP, PS, PET), e.g., defined as DKR-310, -324, -328, -329, and -350 by the German Plastic Recyclers (DKR) and illustrated in Figure 2e.[20] These efficient sorting technologies appear to recover more plastic than manual household sorting[21] and lead to more efficient and cheaper logistic by transporting the whole waste stream instead of individual sorted fractions. All of these elements promise to make central postsorting of plastic wastes more efficient and cheaper than presorting at the household level. Hence, postsorting of postconsumer waste is expected to gain popularity globally and be increasingly adopted throughout the world.

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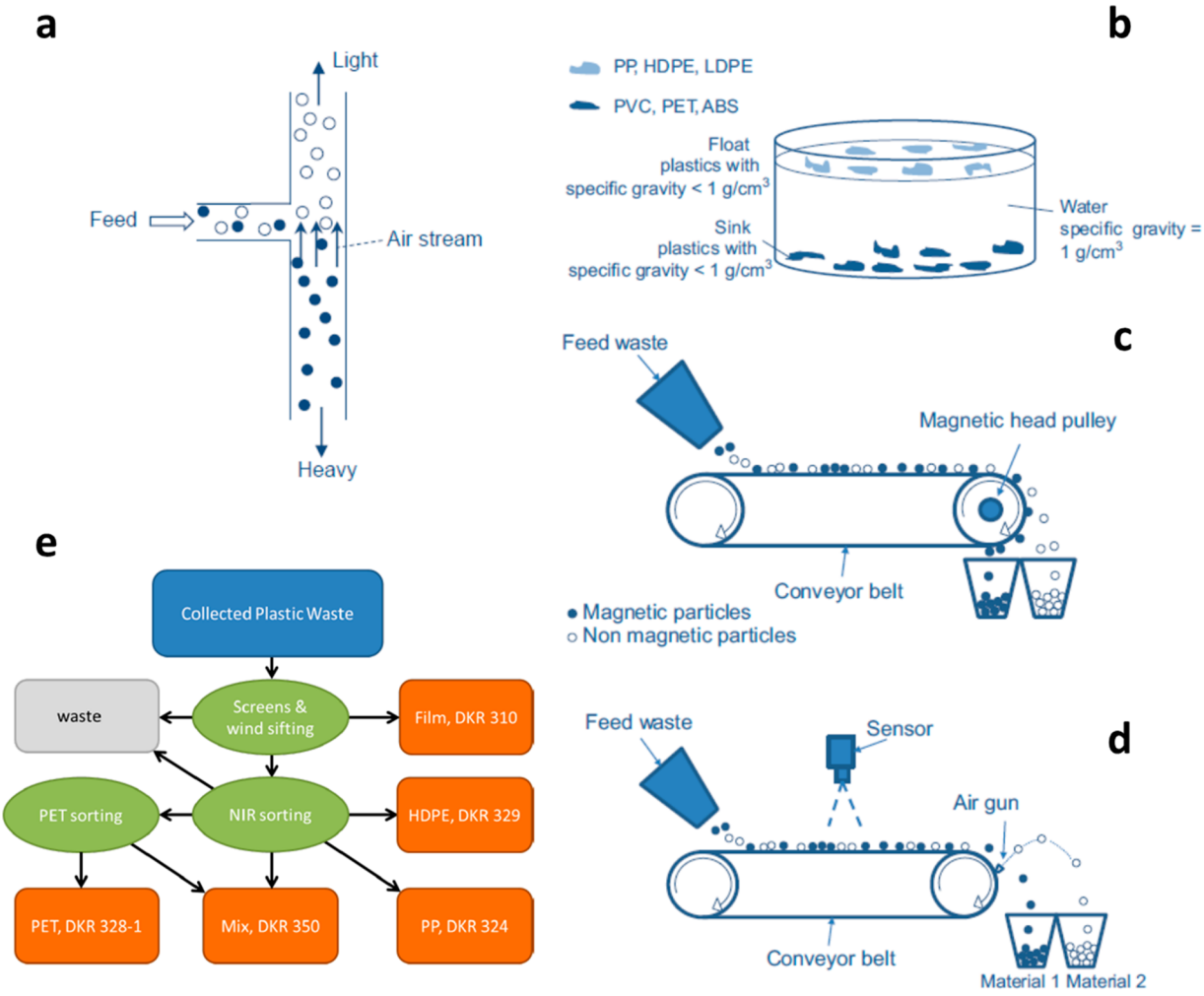

Figure 2. Archetype sorting technologies: a, air classifier; b, sink-float sorting; c, magnetic sorting of ferrous metals; d, sensor-based sorting; e, DKR plastic fractions. (Parts a–d adapted with permission from ref 19. Copyright 2019 Elsevier. Part e adapted with permission from ref 20. Copyright 2017 WUR.)

But new sorting technologies are being developed and demonstrated. One of them, tracer-based sorting, uses fluorescent pigments incorporated into the plastic substrate or in the sleeve. These are only visible under UV light at the sorting plant.[22] Another technology uses digital watermarks, i.e., codes that are integrated into the design of the packaging, and can be detected by cameras on high-speed sorting lines.[22] A watermark can carry a lot of information about the product and its packaging. Beyond assisting the waste sorting, watermarks could also contain nutritional information and provenance details that could be made smartphone-readable for consumers. More than 85 European companies across the consumer packaging value-chain have joined force in the Digital Watermarks Initiative HoleyGrail 2.0.[23] A third emerging technology, robotic sorting, applies artificial intelligence to help cameras + robotic arms to sort plastics from a conveyor belts.[24]

More progress in accurate sorting is to be expected soon. Until then, however, sorting technologies will produce a limited fraction of monostreams while leaving much as mixed plastic wastes. For instance, a pilot program in the UK compared the sorting of mixed plastic waste by manual sorting of whole goods and by mechanical sorting, after chipping the goods to flakes and removing the films.[25] They recovered 67 and 62 wt % as monostreams, respectively, with the rest remaining as mixed plastics. The monostreams can be sold for reprocessing and blending into new plastic products. It should be noted, however, that this reprocessing often starts with a finer sorting that further reduces the volume of plastic that is effectively recycled.

Plastic Washing. Sorted plastics may still not be suitable for direct reprocessing. It may require cleaning to remove dirt and other contaminants, e.g., from packaged food or from the mixed consumer waste. Such cleaning is generally imperative for mechanical recycling but might be important for chemical recycling as well.

Plastic waste is generally cleaned with hot or cold water, with the assistance of caustic agents or detergents.[6] The cleaning is often integrated in the sorting chain, e.g., after shredding and combined with a sink-float sorting step. Such washing can be costly as it requires dedicated washing equipment but also a drying step and a wastewater treatment. It may furthermore lack the efficiency required. For instance, odorous components appear to be only partly removed by a caustic wash; the most apolar components require the use of detergent or organic solvent to be removed.[26,27]

Various dry-cleaning approaches are also being investigated in an attempt to avoid the cost and water demand of

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conventional wet cleaning. They vary from mechanical cleaning with compressed air assisted with mechanical action such as a rotor disk, scrapping, or fluidized sand bed.[28−30] These dry cleaning techniques are reported to match the effectiveness of a caustic wash.

MECHANICAL RECYCLING

Principle and Challenges for "Monostreams". So far, plastic recycling consists mainly of mechanical recycling and is focused on the three dominant packaging polymers PE, PP, and PET. The recycling processes rely on cautious sorting of the clean and pure monostream fraction, compounding it to granules, and blending them with a virgin polymer of the same family, together with compatibilizers and additives to mitigate the shortcomings of recycled material.[5,6,31,32]

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 recycled/downcycled once, from bottle to textile.[33] PP is claimed to technically support up to four recycles but is practically recycled/downcycled once, to textile and playground equipment.[34] Apparently, mechanical recycling mainly consists of downcycling today. Hence, there is a need for complementary recycling options, particularly chemical recycling. So, let us review the limitations of mechanical recycling.

First, recycled materials, particularly postconsumer plastics, generally present lower performance than virgin ones. There are several reasons for that. The sorted material may not come as single grade plastic but as the market-average grade. Sorted plastic may therefore not meet the requirement for high-end applications.

Second, plastic products may contain additives such as fillers, antioxidants, plasticizers, pigments, flame retardants, etc., which have been selected and dosed for specific applications. Recycled materials will therefore contain the market average of these additives.

Third, sorted waste may not have the same purity as virgin material. It may contain minor fractions of foreign polymers, for instance, traces of PET or PP in a sorted PE stream, e.g., because of imperfect sorting. As polymers are practically immiscible with one another, these polymer impurities tend to segregate into small foreign domains that create weak spots into the recycled material. These shortcomings can be mitigated by 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).[5,6,31,32] Alternatively, the compatibilizers contain a main chain that resembles the target matrix and a reactive end group that can react with the functional group of the polymer impurity, for instance, one that can react with an alcohol group of PET or EVOH (ethylene-vinyl alcohol) polymers.

Fourth, recycled polymer chains may be partly degraded, e.g., through oxidation or UV radiation upon use, or through thermal degradation upon repeated hot processing.[5,6,31,32] Indeed, hydrocarbon polymers and PVC are reprocessed at 160−260 °C, and performance polymers such as PA and PET are reprocessed at 220−320 °C.[6] Such processing temperatures are not benign, particularly when the polymer chains has been damaged during use. As a result, the polymer chain may exhibit minor amounts of polar groups that need compatibilization. But recycled polymers may also exhibit an increased Mw and higher viscosity. The resulting shortcomings can be mitigated by means of various additives.[5,6,31,32]

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

These shortcomings are particularly pronounced for postconsumer wastes. Some of them may be of lesser concern for well-defined postindustrial waste. Hence, there is pronounced interest by the recycling industry for postindustrial waste streams. These shortcomings have been recognized for recycling today's fossil plastics. In principle, however, they also apply to the recycling of biobased plastics.[35]

Obviously, the addition of compatibilizers and additives to blend recyclate with virgin resin is increasing the level of impurities in the recycled resins. It will further increase upon multiple recycle loops, to the point where it will disqualify the material for further mechanical recycling. More sophisticated recycling technologies are then required, e.g., dissolution/precipitation or chemical recycling, which will be discussed in later sections.

Challenges for Thermosets, Tires, and Textiles. 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 1/3 of the polymeric materials,[36] spent products are generally recycled/downcycled by chipping and use as a filler in new products. This applies to rubber,[37] epoxy blends,[38] and polyurethane.[39] These materials are not prone to recycling by dissolution either (see next section). Hence, further recycling will require deep deconstruction, i.e., chemical recycling.

But alternative approaches are also being explored. For instance, flexible PU foams have been reported to be recycled into PUR films, fibers, or rigid foams by swelling them with a solution that contains a minor amount of Sn catalyst and, then, reprocessing the material at a high temperature in a twin-screw extruder. The catalyst facilitates the reorganization of the cross-link by catalyzing carbamate exchange.[40]

Textiles is a second sector that poses challenges in waste management and recycling. Textiles are the second largest contributor to pollution and have a modest recycling rate of 13%:[41] 1% is truly recycled to cloths; the rest is downcycled to industrial cleaning cloths or stuffing for matrasses and car seats.[42] Recycling textile fibers is very limited. They are rather downcycled to carpets or insulation because of the shortening of fibers and a loss of strength.[42] As if it was not challenging enough, textiles often consist of mixed fibers, e.g., cotton, polyester, and/or acrylate in varying ratios, and contain pigments and dyes of all sorts and colors. Despite all these challenges, the Nordic European countries have developed a comprehensive strategy for textile recycling, which is available on the web.[43]

Dissolution/Precipitation. The challenge that additives and contaminants pose to mechanical recycling can also be tackled by removing them, e.g., by extraction or dissolution/reprecipitation.[7,44,45]

In the former case, the extraction, the waste polymer is washed by an appropriate solvent or supercritical fluid.[45] The solvent is selected for high affinity for the additive to dissolve

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and moderate affinity for the polymer to swell it without dissolving it. But the solvent also needs to exhibit high diffusivity through the polymer to allow compact equipment. Needless to mention that the value of extraction may be limited to simple cases with low molecular weight additives. It may indeed encounter difficulties in removing a multitude of additives with varying solvency properties or removing high-molecular weight or insoluble materials. Such more challenging cases may require dissolution/precipitation.

In the case of dissolution/precipitation, the spent polymer is fully dissolved in an appropriate solvent. The polymer solution is separated from the insoluble impurities and additives, and the polymer is reprecipitated upon the addition of an antisolvent. The solvent and antisolvent are then separated for reuse at the dissolution or precipitation stage of the process. Dissolution processes have been developed for recycling PS,[31,46] PVC,[46,47] nylon,[48] PMMA,[46,49] PE/PP,[46,47,50] cotton/PET mixed fibers,[47] PLA/PET mixtures,[47] and multilayer films.[46,51] Some of these technologies are in commercial operation, e.g., APK's dissolution of the multilayer film[52] or the Re:newcell and OnceMore technologies for recovering cellulosic pulp from textiles.[53] Solvay's VinyLoop process for PS purification by dissolution has been run on a commercial scale for 16 years but, eventually, closed in 2018 because of the cost of renewing the permit for handling toxic phthalate plasticizers.[47] The other dissolution/precipitation technologies are at the pilot or demonstration stage.[7]

The recovery of solvent and antisolvent is likely energy demanding, particularly when operating at a high solvent/polymer ratio. Hence, one needs to ensure that the energy needed for solvent evaporation remains much lower than the energy needed to depolymerize the polymer back to its monomer. The heat of evaporation of organic solvents typically increases with polarity, from 0.3 kJ/g for hydrocarbons to 0.9 kJ/g for alcohols. This represents a small but significant fraction of theoretical depolymerization energy of polyolefins, e.g., 3.5 kJ/g for PE and 2.1 kJ/g for PP. But it exceeds that of some condensation polymers (e.g., 0.13 kJ/g for Nylon-6). Consequently, the use of a solvent/polymer (or antisolvent/polymer) ratio of 2:1−10:1 may eventually destroy much of the advantage of dissolution/precipitation of polyolefins over their depolymerization by leading to comparable energy demand. This concern is nicely illustrated in two papers. The first one[50] reports a plant designed to recycle LPDE bags by dissolution in toluene and precipitation with IPA addition. This plant appears to consume the equivalent of 23.5 kJ of energy per gram of LDPE (i.e., 10 g of steam and 0.4 Wh of electricity per gram LDPE). This largely exceeds the theoretical depolymerization energy mentioned above and still exceeds the practical energy demand of a steam cracker of 14−17 kJ/g of olefins and aromatics.[54] The second paper[51] developed a sequence of dissolution/precipitation to separate a multilayer film of PE:EVOH:PET into its constituting polymers. The process was reported to require 80 kJ/g of energy. This very high energy penalty can be further reduced with improved design[55] and recovers high-value polymers, mainly PET with minor amounts of EVOH and PE.

CHEMICAL RECYCLING

The mechanical recycling will likely be limited to deserving a fraction of the plastic markets and recycling a fraction of the plastic waste. Some markets may be too demanding, e.g., in terms of mechanical performance (strength or stretch), optical quality (transparency and colorless), or chemical purity (free of toxic contaminants). Similarly, recyclers extract the top-quality materials from the plastic waste and reject a sizable, if not dominant, fraction of mixed or contaminated plastics. Chemical recycling may help extend the market reach and/or the recyclable fraction.

Some polymers can and should be depolymerized back to their monomers. Other can only be converted to a general feedstock. Still others cannot fit either of these loops in an attractive manner and need to be discarded. But how to decide which recycling loop to apply? The basis for such a choice is illustrated by Figure 3.[16,56] The horizontal axis helps identify

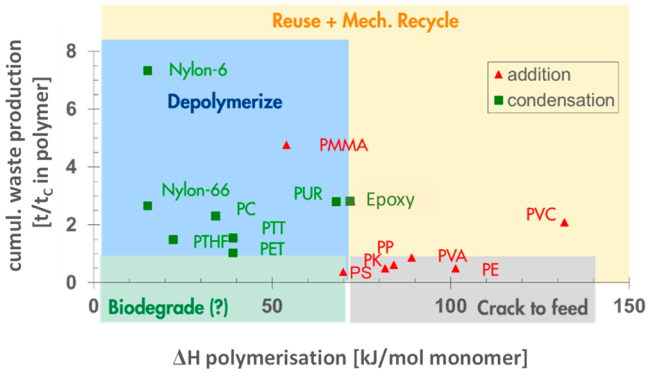

Figure 3. Options for plastic recycling (PC, p-carbonate; PTHF, p-tetrahydrofuran; PTT, p-trimethyleneterephthalate; PET, *p*-ethyl-eneterephthalate; PMMA, *p*-methylmetacrylate; PUR, p-urethane; PS, p-styrene; PP, *p*-propylene; PK, p-ketone; PVA, p-vinyl alcohol; PE, *p*-ethylene; PVC, p-vinyl chloride) Adapted with permission from ref 16. Copyright 2002 Royal Society of Chemistry.

the polymers that are easily depolymerized back to their monomer from those that are only cracked to a general hydrocarbon through more severe pyrolysis. The former show a low-to-modest heat of depolymerization (dH < 70 kJ/mol of broken bonds) and generally consist of condensation polymers. The latter show a high heat of depolymerization (dH > 70 kJ/mol) and represent addition polymers. The *y*-axis represents the cumulative amounts of resources that are consumed when producing the polymer (i.e., tons of inorganic, organic, and fuel consumed per ton of carbon present in the polymer). It, thereby, represents the "incentive" to recover the monomer rather than degrading it back to hydrocarbon and having to consume a lot of resources again to generate the monomer. This simple mapping readily recommends cracking polyolefins back to general feedstocks (lower right quadrant) but depolymerizing PET and polyamides back to their monomers (upper left quadrant). Polymers falling in upper right quadrants (e.g., PVC) are demanding to make and 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 candidates for biodegradation, if they would be biodegradable, as this would waste only limited energy and chemistry invested in making them. Although not shown here, today's biodegradable plastics (e.g., p-hydroxyalkanoate (PHA), p-lactide (PLA), and p-caprolactone (CPL)) fall in the upper left quadrant as they are easily depolymerized but are fairly demanding to produce. They indeed show a low polymerization enthalpy <50 kJ/mol, likely close to the esterification

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enthalpy of acetic acid/ethanol to ethyl acetate/water of −20 kJ/mol. However, the production involves demanding recovery of the diol, diacid, or hydroxyacid monomers from fermentation broth, e.g., in terms of energy and chemicals such as acid to convert the carboxylate salt to the desired acid and solvent to extract it from the broth.

Solvolysis 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 PUR (Figure 4), which are well advanced.[7,31,49]

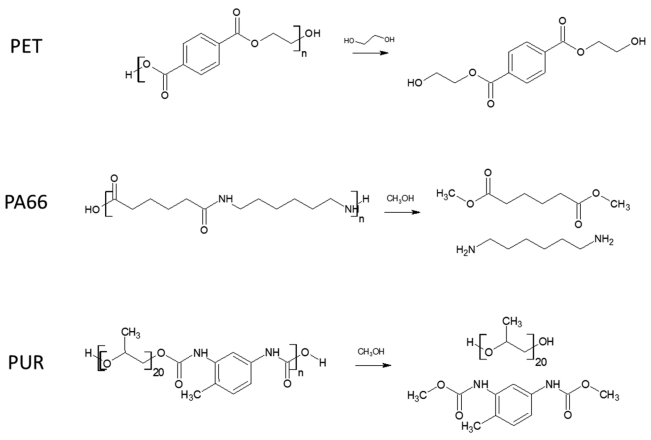

Figure 4. Glycolysis of PET and methanolysis of PA66 and PUR.

The polyester PET is commonly depolymerized by alcoholysis, i.e., methanolysis (with methanol) to dimethyl terephthalate of glycolysis (with ethylene glycol) to bishydroxyethylene terephthalate BHET.[57,58] The reaction is generally carried out at an elevated temperature (~200 °C) in the presence of catalysts, traditionally a Lewis metal salt such as Zn acetate.[59] The methanolysis requires a complex product recovery and purification train, which becomes very challenging when dealing with copolymers, e.g., that contain some isophthalate (besides terephthalate) or some diethylene glycol (besides ethylene glycol). Deep solvent removal is necessary since the monoalcohol solvent would terminate the growing chains during polycondensation polymerization. Glycolysis does not suffer these drawbacks and holds therefore more promise. It furthermore enables partial depolymerization to low-viscosity oligomers that can be fed back to the polymerization reactor, thereby facilitating also the repolymerization. Many companies are piloting or demonstrating PET depolymerization processes with the aim of providing high-quality recycled materials for food packaging applications.[60] A depolymerization process scheme could look as presented in Figure 5.

Polyamides (PA) are depolymerized in water at ~300 °C in the presence of inorganic acid.[62] 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[63] but does not seem effective for nylon-66.

Polyurethane (PUR) can also be depolymerized by alcoholysis, glycolysis, and hydrolysis. However, it can also undergo aminolysis.[64,65] In contrast to the previous cases, however, PUR depolymerization does not release the constituting monomers, i.e., propylene oxide and diisocyanate. Instead, it releases high molecular-weight products, namely, the oligomeric polyols and the aromatic N-containing oligomers. These high molecular-weight products may also be difficult to separate and purify. In the best cases, the polyols can be purified and 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 may 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 logistic and reprocessing. This is surely the case when mixed with other plastic waste. But the small-scale reprocessing likely applies to industrial waste as well.

The new and emerging biobased polyesters such as PLA, PHB, PBS, and PEF are compatible for alcoholysis to a monomer.[35] This opportunity will become interesting when these materials are used in significant volume and can be sorted properly. In the meantime, however, they may remain in an unsorted residual stream or, worse, get erroneously sorted as impurities with related material and jeopardize their recycling.

In some cases, solvolysis can be applied to reprocess composite materials by selectively separating their constituents. For instance, aliphatic polyesters such as PLA are much more prone to hydrolysis than aromatic polyesters such as PET. Consequently, hydrolysis conditions can be selected such as to depolymerize and dissolve the PLA component of a composite

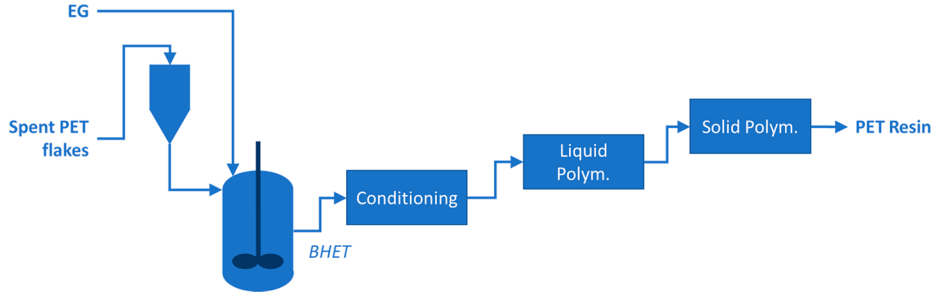

Figure 5. Process concept for PET chemical recycling (EG, ethylene glycol; BHET, bis-hydroxyethylene terephthalate). Adapted with permission from ref 61. Copyright 2018 Wiley.

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polymer without attacking the PET constituent.[47] The undissolved PET residue can then be subjected to glycolysis under harsher conditions to be depolymerized and recycled. A similar approach is applied to cotton/PET mixed fibers, where PET is dissolved to recover cotton as cellulosic pulp.[47]

At this point, it should have become clear to the reader that solvolysis still requires waste polymers of minimum quality and cleanliness. Solvolysis may remove additives, including foreign polymers. However, the purification train may become very complex and expensive if it needs to recover the monomers free of too many undesired low-molecular weight components such as comonomers, degraded monomers, or functional additives such as dye, antioxidant, etc.

Pyrolysis. *Melt Pyrolysis of Polyolefins.* Polyolefins cannot be depolymerized back to their monomeric constituents. Depolymerization requires harsh pyrolysis conditions and generally lead to a complex mixture of hydrocarbons, i.e., a general feedstock (lower right quadrant of in Figure 3). The pyrolysis of polyolefins produces paraffinic/olefinic waxes under moderate temperature (450 °C) conditions, an aromatic product at more severe conditions, and olefin-rich gas and char at the highest temperature (~700 °C).[6,49,66−68] Such a hydrocarbon product can be processed into a synthetic fuel. But fractions of aliphatic products produced under mild conditions can also be used as chemical feedstock and 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 a coproduction of ~10 wt % fuel gas, ~10 wt % aromatic gasoline, and 15 wt % aromatic fuel oil.

Pyrolysis is no new technology. Oil refineries have been applying it on a large scale in various forms for decades for upgrading heavy oil fractions into gas and distillates. These technologies are then called thermal crackers, visbreakers, or cockers.[69] Pyrolysis has also been explored for processing plastic waste by major chemical producers for some 30 years. Although technically successful, these technologies were not commercialized because they could not compete with cheap crude oil. The rise in oil price in the early 2000s encouraged start-up companies to revisit plastic pyrolysis, which led to a plethora of technology providers today.[7,31] More recently, 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 that it was processing a first truck of plastic pyrolysis oil in its cracker at Norco, US, and announced its ambition to ramp up the volume of plastic recycling fed to the cracker to 1 Mt/a by 2025.[70] Numerous chemical producers have embarked on this journey and made similar pledges.

Polyolefins are generally pyrolyzed by so-called melt pyrolysis.[64,65] A conceptual process scheme is provided in Figure 6 (top). Accordingly, the plastic is fed and melted into an extruder, optionally with recycled liquid, then fed to a large vessel that is heated to 450−500 °C and is 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. The pyrolysis of polyolefins produces a waxy liquid product with 75−80 wt % yield and consumes about 1.5−2 GJ of energy per ton of liquid product, which represents less than

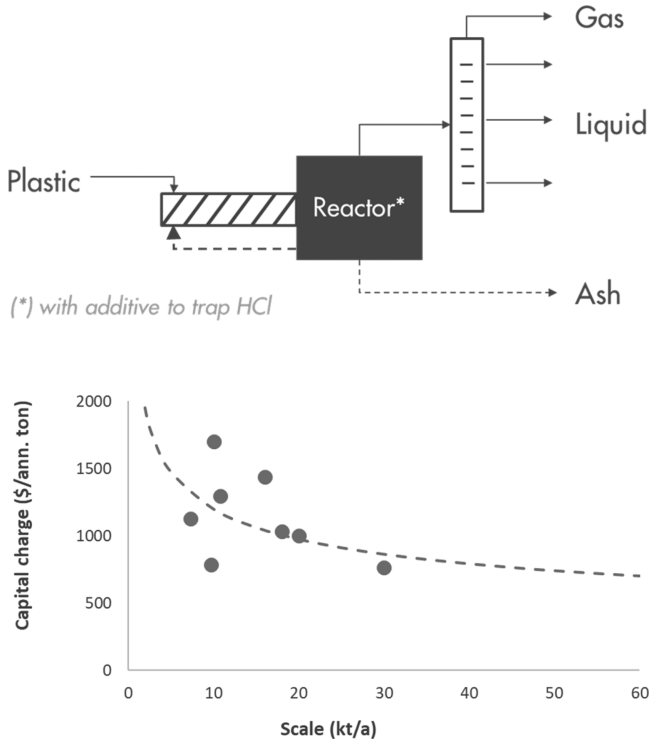

Figure 6. Melt pyrolysis of waste plastics—typical process concept (top) and reported investment costs (bottom; the dotted line illustrates a typical economy of scale and is meant to guide the eyes).

half the energy available in the 10−15 wt % of gas produced during pyrolysis.[64] Hence, the pyrolysis process can be run autosufficiently on its own byproduct. Tight temperature control and extensive agitation seem essential to minimizing coke deposition and achieving high oil yields. Kinetic modeling and the role of heat and mass transfer in pyrolysis is discussed extensively in the literature.[66] These requirements seem to limit the scale of pyrolysis reactors at some 15−20 kt/a, a scale that is very small when compared to the 3 Mt/a of liquid that steam crackers are processing. The small scale is clearly harming the economic competitiveness of the process as it leads to high capital and operating costs (Figure 6, bottom).

The resulting pyrolysis oil and waxes can further be cracked to olefins and aromatics (so-called high value chemicals) with about 65 wt % yield. But not all steam crackers are capable of processing feedstock with such a broad range in boiling points. Some may indeed be limited to processing the naphtha fraction of the pyrolysis oil. This 1.5−2 Gj/t of energy consumed by the pyrolysis step is dwarfed by the 14−17 GJ/t of energy needed to further crack the pyrolysis to high value chemicals in a steam cracker[54] and comparable to the energy needed to produce the standard hydrocarbon feed from crude oil. Hence, recycled olefins are not disadvantaged over virgin ones, as will be discussed in a later section (LCA section).

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. The pyrolysis of polymers other than polyolefins will be briefly discussed in a later section. Small amounts of PVC in the feed are particularly detrimental, as it liberates HCl that corrodes the equipment and makes the oil unsuitable for feeding into a steam cracker. One element of mitigation consists of heating

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the plastic waste in the feeding system and recovering the HCl-rich gas prior to feeding the plastic melt to the reactor. Another and complementary approach is to feed caustic elements such as $CaCO_3$ to the reactor to trap and neutralize remaining chloride. The resulting salt is then removed together with the coke.

Alternative Pyrolysis Processes. Beyond melt-pyrolysis, other technologies are also being developed to convert waste plastics into liquid hydrocarbons.

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 a monomer.[64,65] For instance, the Synova technology cracks plastic waste in a hot fluidized sand bath, cools the product, recovers the tar and liquid for recycling back to the cracker, and delivers an olefin-rich gas for further purification.[71] Such purification will likely require the removal of various contaminants and, subsequently, cryogenic fractionation to deliver polymer-grade ethylene, propylene, and butylenes.

The pyrolysis can also be assisted by a catalyst, typically an acidic zeolite, to convert the pyrolysis vapors to lower olefins and waxes.[49,64] Anellotech[72] and BioBTX[73] have developed such processes, based on their earlier learnings on lignocellulose upgrading to aromatic biofuels. Catalyst deactivation requires complex reactor design, e.g., based on riser-regenerator applied in fluid catalytic cracking,[67] to allow continuous catalyst regeneration.

Hydrothermal liquefaction, as performed by Licella, is another process that has been developed for biomass and adapted for plastic waste.[74] Accordingly, the plastic waste is thermally cracked in near/supercritical 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 low-carbon fuel (see Waste Destruction and Disposal).

Finally, the IH^2 hydropyrolysis technology that is being developed by GTI and Shell runs the pyrolysis in the gas phase, in the presence of a hydrogen atmosphere and a hydrogenation catalyst (Figure 7). It is presently being demonstrated on a 2000 L/day scale.[75] 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 fuels (RDF).[76] However, it remains unproven for pure waste plastic feedstock. Further discussion of this technology will therefore be moved to Waste Destruction and Disposal that also considers gasification to valorize RDF.

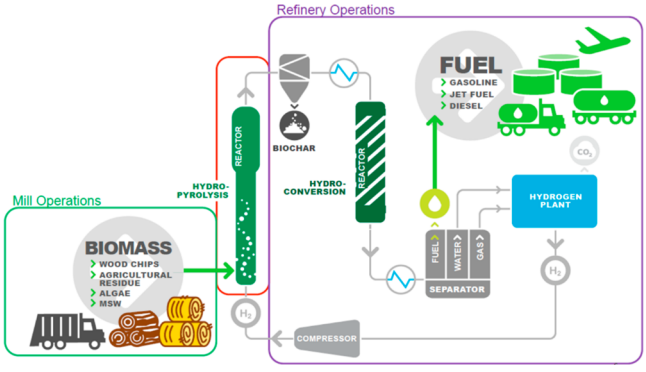

Figure 7. IH^2 hydropyrolysis process, developed by GTI and Shell, converts MSW and RDF to hydrocarbon feedstock[74]

Pyrolysis of Polymers Other than Polyolefins. Pyrolysis has also been investigated for other polymers than polyolefins, e.g., PS, PVC, PET, PA, and even thermosets such as PUR, rubbers, and epoxy composites.

Pyrolysis appears particularly promising for PS and PMMA waste. These addition polymers indeed crack back to their constituting monomer with reasonable selectivity at moderate temperatures (<400 °C), as suggested by Figure 3. For instance, PS pyrolysis can deliver some 70 wt % of styrene and some additional 10 wt % of other monoaromatics.[77,78] Similarly, PMMA pyrolysis can deliver an MMA yield of 50−80 wt % in melt pyrolysis or heated screw feeders and up to 97 wt % in a heated fluidized bed or conical spouted bed.[79,80] Moreover, the product can be condensed out of the gaseous byproducts. Various processes are being developed and demonstrated for these streams.[46,49] The small scale of pyrolysis might not be a critical limitation here since these waste streams are available in limited volume any way. But it will still hurt the economic viability of the process.

Pyrolysis seems to also be promising for depolymerizing some condensation polymers. For instance, Nylon-6 pyrolysis has been reported to deliver the cyclic monomer caprolactam with more than 90 wt % yield, with only minor amounts of byproducts such as its cyclic dimer as well as some nitriles and acido-amides.[61]

Other thermoplastic polymers are less suitable for pyrolysis.[81] PVC is particularly reactive under pyrolysis conditions as it release HCl at mild temperatures, starting at ∼250 °C. This proceeds in an autocatalytic manner since HCl catalyzes further dehalogenation. PVC pyrolysis also delivers little hydrocarbon oil (<15 wt %). The main products are HCl (up to 58 wt %) and char (>25 wt %).[82] Furthermore, the oil is contaminated with Cl components, e.g., chlorobenzene. Small amounts of PVC can even contaminate the pyrolysis of polyolefins, e.g., by the addition of HCl to the olefins produced from polyolefin pyrolysis.[79]

PET is another polymer that is not suitable for pyrolysis.[83−85] Upon thermal degradation, it liberates much gas (20−40 wt %) and an oil that is rich in oxygenated fragments, such as 4-(vinyloxycarbonyl) benzoic acid and benzoic acid.

Pyrolysis processes have also been explored for recycling thermoset resins such as PUR, rubber tires, or even epoxy composites.[37−39] While technically feasible, the product yield and/or quality does not appear very attractive so far. The pyrolysis of vulcanized rubbers[86] leads to ∼70 wt % highly aromatic oil and ∼25 wt % sulfur-rich gas. The addition of acidic and metal catalysts does not seem to change the product slate significantly.

Alternative Chemical Valorization. Research groups have started exploring the possibility of using waste plastic as a feedstock for manufacturing chemicals other than their constituting monomer or polymer. For instance, PE appeared to be converted to C_{25-35} alkyl-benzenes and alkyl-naphthalenes with 80 wt % yield when contacted with a Pt/Al_2O_3 at 280 °C without a H_2 atmosphere.[87] In the presence of H_2, however, PE can be converted to paraffinic waxes and/or lubricants in the presence of Pt- or Ru-based catalysts.[88,89] The result is expectedly more valuable that the more traditional pyrolysis oil, but the conversion process is also more

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challenging and, likely, more expensive. This could easily offset most of the added value of the product.

Oxidative valorization is also being investigated. Hydroxyl-terminated polymers such as polyetherpolyols have been converted to formic acid and alkyl formate in the presence of O_2 under LED irradiation.[90] The authors proposed to valorize the formate product for fuel and chemicals applications. They, thereby, seem not to have fully recognized that they have destroyed most of the energy content of the original polymer while making the fuel or are targeting a very small chemical market to accommodate significant amounts of plastic waste.

Postsynthesis functionalization of polymers is being explored in order to modify their properties, e.g., for improved surface adhesion. For instance, PE has been partly functionalized with keto and hydroxyl groups by post synthesis oxidation.[91] Similarly, functionalization of PP with xanthate groups (RO-C(S)S-) confers it improved adhesion properties.[92] However, one should watch out not to confuse such polymer-upgrading technologies with waste recycling or upcycling. First, the feedstock likely needs to be of high purity to deliver a high-quality product. Second, the resulting high-quality product will likely target niche applications that are too small to valorize a sizable fraction of the plastic waste.

At this point, it seems valuable to spend a few words on the concept of upcycling that is confusingly used in the scientific press and scientific literature. Upcycling seems to occasionally be used as a synonym of *recycling*, while it should more restrictively mean the opposite of *downcycling*, i.e., *recycling to higher-value product that the original polymer*. But high-value products typically are marketed in limited volumes. For instance, ethylene vinyl alcohol (EVOH), the adhesive-version of PE, represents about 0.1% of the global PE market. Hence, one should ensure that the target application can assimilate a sizable fraction of the plastic waste considered to truly contribute to the circular economy.

WASTE DESTRUCTION AND DISPOSAL

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 diolefins and to remove residual oxygen and nitrogen. It may also need fractionation to select the desired boiling range and may also need dewaxing to avoid the gasoil-range product to crystallize at low temperatures.

But transportation fuels can also be produced from a more contaminated and cheaper stream such as the whole MSW or its sorting rejects, namely, the refused derived fuel (RDF) or the solid recovered fuel (SRF) that contains unsorted plastics still mixed with unsorted textile, paper/cardboard, and other organic fractions. These fractions can be upgraded to hydrocarbon fuel 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.[9] For instance, Shell has partnered with other companies to help demonstrate Enerkem's gasification technology to convert MSW to syngas and, eventually, methanol.[93]

Gasification technologies can, of course, be applied to mixed plastic waste or even well-sorted plastic waste. However, gasification technologies are expensive and, thereby, require large scale. Furthermore, they deliver a low-value product, syngas, that needs further conditioning and conversion to get to hydrocarbons. For instance, the fuel manufacturing plants based on a much cleaner and easier feedstock, natural gas, have been reported to require investment costs of $1500−2000 per annual ton of fuel (in 2003 currency and likely 50% more in today's currency) on the scale of ∼500 kt/a.[94] Such capex intensity is comparable to that reported above for plastic pyrolysis at 1/50 of the scale. 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.[73] 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.[72]

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 gas cleaning technologies to free the exhausted gas from harmful components such as polyaromatic hydrocarbons, dioxins, NO_x, and SO_x prior to release to the atmosphere.[95]

In contrast, field burning of waste is infamous for its air pollution, for the release of toxic components, and for wasting the energy content of the waste. But it is a low-cost way to destroy the waste, making it popular in low-to-medium income countries that lack infrastructure for better waste treatment.

Biodegradation. Biodegradation, i.e., biological conversion to CO_2/H_2O/biomass, is another way to destroy organic waste. It is often perceived or presented as ideal waste management. But this does not recognize the fact that biodigestion is truly wasting the energy and chemistry embedded in the polymer or is, at best, converting it to low-value compost. It is therefore no recycle option but rather a waste destruction option. It belongs to the bottom of the waste hierarchy. It can nevertheless be valuable in a few occasions. For instance, biodegradation can help minimize the pollution of 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 much films, or in plastic waste that is heavily spoiled with food rests (e.g., single-use food packaging and disposable cutlery).[96]

Anaerobic biodigestion, i.e., biological conversion CO_2/CH_4/biomass, is more valuable when run in a well-controlled industrial setting, for it delivers CH_4 that can be used to generate electricity and be fed into the gas pipeline for domestic and industrial use. It thereby falls among the energy recovery options discussed above.

Both aerobic and anaerobic biodigestion are applicable to a limited set of polymers. This requires the polymer to be hydrophilic to allow microbial film to grow on, to have low crystallinity to be accessible to enzymes, to be prone to enzymatic hydrolysis, and, finally, to release monomers that can be metabolized by microorganisms. Amorphous aliphatic polyesters such as p-caprolactone (CPL), p-hydroxyalkanoate (PHA), and p-butylsuccinate (PBS) are renown examples of biodegradable polymers.[93] p-lactide (PLA) and *p*-ethylenefuranoate (PEF) show a higher crystallinity and higher hydrophobicity and are, thereby, slower to biodegrade.

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Landfill. Despite all the options discussed above, the dominant form of waste disposal is arguably landfill. It accounts for 40−60% of waste disposal, depending of the income level of countries,[8] but has been decreasing significantly over the past decades, particularly in regions of high income and high population- density such as Western Europe and Japan.[2,11] Some could argue that plastic landfill is a responsible method of carbon sequestration. This would be reasonable when landfills would have no other environmental impact than the occupying a modest fraction of the land. But this is not the case. It is also contaminating the air by the release odorous components and greenhouse gases (biogas, a mixture of CO_2 and CH_4) through decomposition of organic matter such as food waste. It is also contaminating the land and aquifer through release of leachable components trapped in the plastic and washed of by rainwater. Examples include the leaching of bisphenol A from PVC,[97] phthalate plasticizers,[98] brominated flame retardants from electric and electronic equipment (WEEE),[99] as well as heavy metals such as Pd, Ni, Sn, Zn, and Sb from WEEE.[100,101] The leaching seems to be further promoted by the humic acids, short-chain carboxylic acids, and amino acids that are coextracted from the waste itself. Landfills would obviously need to meet very strict gas and leachate containment criteria to qualify as a responsible disposal method.

Existing landfills have also been considered as potential resources to be mined.[102−104] Unsurprisingly, the excavated waste requires extensive sorting and washing to deliver a plastic-rich fraction, and this remained still very contaminated. Excavated plastics showed extensive surface contamination, surface degradation/oxidation (e.g., expressed as carbonyl index), and increased crystallinity. All this makes them, at best, compatible for recycling by pyrolysis and, at worst, and more likely, only valuable as RDF for incineration with energy recovery.

Micro/Nanoplastics. We cannot discuss the end-of-life of plastic without addressing the spread of microplastics that eventually escape collection/recycling and impact the environment and health.

Micro/nanoplastics are millimeter to submicron pieces of plastic that end up in the environment for varying reasons. The majority are debris generated and released during normal use of the plastic (e.g., short textiles fibers or tire dust) or are intentionally added to specific products e.g. as abrasive additives (e.g., for cosmetic, laundry, or paint).[105] A minority are debris from land or ocean litter.

Microplastics can be dispersed by wind or water streams and get assimilated by living organisms via inhalation or through the food chain.[102,106] They are indeed found along the food chain, with occasional evidence for reduced feeding in invertebrates. Microplastics have been found to penetrate tissues and cells and to distribute to fluids and organs.[103] But ingested microplastics seem to also get eliminated after a while, e.g., through body fluids.[102,103]

There is no evidence yet for acute toxicity or severe long-term effects of microplastics on human health, although much is still poorly understood.[107] As such, microplastics are a cause of inflammations, through mechanical/physical irritation.[103] They have not been proven to cause cancer. However, microplastics also carry leachable components that are potentially toxic. These could be residual monomers, leachable additives (e.g., plasticizers), as well and hydrophobic pollutants and biofilm/planktons that have accumulated over time.[102,103] These leachable components are likely of bigger concern.

The spread and impact of microplastics has come under scrutiny. First, intentional microplastic additives are being considered for ban. Second, products that release microplastic upon normal use may eventually need to switch to non-persistent polymers that biodegrade in the environment within a finite and acceptable time span.

CIRCULAR PLASTIC ECONOMY

Now that the life cycle of plastics has been reviewed, it seems timely to assess the progress made toward a circular plastic economy. The following section will therefore review some life-cycle analyses (LCA) on the use and recycling of plastics. But a circular plastic economy needs more than waste recycling and responsible disposal. It also needs to have products redesigned to maximize material recycling. This will be addressed in a subsequent section. Beyond all that, a circular economy also needs to recognize the inevitability of losing material along the life cycle. It therefore must ensure that these losses are harmless for the ecosystem. This calls for the eventual switch to renewable carbon as a feedstock, the last subject of this review.

LCA. The scientific literature and the web offer a wealth of life-cycle analyses (LCA) 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 biobased to fossil-based plastics, and still others aim at comparing various end-of-life (EoL) scenarios such as landfills, incineration, conversion to fuel, or recycling to plastics. These studies also vary in their scope. Some limit their analysis to the carbon footprint or GHG emissions, while others also consider other planetary boundaries such as land and water use, water and air pollution, biodiversity, etc. I personally find it very delicate to draw solid conclusions from such studies, for the overall conclusions heavily depend on too many factors, premises, boundaries, substitution scenarios, etc., which are often hidden in the small print of the study, e.g., in their Supporting Information. I will nevertheless take the risk to extract a few important messages to be used in an indicative, at best semiquantitative manner.

Overall, the carbon intensity or GHG/CO_2 emissions of plastics seems to amount to 4−5 $t_{CO2}/t_{plastic}$,[36,108] half of it being due to the production stage and the other half due to the incineration at the end of life.[36] 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 6 t_C/t_C for the major engineering plastics and likely more for high performance polymers.[16,54]

Recycling is generally seen as delivering significant GHG emissions savings, when compared to incineration.[105,109−111] Obviously, the GHG savings vanish if one compares recycling with landfill, which could be considered as a form of carbon sequestration if done responsibly, as discussed above. Considering the chemistry and energy requirements of the various recycling options for polyolefins, 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.[25,46] Mechanical recycling is particularly effective when delivering high-quality

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recyclate at high yield (>70%).[25,108] But this may apply to a very limited fraction of the waste, thereby making chemical recycling very competitive for polyolefins.[108] 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 8.[112] These data are in

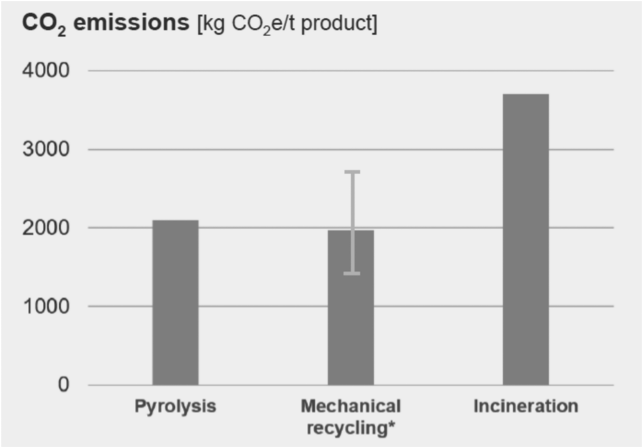

Figure 8. CO_2 emissions of various end-of-life scenarios for polyolefins (the error bar reflects different scenarios of sorting quality and losses). Published with permission from ref 109. Copyright 2017 BASF.

line with estimates made by Shell and reviewed by CE Delft. Vollmer et al. also confirm the savings of 1 $t_{CO2}/t_{plastic}$ for pyrolysis of PE and report significant savings for chemical and mechanical recycling of ABS, PA, and PET, when compared to incineration.[7] They even find some savings when compared to landfills. They also report the lowest C-footprint for the dissolution/precipitation approach, which is intriguing in light of the earlier discussion.

It should be realized that the chemical recycling by pyrolysis is likely not producing a pure recycled product rather a mixture of virgin and recycled chemicals, for the recycled pyrolysis oil will most likely be coprocessed with virgin hydrocarbon in the steam cracker. Hence, the benefit in carbon footprint is effectively spread over the whole product slate. Depending on legislation and consumer support, it could fully be assigned to a specific product fraction, following the so-called mass balance approach.

The carbon footprints estimated above are no ultimate footprint. Much progress can still be made to reduce the CO_2 emission of recycling by refining and integrating the technologies, and by applying renewable energy (e.g., renewable electricity), to name but a few.

It seems valuable to devote, here, a few words to the end of life by biodegradation. Qualitatively, we can expect biodegradation to deliver the highest C-footprint of all end-of-life options. Like incineration, biodegradation is converting the plastic to CO_2 and H_2O. Unlike incineration, however, it does not allow the recovery of the energy bound into the material and, thereby, does not save on other fuels. This conclusion is indeed confirmed by Posen et al., who report the CO_2 savings of PLA and PHB to decrease in the order of recycling > incineration > composting.[113] They also found CO_2 savings when substituting fossil polymers by PLA or PHB in case the polymers are incinerated at EoL. No significant savings were found when the waste polymers were recycled.

Design for Recycling. *Guidelines.* While being critical to the sustainability and circularity of plastics, improved technologies for collecting, sorting, and recycling the material will not suffice. Deep circularity will also require new product design that facilitates the recycling. The design for recycling may require reducing the diversity of polymer materials; revisiting the use of and choice for additives; reconsidering composite materials such as multilayer films; rethinking product accessories such as caps, labels, and sleeves; and much more.

Various design guidelines have been defined to facilitate recycling. Plastic Recycler Europe proposed RecyClass guidelines for a variety of plastic products.[114] For instance, HDPE containers are recommended to consist of >90% (preferably > 95%) HDPE, contain a minimal barrier layer (<3% EVOH that is stabilized with <1% PE-graphed maleic anhydride tie layer), contain only unavoidable additives, and bear labels and sleeves made of PE. Similarly, clear PET bottles should consist of >90% (preferably >95%) PET; contain no barrier layer or only an internal coating of SiO_x; avoid the use of additives; and bear caps, labels, and sleeves made of low density materials such as polyolefins or PET foams. Similar guidelines are proposed by the Ellen McArthur foundation[115] and by Ceflex,[116] a large consortium for a circular economy for flexible packaging. But this represents only the beginning of the journey.

Design guidelines have so far been defined to facilitate mechanical recycling. They may soon need to be revisited to accommodate the preference of chemical recycling as their second or third choice, now that chemical recycling is taking off. Guidelines should furthermore be sharpened to mandate slow biodegradation to avoid accumulation in the environment for those products that present significant risks to escape collection and end up as litter in the environment because of, e.g., their application, their size, or their contribution to microplastic release. Finally, guidelines for durable products need to recognize the possibility of sorting technologies to evolve during the lifetime of the products and become inadequate when they eventually get collected as waste. This issue has been reported for computer recycling in 2002. Design guidelines were defined to facilitate manual disassembling and manual sorting of the constituting plastics but became ineffective when the decreasing revenues and technology development enticed recyclers to switch to shredding and automatic sorting of the plastics.[117]

Novel Materials. Design for recycling should obviously look beyond product reformulation based on existing materials. It should also consider novel polymers that are intrinsically easier to recycle. Quite some research is indeed devoted to developing new opportunities. Let us review a few examples for illustration.

Cross-linked condensation polymers, i.e., thermoset resins, have been designed to be recyclable by hot remolding like thermoplastic. This is achieved by incorporating one of the condensation functions in excess, e.g., the alcohol or amine in polyester or polyamide, respectively. This allows transesterification at elevated temperatures and, thereby, enables reshaping the material upon heating without losing network integrity.[118,119] Such materials are called vitrimers or a covalent adaptable network.

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Long-chain polyesters and polycarbonates have been shown to offer properties that match those of polyolefins while being intrinsically depolymerizable as are condensation polymers.[120]

Wood and other lignocellulosic feedstock have been converted to recyclable thermoplastic composites by means of liquefaction, recovering the liquefaction residue as a thermoset matrix and reinforcing it with natural fibers.[121] Spent composites can be reprocessed in the liquefaction to convert the natural fibers into a thermoset residue to be subsequently reinforced with fresh natural fibers to form recycled composites.

With all of these exciting developments emerging, one needs to recognize that novel materials will only become collectable and recyclable when applied in enough volume. Otherwise, they may not be sorted and may end in the RDF fraction (residue derived fuel) or, worse, as annoying impurities in a sorted plastic fraction that spoils recycling. The exploration of novel materials seems, in fact, to oppose the first guideline in design for recycling: material simplification. Although elegant at the technology level, novel materials may become inefficient at the system level. It may be wise to remember here an important lesson in metal recycling: the metals that get recycled at a high rate (>50%) are either produced and collected in a very large volume and high concentration (e.g., Fe, Co, Ni Cu) or have a very high market value (e.g., noble metals).[122] Recycling other metals is often economically challenging and proceeds at a modest rate.

Closing the Cycle with Renewable Feedstock. The definition and implementation of well-thought-out recycling guidelines and the deployment of performant collection, sorting, and recycling technologies will still not make the plastic economy fully circular. The recycling will inevitably suffer from material losses at various stages of the cycle, from collection to sorting, to mechanical recycling of the high-grade fractions and chemical recycling of the low-grade fractions. Let us try to estimate a number around recycling efficiency, at least a crude one, for a well-functioning recycle scheme by 2050:[123]

Assuming optimistic efficiencies of 90% for collection, 80% for sorting (20% to high-grade, 60% to low-grade), a realistic efficiency of 90% for mechanical recycling, and realistic efficiencies of 80% and 80% for the pyrolysis and steam cracking steps of chemical recycling of polyolefins, we arrive at an overall efficiency of 50% (Figure 9).[120] This also means that

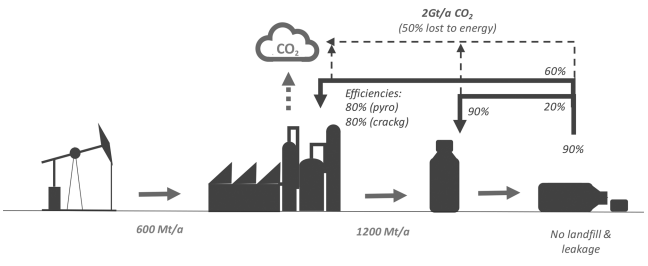

Figure 9. Possible recycling efficiency by 2050[120]

~50% of the material is still lost. Ideally, the losses after collection would not end up in the environment as uncontrolled litter or controlled landfill but would be valorized as energy or fuel and be released as CO_2. This does not apply to the collection losses that are inevitably leaking into the environment in one form or another. Material losses will likely remain very significant for a while: if the demand for plastic keeps growing at 4% per year, it could triple by 2050, and the CO_2 release could amount to some 2 Gt/a.

Accordingly, the recycling loop must be replenished with a sizable fraction of fresh carbon. Fossil hydrocarbons will likely supply it for some decades ahead[120] and should be complemented by a comparable volume of CO_2 capture and sequestration to mitigate the resulting CO_2 emissions, either artificially (CCS) or naturally by planting and preserving trees (nature-based solutions, NBS). But this will make the industry only partly circular. A fully circular economy will require fresh carbon input being supplied by renewable carbon, i.e., by atmospheric CO_2.[120]

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.[124,125] Other groups are exploring biomass. In fact, plants are already doing most of the work: they capture the CO_2 from the atmosphere and reduce it from C^{4+} carbon to C^0.[120,126] Biomass appears indeed to be economically a much more attractive source of renewable carbon in the short-to-midterm, and opponents to biofuels are no opponents to biobased chemicals. On the contrary, they are recommending to use biomass for chemical applications.[127] A number of biobased plastics are already being deployed, with polylactide PLA and biobased polyethylene as front runners, while many more are being developed, e.g., polybutylenesuccinate PBS, polyethylenefuranoate (PEF), or polyhydroxyalkanoates PHA.[20,93,128−130] Moreover, a number of biobased monomers such as ethylene glycol, 1,3-propylene diol, 1,4-butanediol, and epichlorohydrin are being incorporated into existing polymers.[131] In fact, several existing monomers promise to be produced from sugars in a cost-competitive manner. A very simple but still insightful economic analysis reveals indeed that some biobased routes could be economical at an overall target selectivity (eq 1) that is lower than the overall stoichiometric selectivity (for given economic premises).[125,132]

$$\text{target selectivity [g/g]} > (\text{feed price} + \text{conversion cost})/\text{product price} \quad (1)$$

For instance, the conversion of sugars to acids and diols can afford target selectivity below the stoichiometric one, because these routes allow high weight-based stoichiometric selectivities and deliver high-value products (see as green symbols in Figure 10).[125] In contrast, the production of olefins, aromatics,

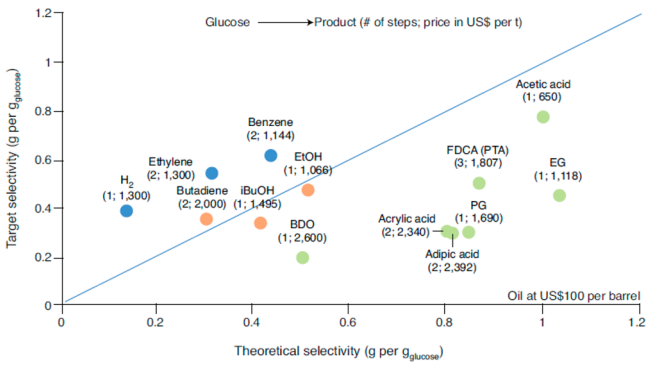

Figure 10. Economic viability of converting glucose to chemicals by comparing the target selectivity (eq 1) with the stoichiometric selectivity (FDCA, 2,5-furandicarboxylic acid, EG, ethylene glycol, PG, propylene glycol; BDO, 1,4-butanediol[125]).

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and H_2 appears prohibitive, because their lower stoichiometric selectivities and low-value products require target selectivities that exceed the stoichiometric selectivity (see red symbols in Figure 10).[125] These conclusions will also apply to the valorization of the nonedible sugars that are hidden in lignocellulosic biomass in the future. But this will require the lignocellulose fraction technologies to be further improved for them the deliver cellulosic sugars at competitive prices.[133−136]

But future materials will not be limited to biobased plastics. More traditional biomaterials such as wood, paper/cardboard, cellulose (e.g., cellulose acetate), and starch are also reconquering the stage while novel materials and composites based on, e.g., nanocellulose and lignin are being developed.[137−143] Such materials promise to access the large-volume and low-price markets as they rely on low-cost feedstocks with low-cost processing.

Overall, the polymers of tomorrow may eventually deviate from today's favorites. As the industry transitions from reduced carbon (e.g., ethane and naphtha) to oxidized carbon (sugars and CO_2) as a feedstock, it may also transition to oxygen-rich plastics and materials (e.g., PLA and paper). Of particular interest will be those that offer high biomass utilization (thereby, low land requirement), that require simple processing (for low manufacturing costs), that are easily recyclable, and that are sufficiently biodegradable to be nonpersistent in the environment. However, such new materials will need to prove themselves in the market. Their full deployment may, therefore, lag that of drop-in biobased plastics in coming decades and fully materialize around 2050.

CONCLUSIONS AND OUTLOOK

Over the years, the petrochemical industry has developed a plethora of polymers that are contributing to the well-being of modern society. Irresponsible disposal of used plastics has, however, led to the buildup of litter, which is fouling the environment, harming wildlife, and wasting valuable resources. The industry has been struggling for a few decades to collect and recycle waste plastic but could not make it economically viable. The litter problem has now become so prominent in certain parts of the world that society and industry have moved to action. For instance, a broad coalition of industries along the whole plastic value chain, from manufacturers, to brand owners, to waste processors, has launched the *Alliance to End Plastic Waste* to solve this problem by supporting programs on education, legislation, innovation, and environmental cleaning.[144]

The present paper focused on technology innovations in sorting, recycling, and disposal. But it also complemented it by discussions on microplastics, LCA, design for recycling, and renewable carbon feedstock. Overall, these new technologies show the potential to close the carbon loop and, thereby, convert the linear plastic economy into a truly circular one. But there is no unique solution to this challenge. It requires innovations in all segments and a cascaded approach to waste valorization.

We need to design new products for recycling, through a reduction of the number of materials and grades, as well as through simplification of product formulation. Design rules need to anticipate the emergence of new technologies in identification/sorting and in chemical recycling. They also need to consider biodegradation of the small fraction of products that, despite all efforts, will still be released into the environment and will generate microplastics.

Waste sorting will further improve through refinements in identification and sorting technologies and through the emergence of new technologies, e.g., based on watermarks and AI. But cleaning and conditioning technologies should not be forgotten.

Mechanical recycling has been so far limited to downcycling of a small fraction of the waste, and to producing resins with a modest recyclate content. Progress in product design, waste sorting, and conditioning as well as in recycling reformulation will undoubtedly allow mechanical recycling to supply more demanding applications and to accommodate larger recycling fraction.

Chemical recycling will likely take over, where mechanical recycling is struggling, e.g., in delivering top-grade products and recycling mixed, contaminated, or degraded reject streams. Numerous technologies are now close to deployment, being for recycling to monomers or to feedstock. To be affordable, these technologies will require scale. This seems achievable for mixed polyolefins and PET. The other plastics will be more challenged and may have to deliver high-value product/monomers to compensate for the lack of economy of scale.

The streams that are still refused by chemical recycling will eventually have to be disposed of responsibly. Landfill could be considered as responsible carbon sequestration where land is largely available and when it is done such as to avoid toxic leachate from contaminating the soil and aquifers and avoid biomethane from leaking to the atmosphere. In all other cases, a last valorization with energy recovery is likely the most responsible option. This includes direct incineration, indirect incineration via biogas or syngas, and conversion to fuels. Energy valorization may not require separating the plastic waste from organic waste, being food, paper, wood, or textiles. New technologies are indeed being developed to process them mixed.

But the carbon that is refused and disposed of will need to be compensated for by fresh carbon entering the cycle. This may still come from fossil resources for a while. But it eventually needs to come from renewable carbon, namely, atmospheric CO_2. This can be achieved by carbon capture and utilization (CCU) but will likely start with biomass in the short-to-medium term.

Overall, the industry is on the verge of closing its material cycle. Many technology developments are still needed at all segments of the value chain to make the closure of the material cycle affordable.

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Biography

Jean-Paul Lange is a principal research scientist at Shell Projects and Technology in Amsterdam, The Netherlands, where he has been exploring novel catalytic processes for producing fuels and chemicals, initially from natural gas and oil and, for more than 20 years, from biomass and plastic wastes. His research embraces heterogeneous catalysis, chemical engineering, conceptual process design, manufacturing economics, and technology strategy. Jean-Paul Lange is also Professor in Chemical Biorefining at the University of Twente, The Netherlands, where he is investigating thermo-chemical and -catalytic routes to convert biomass to fuels and chemicals and to recycle plastic wastes. Before joining Shell, he was a postdoctoral fellow at Lehigh University in Bethlehem (Pennsylvania, USA), got his Ph.D. at the Fritz-Haber Institute (Max Planck Society) in Berlin (Germany), and graduated at the University of Namur (Belgium). Jean-Paul Lange is coauthor of more than 100 patent series, more than 60 scientific publications, and seven book chapters and is working on coediting a scientific book. He is also contributing to public science through various advisory boards in The Netherlands and Europe and for the European Commission.

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