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The Critical Role of Process Analysis in Chemical Recycling and Upcycling of Waste Plastics

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Abstract

There is an urgent need for new technologies to enable circularity for synthetic polymers, spurred by the accumulation of waste plastics in landfills and the environment and the contributions of plastics manufacturing to climate change. Chemical recycling is a promising means to convert waste plastics into molecular intermediates that can be remanufactured into new products. Given the growing interest in the development of new chemical recycling approaches, it is critical to evaluate the economics, energy use, greenhouse gas emissions, and other life cycle inventory metrics for emerging processes,

relative to the incumbent, linear manufacturing practices employed today. Here we offer specific definitions for classes of chemical recycling and upcycling and describe general process concepts for the chemical recycling of mixed plastics waste. We present a framework for techno-economic analysis and life cycle assessment for both closed- and open-loop chemical recycling. Rigorous application of these process analysis tools will be required to enable impactful solutions for the plastics waste problem.

INTRODUCTION

Plastics have become ubiquitous in modern society given their versatility for a massive range of applications at low cost (1). Today, humankind primarily employs synthetic polymers in a linear materials flow via a model of extract, manufacture, use, and discard. This approach has led to a global pollution crisis caused by the accumulation of plastics in landfills and the natural environment (2–5). Moreover, virgin plastics manufacturing is also contributing to anthropogenic climate change. It is estimated that nearly 4% of the global carbon emissions in 2015 were from plastics manufacturing and that, if humankind continues on the current trajectory, global carbon emissions could increase by up to 20% by 2050 (6). Other studies of plastics greenhouse gas (GHG) emissions make similar conclusions regarding the potential for virgin plastics manufacturing to contribute significantly to global carbon emissions (7–9).

Although some forms of several commodity plastics are mechanically recycled today, these processes often produce materials with diminished properties and lower value (10). However, more often plastics are simply not recycled or are not able to be mechanically recycled owing to contaminants, additives [e.g., green poly(ethylene terephthalate) (PET) bottles], their inability to be reprocessed (e.g., thermosets like tires), and/or their hierarchical structure containing multiple polymers (e.g., multilayer films). The lack of available recycling thus ends plastics' useful lifetime in a landfill or in the natural environment, where most synthetic polymers are projected to persist for decades or longer (11, 12). Given recent public awareness surrounding the plastics pollution crisis and the inherent limitations of today's mechanical recycling methods, there is now reinvigorated interest in the development of new recycling technologies that enable a shift from a linear approach to one based on circular plastic materials flows (10, 13–21).

In a circular economy model for plastics, synthetic polymers become feedstocks for remanufacturing at the end of life for use in the same or another application, such that the raw materials remain in use. Beyond mechanical recycling, emerging methods aim to repurpose the polymer structure, such as compatibilization of discarded, mixed plastics to create new materials (22) and chemical functionalization of waste polymers (23). Other promising approaches, such as solvent-based recycling, aim to keep the polymer structure intact during processing and have especially found use to date for multilayer packaging recycling (24, 25).

Additionally, there is substantial momentum in the community toward the broad concept of chemical recycling of plastics. Here, we define chemical recycling as the deconstruction of synthetic plastics to processable molecular intermediates that can be converted into new products. As illustrated in **Figure 1**, we further define closed-loop chemical recycling as a process that deconstructs a waste plastic and remanufactures it into a chemically identical polymer with virgin-like material properties. Alternatively, open-loop chemical recycling is defined as the deconstruction of waste plastics into molecular intermediates that are manufactured into products that differ from the starting polymer feedstock. Lastly, we define the term chemical upcycling, which is often used quite loosely, as an open-loop chemical recycling process in which the remanufactured product

Chemical recycling: the deconstruction of synthetic plastics (macromolecules) to processable intermediates (molecules) that can be converted into new products

Closed-loop chemical recycling: a process wherein the chemically identical material is produced with virgin-like material properties via chemical recycling methods, namely, deconstruction and remanufacturing into the same polymer

Open-loop chemical recycling: the deconstruction and conversion of plastics into different products than the starting materials

Chemical upcycling: an open-loop chemical recycling process where the remanufactured product exhibits a higher value than the original waste plastic



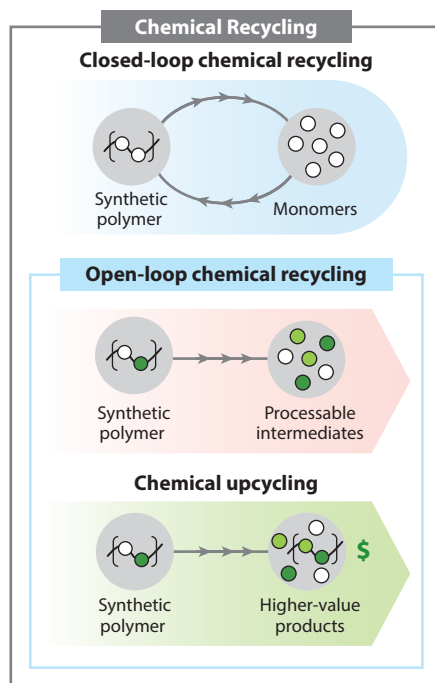


Figure 1

Illustrative definitions used in this review. See text for proposed definitions for chemical recycling, closed-loop chemical recycling, open-loop chemical recycling, and upcycling.

exhibits a higher value than the waste plastic feedstock (**Figure 1**). Some waste plastics today have either zero or negative value (i.e., disposal costs), but as advanced recycling technologies are developed, it is anticipated that waste feedstocks will become valuable, similar to a few plastics today in the mechanical recycling industry. In a chemical processing context, the value of an upcycled product is typically economic, but other value metrics, including carbon intensity, environmental impacts, and other technical measures of value, are factors that may play a role in future waste management and climate-related legislation for plastics (26, 27).

Early chemical recycling technologies, several of which are being scaled today, employ thermal deconstruction methods such as pyrolysis and gasification (28–30). The resulting intermediates from these methods are typically destined to enter petrochemical processes, where they can be either directly converted into fuels and chemicals or combined with virgin petrochemical feedstocks for synthesis of fuels and chemicals, including some fraction that makes its way into new polymers. Beyond thermal deconstruction, a central theme of many emerging strategies in chemical recycling is the use of catalysis-enabled approaches (10, 14–18). Technologies that employ catalysis offer the possibility to recycle or upcycle plastics that include and go beyond polyolefins and polyesters, which are the polymer classes of primary focus to date. This expanded substrate scope, enabled by advances in chemical recycling, could include polymers that contain substantial heteroatom content; that are crosslinked; and that almost universally comprise heterogeneous formulations, including comonomers, small-molecule additives, catalysts, and additional components (31). Developing new methods for recycling polymers that are not recyclable today is a key step toward circularity. However, to realistically develop catalysis-enabled chemical recycling, the community must urgently focus resources on the development of technologies that can process

complex plastics waste streams and deliver beneficial economic, environmental, and social incentives for investment and scale-up (32).

To that end, here we highlight the critical role of process analysis in enabling chemical recycling for waste plastics. This focus is intended to be complementary to the authoritative catalysis-centric reviews that have been published recently (10, 14–18, 20, 21). We intend this review to be a resource for the broad communities focused on developing new approaches for plastics recycling and upcycling as a framework for analyzing new processes of interest. We first discuss and review illustrative process frameworks for plastics chemical recycling in the context of mixed plastics waste. We subsequently remark on the importance of techno-economic analysis (TEA) and life cycle assessment (LCA) in judicious process development. Specifically, we present analysis frameworks, taken from the analysis literature, to examine closed- and open-loop recycling relative to the linear extract–manufacture–use–discard processes employed today. We end by describing important considerations for data inputs to analysis and highlight key gaps in the literature that represent opportunities for future research.

PROCESS FRAMEWORKS FOR CHEMICAL RECYCLING

We first consider several exemplary process frameworks for chemical recycling of waste plastics. This framework starts from the basis that waste plastics feedstocks are mixed substrates, which is commonly the case for postconsumer waste in materials recovery facilities (MRFs), in municipal solid waste (MSW), or when sourcing waste plastics from landfills or the natural environment. In some cases, waste plastics can be sourced as pure substrates from various point sources, as in the case for waste generation during industrial plastics manufacturing or fines from mechanical recycling (33). When sourcing pristine waste plastics, the closed- and open-loop recycling analysis frameworks (see below) remain applicable.

The overall goal of plastics chemical recycling is to cost effectively convert a stream of plastic waste to valuable products while minimizing material and energy inputs, waste generation, and environmental impacts. **Figure 2** presents three primary process frameworks for the chemical recycling of mixed plastics streams, including:

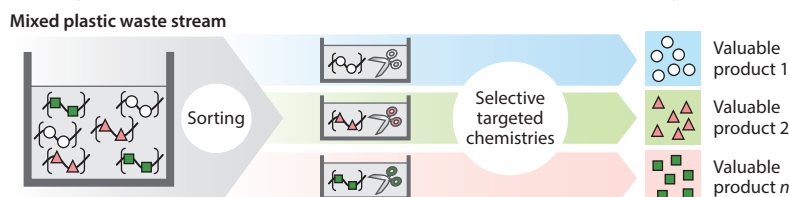
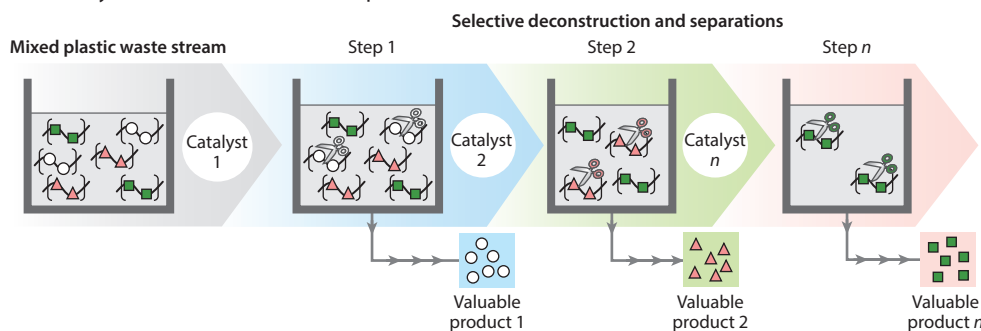
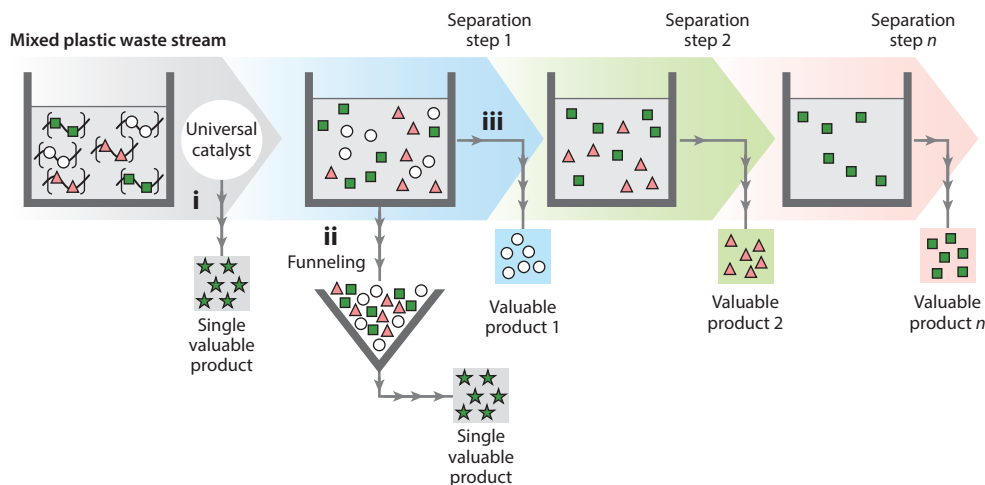
1. polymer separations, followed by targeted chemical processing of individual polymers in parallel process trains (**Figure 2a**);
2. catalytic fractionation and separation of molecular intermediates from intact polymers (**Figure 2b**); and
3. deconstruction of a mixed plastics stream to produce a mixture of molecular intermediates for (a) consolidated deconstruction and upcycling of mixed plastic waste to a single valuable product, (b) catalytic funneling of a mixture to a single valuable product, or (c) conversion to valuable product streams through separations (**Figure 2c**).

These process concepts are discussed below, with several demonstrated or hypothetical examples for each. Although these process frameworks do not encompass every conceivable process iteration for chemical recycling, they offer a generalizable classification scheme for many chemical recycling processes.

Polymer Separations and Parallel, Single-Substrate Chemical Recycling

As shown in **Figure 2a**, potentially one of the simplest conceptual process approaches to chemical recycling is the upfront separation of polymers and treatment of individual plastics streams in parallel targeted deconstruction processes. Much of the catalysis-focused chemical recycling literature fits in this framework, given that many studies focus on either single plastic materials



a Polymer separations and parallel, single-substrate chemical recycling**b** Catalytic fractionation of mixed plastics**c** Mixed plastics deconstruction and downstream processing**Figure 2**

Process frameworks for chemical recycling. (a) Polymer separations and parallel, single-substrate chemical recycling. Mixed plastics waste streams can be separated into single polymer streams that are highly enriched in the target polymer, and subsequently, chemical recycling processes can be conducted in parallel and in a targeted manner for each polymer to produce valuable products. (b) Catalytic fractionation of mixed plastics. Mixed plastics waste can undergo selective catalytic fractionation chemistries in which sequential steps selectively deconstruct individual plastic materials. (c) Mixed plastics deconstruction and downstream processing. A mixed plastic waste stream could undergo a single-step deconstruction and upcycling approach to a valuable product (i) or be deconstructed simultaneously to molecular intermediates, which would then undergo either (ii) a catalytic funneling process to a single valuable product or (iii) separation processes to isolate target products.

or a few similar plastics at a time. To enable this process from mixed feedstocks, separations of some plastics are technically feasible via mechanical means (mostly applicable when plastics are not multicomponent materials) (10) or solvent-based separations (24, 34, 35) or through preprocessing to separate multicomponent materials (36, 37). Today, physical polymer separations are practiced routinely, and being continually advanced, at MRFs (10), for which TEA and LCA studies have been reported (38–41). Bolt-on chemical recycling processes that rely on current and/or emerging MRF-based separation methods could harness these technologies to enable the process framework shown in **Figure 2a**. Additional information regarding materials flow analyses for MRFs and other plastics waste sources is reviewed below.

Catalytic Fractionation of Mixed Plastics

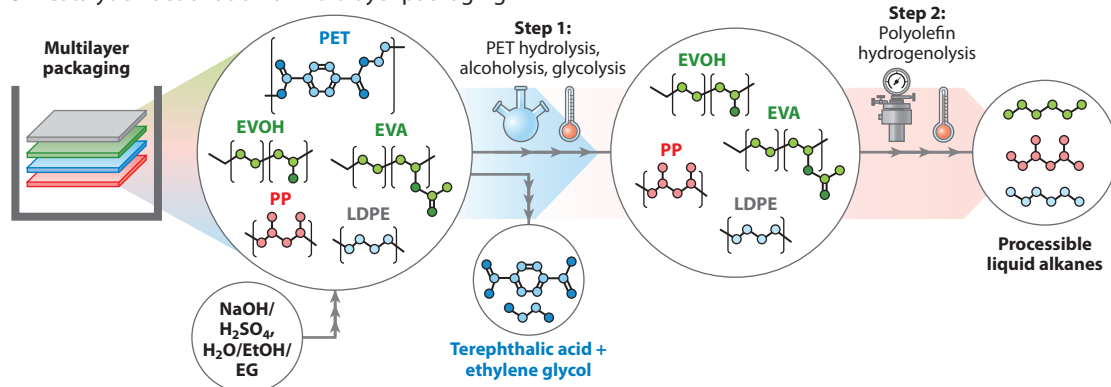
Another envisioned process framework, illustrated in **Figure 2b**, is the recycling or upcycling of mixed plastic waste via catalytic fractionation. This involves sequential depolymerization and separation steps that employ selective catalysts under particular reaction conditions to target specific plastics, leaving other polymers intact. This approach eliminates the need for upfront separation of mixed plastics as solids and is also potentially applicable to multicomponent plastics, such as multilayer packaging or textiles. These sequential techniques could exploit reactivity differences in the types of polymer linkages, solvation properties of the materials, physical and mass transport properties, or adsorption properties of the different polymer materials to enable depolymerization and separation at each stage.

From a catalysis perspective, the diversity of polymer backbone chemistries provides a convenient target for selective catalytic fractionation. For example, the C–O bonds in ester and carbonate linkages of plastics such as PET and polycarbonates exhibit relatively more labile linkages than the C–C-linked backbones of plastics such as polyethylene (PE), polypropylene (PP), polystyrene (PS), and poly(vinyl chloride). Among plastics with C–C backbones such as PS, PP, and PE, the differences in bond dissociation energy due to the presence of different functional groups also provide a handle for catalytic fractionation. The weaker bonds can be targeted via depolymerization strategies at milder conditions or catalytic conditions tailored toward particular bonds or functional groups. The difference in physical properties (solubility, melting point, boiling point) of the depolymerized products could then be exploited for separations via solvent extraction (24), liquid–liquid separation, or gas–liquid separation (e.g., reactive distillation) (42).

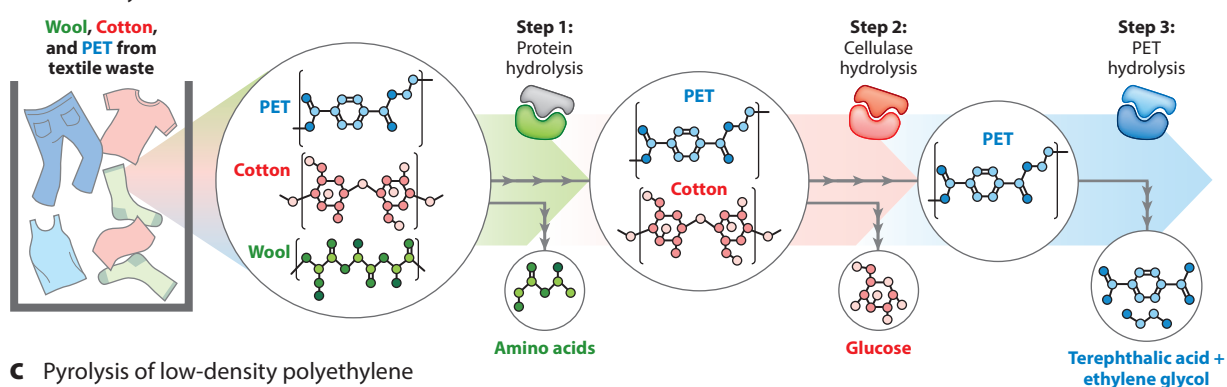
As one example of this concept, catalytic methods employed to deconstruct polymers with ester linkages, such as aminolysis, hydrolysis, methanolysis, and glycolysis, are often completely unreactive toward polymers with aliphatic C–C bonds (15, 43). As shown in **Figure 3a**, catalytic fractionation could be applied first using an ester bond–specific deconstruction approach to depolymerize PET in multilayer packaging that also contains C–C-linked polymers such as ethylene vinyl alcohol, ethylene-vinyl acetate, and PE (44), as shown by Ügdüler et al. (45, 46), followed by a C–C bond–specific approach, such as polyolefin hydrogenolysis (47–51). In the context of mixed ester and ether-based polymers, Jehanno et al. (52) demonstrated this concept (in a hybrid open- and closed-loop recycling process) using glycolysis of bisphenol A–based polycarbonate and PET with an amine–based organocatalyst. In another example, albeit not wholly for synthetic polymers, Quartinello et al. (53) demonstrated the sequential application of enzymes for mixed textile recycling to break down wool to amino acids with proteases and cotton to glucose with cellulases, leaving behind pure PET polymer. Although not demonstrated in their work, application of either PET hydrolase enzymes (potentially with some thermomechanical preprocessing of the PET fibers) or chemo-catalytic strategies likely could also enable PET deconstruction in this context (14, 54–56), as conceptually illustrated in **Figure 3b**. Similarly, Palme et al. (57) used



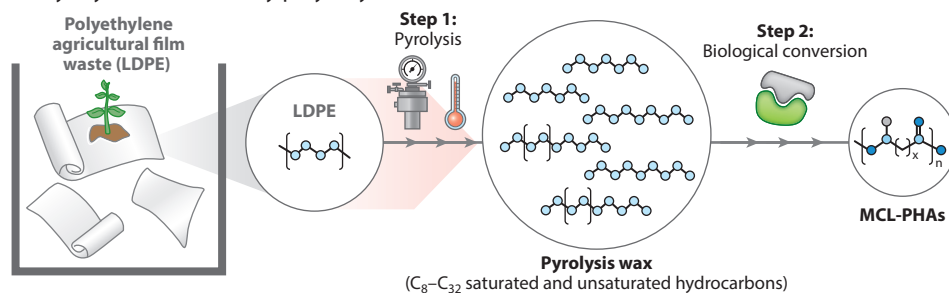
a Catalytic fractionation of multilayer packaging



b Biocatalytic fractionation of mixed textile waste



c Pyrolysis of low-density polyethylene



d One-pot deconstruction of low-density polyethylene followed by downstream separations

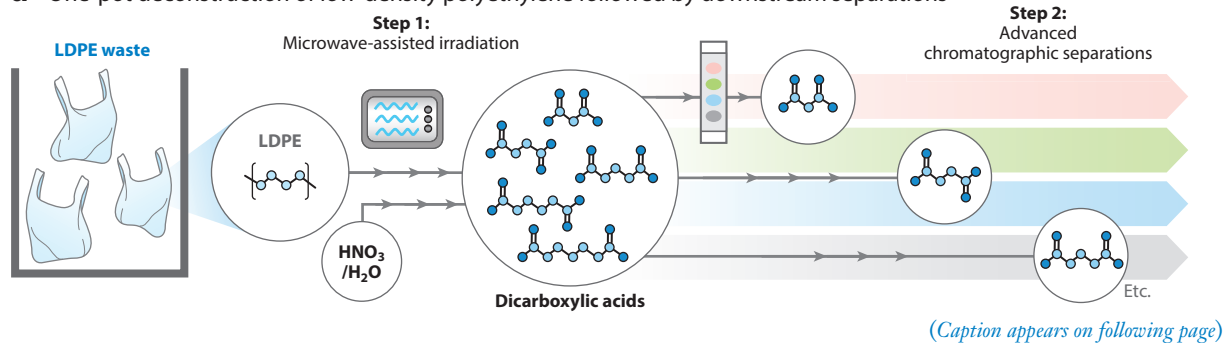


Figure 3 (Figure appears on preceding page)

Illustrative examples of process frameworks for the chemical recycling of waste plastics. (a) Catalytic fractionation of multilayer packaging. (b) Biocatalytic fractionation of mixed textile waste. (c) Pyrolysis of low-density polyethylene followed by biological funneling to produce MCL-PHAs. (d) One-pot deconstruction of low-density polyethylene followed by downstream separations. Abbreviations: LDPE, low-density polyethylene; MCL-PHA, medium-chain length polyhydroxyalkanoates; PET, poly(ethylene terephthalate); PP, polypropylene.

alkaline hydrolysis to selectively deconstruct PET to terephthalic acid and ethylene glycol from mixed PET–cotton textile waste, leaving behind intact cellulose for reuse.

There are also multiple parallels in the field of biomass conversion to the catalytic fractionation of plastics, as this is a common approach to valorize lignocellulosic biomass through multistage extraction and depolymerization processes (58, 59). Process analysis insights in this field offer direct guidance for the catalytic fractionation of plastic waste. For example, Won et al. (60) used TEA to compare multistage thermal biomass decomposition and catalysis to single-stage pyrolysis to identify key cost drivers. They predicted that improved selectivity to a slate of higher-value products afforded by multistep processes could outweigh the increased capital costs necessitated by additional unit operations. Bartling et al. (61) performed TEA and LCA on biomass valorization via reductive catalytic fractionation, revealing insights into the major contributors to operating and environmental costs. In that case, such factors, including solvent recovery, capital costs, and reactor pressure, were predicted to play a major role in both the economics and environmental impacts, which may envisage targets and challenges in using similar chemistries for plastics recycling and upcycling with catalytic fractionation.

Mixed Plastics Deconstruction and Downstream Processing

A third process option is the catalytic deconstruction of mixed plastics in the same reactor to produce molecular product mixtures, as illustrated in **Figure 2c**. The mixture of products themselves may be inherently valuable (e.g., as a fuel or a lubricant) and therefore sold directly. Often, especially for chemicals production, purity is key; thus, at least two options exist for dealing with product mixtures: separations to isolate valuable compounds from a mixture or convergent funneling approaches that convert mixtures to single products.

The framework in **Figure 2c,i** shows the simultaneous chemical deconstruction and upcycling of mixed plastic waste to produce a single valuable product. Reported studies to this end include the gasification of mixed plastic waste to produce syngas (62, 63) and the complete hydrogenolysis of plastic waste to methane (64). The conversion of polyolefin plastics into fuel-range hydrocarbons is also an example of this approach (65–68). As another example, ruthenium-based catalysts have been employed by Rorrer et al. (69) for the one-pot depolymerization of mixed polyolefins (PE, PP) to isoalkanes and by Jing et al. (70) for conversion of mixed aromatic plastics [PET, PS, polycarbonate, poly(phenylene oxide)] to arenes, the latter study demonstrating cleavage of both C–O and C–C bonds.

Mixed intermediates derived from plastics deconstruction can also be valorized via funneling to a single valuable product, as illustrated in **Figure 2c,ii**. The funneling concept involves the use of either whole-cell biocatalysts (71) or chemical catalysis (72, 73) to convert heterogeneous mixtures of substrates into single valuable products. This funneling concept was coined as such in the lignin valorization field (71). Guzik et al. (74) demonstrated this concept in the case of biological conversion of plastics-derived intermediates, using pyrolysis to deconstruct PE and subsequently feeding the hydrocarbon-rich mixture to a bacterial *Pseudomonas* strain to produce polyhydroxyalkanoates, as illustrated in **Figure 3c**. The same group also conducted similar work with PS-derived pyrolysis oil (75). More recently, Utomo et al. (76) employed a coculture of engineered pseudomonads

to funnel polyurethane-derived intermediates to surfactants. In 2021, Guzik et al. (77) also presented a proof-of-concept study that employed tandem PE pyrolysis, chemical oxidation of the PE-derived wax, and biological funneling of the purified fatty acid mixture to produce polyhydroxyalkanoates. These authors employed LCA to examine a hypothetical process based on this proposed approach. Similar concepts, using both biological and chemical catalysis, will likely find utility in plastics recycling and upcycling processes.

Lastly, as shown in **Figure 2c,iii**, another option for recovering valuable products from plastics-derived intermediates involves the use of downstream processing techniques to separate product mixtures to obtain pure compounds. When deconstructing hydrocarbon plastics, distillation may offer a reasonable separations approach with volatile organic compounds, but many plastics waste streams will likely contain compounds with high boiling points, thus limiting the use of direct distillation. The application of advanced separations technologies to this end, including condensed phase separations methods, likely will have utility. For example, Bäckström et al. (78) demonstrated the microwave-assisted oxidative deconstruction of low-density polyethylene in nitric acid to mixtures of monocarboxylic and dicarboxylic acids. Although not demonstrated in their report, the feasibility of chromatographic separations to isolate aliphatic acids and diacids (79), which is illustrated in **Figure 3d**, or the use of crystallization (80) may offer solutions to these types of plastics waste-derived mixtures.

KEY CONSIDERATIONS FOR ANALYSIS OF CHEMICAL RECYCLING PROCESSES

With these process frameworks, we now review the primary considerations for conducting analysis of chemical recycling processes. In the context of chemical processing technologies, analysis can be described broadly as the gathering and interpretation of data and projections about a process to inform development and implementation. As a preface to the analysis frameworks, this section describes the primary metrics associated with TEA and LCA and introduces important considerations for rigorous analysis of chemical recycling, including those related to the establishment of system boundaries and baselines for TEA and LCA.

Robust, quantitative analysis is predicated on precisely defined, specific metrics that quantify some characteristic of the process or system of interest. Once established, such metrics can be compared across multiple processes, systems, or scenarios to quantify the relative differences between them. Metrics applicable to recycling technologies can be categorized into three broad categories:

1. Technoeconomic and financial return metrics. Any chemical recycling facility will require a certain capital investment for installing equipment and see recurring operating expenses, such as feedstock purchases, raw material costs, and utilities (e.g., electricity, steam, water). Estimating the capital and operating expenditure of new processes can help determine the financial return-on-investment metric, such as a minimum product selling price or net present value. Many chemical recycling facilities are in either the research and development or early commercialization stages; hence, economic projections are associated with a degree of uncertainty. To systematically compare emerging approaches, we urge the evaluation of open- and closed-loop recycling technologies against a consistent baseline, as discussed in the following sections (see the section titled Techno-Economic Analysis Considerations below).
2. Life cycle environmental metrics. Many metrics have been developed to quantify the environmental impacts of the life cycle of a product, including nonrenewable energy use, GHG emissions, ecotoxicity, human health impacts, and water consumption, and many others (81).



System boundary: the set of processes or life cycle stages included in a life cycle analysis; the scope

It is important to remember that many of the environmental burdens may originate exogenous to the plant-level system boundary often under consideration in TEA. The cradle-to-cradle system boundary accounts for environmental impacts from all steps of the life cycle of the material, from initial manufacturing through usage, disposal, collection, and remanufacturing (see the section titled System Boundary Considerations below). In practice, certain aspects of the product life cycle that may be identical across compared life cycle scenarios [i.e., the use phase of a (closed-loop) recycled product that is identical to that made from virgin sources] may be excluded from the analysis to focus on aspects of the life cycle that differ between manufacturing systems.

3. Economy-wide and social justice metrics. Impacts of plastics pollution extend beyond the environmental impacts described above to include economic and social impacts, such as employment, gross domestic product, or socioeconomic distribution of environmental impacts (environmental justice). Several reports describe impacts from microplastics entering our ecosystem, including oceans and the food chain, many of which are not yet well understood and thus are challenging to quantify (82). Additionally, recycling can enable added value to the economy and employment generation, as reported in recent studies (83–86). This is an important, emerging frontier of analysis-focused method development and is not reviewed extensively here; readers can refer to top-down models for more information on the methodology for quantifying such impacts (27, 87–89).

System Boundary Considerations

Techno-economic and environmental impact metrics associated with chemical recycling processes are of little use on their own—the analyst must first establish an appropriate baseline against which to compare such metrics. Baseline choice, and by extension the entire analytical framework, is dictated by the type of chemical recycling process under study (**Figure 2**), which determines the system boundary.

TEA of either closed- or open-loop recycling can be best compared with virgin materials production, which requires evaluating mass and energy balances. Making such a diligent inventory of material and energy balance starts with a consistent definition of the system boundary—a description of the set of processes included in or excluded from the analysis (i.e., the scope). This is essential to perform TEA, which determines the capital/operating expenses and financial estimate of the technology within the scope of a single chemical plant. Technologies focused on chemical recycling can define system boundaries from the point when reclaimed or plastic-rich feedstock is fed to the reactor up to the purification and recovery of the final product.

Once a system boundary has been established, the calculation of product flows and material yields, from both the virgin manufacturing process and the recycling process, need to be carefully tracked, because they serve as the basis not just for TEA but also for the LCA impacts, as well as broader socioeconomic impacts. Material losses at both the plant level and broader supply chain level (including collection) must be accounted for to determine the remaining availability of secondary feedstock for subsequent recycling.

In contrast to TEA, the system boundary of LCA analysis typically extends beyond the plant boundary. There are multi-tier effects to be considered on a regional or a global scale, starting from fossil fuel extraction and proceeding to virgin polymer production and then to either recycling or disposal (cradle-to-cradle or cradle-to-grave scopes, respectively). Feedstock production and transport (including collection) may exhibit a significant burden in the environmental impact calculation, so a clearly defined and consistent LCA system boundary ensures that these impacts are not overlooked.

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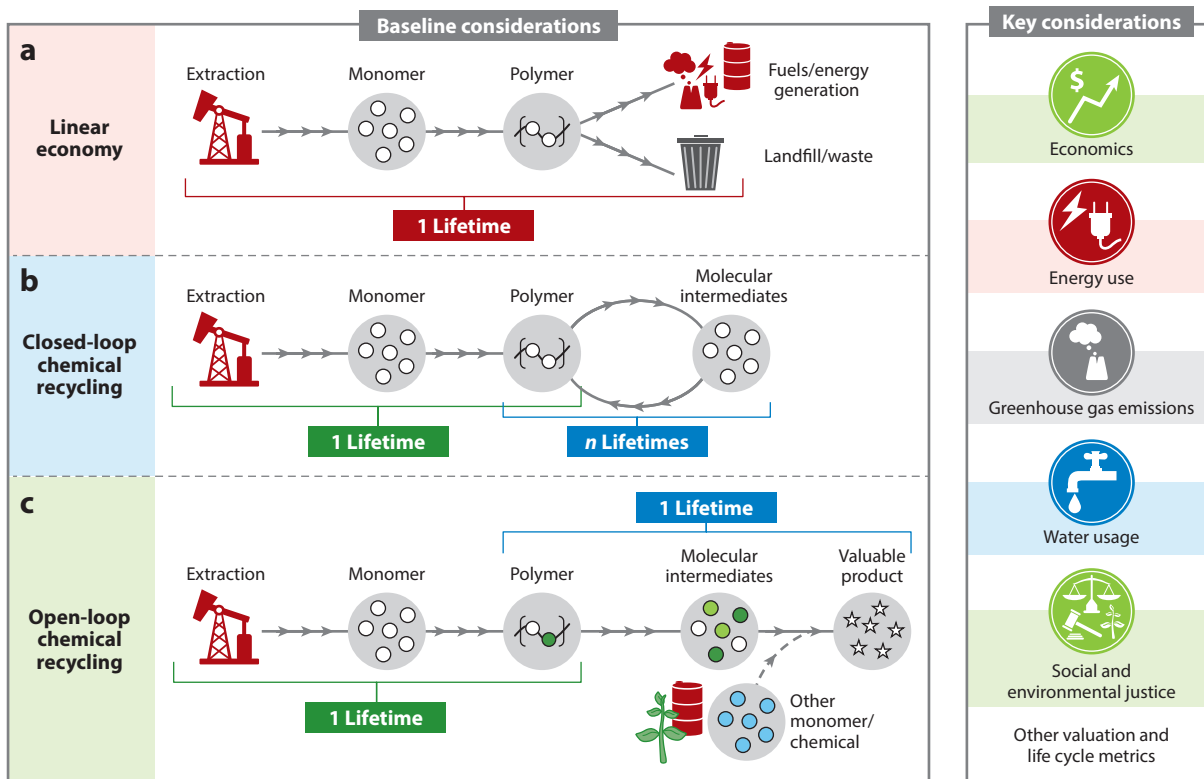


Figure 4

Analysis frameworks for the chemical recycling of waste plastics. (a) Linear economy framework. The conventional single lifetime of a polymer produced from virgin fossil sources, used once and then discarded to landfill or combusted for energy recovery. (b) Closed-loop chemical recycling framework. An identical first lifetime of the product compared to panel a, except that in the end-of-life phase, the polymer is chemically recycled to molecular intermediates, which are then remanufactured to the same polymer, resulting in additional useful lifetimes of the polymer product. (c) Open-loop chemical recycling framework. An identical lifetime of the product compared to panel a, except that in the end-of-life phase, the polymer is deconstructed to molecular intermediates and then converted into a valuable product, possibly with the addition of other monomers or chemicals (which in turn may be derived from virgin sources). (right) Key considerations for comparisons across frameworks.

Baseline Considerations

As shown in **Figure 4**, the logical baseline against which to compare closed-loop chemical recycling is often the analogous impacts associated with an incumbent, linear technology for producing the same polymer from virgin sources (8). In the context of polymer manufacturing, virgin sources are typically fossil-derived petrochemicals, but supply chains starting from bio-based sources could also be used to establish a linear production baseline. For open-loop processes, an LCA baseline may involve an economically derived waste value allocation scheme. Alternatively, system expansion (assigning impacts to specific end products or to the system as a whole, respectively) may be the more intuitive and preferred approach. **Figure 4** illustrates the difference between conventional, linear production of polymers and the closed- and open-loop chemical recycling systems. Each of these analysis frameworks is discussed below.

Other baselines can be established for chemical recycling impacts besides virgin polymer production, such as to other types of recycling (e.g., mechanical processes). Indeed, a considerable

Allocation: a method of assigning to a single output some fraction of a quantified life cycle impact associated with a single process with multiple outputs (coproducts)

System expansion: consideration of life cycle impacts associated with a single process with multiple outputs as attributable to the full set of those outputs (i.e., a combined functional unit with multiple coproducts), without attributing impacts to any one within the functional unit; can avoid challenges of choosing an appropriate allocation method

number of treatment scenarios have been proposed in the literature—Meys et al. (90) considered 75 such scenarios in a recent study, whereas Schwarz et al. (91) considered 250 scenarios (10 recycling technologies across 25 polymer types). In another review of chemical recycling LCA studies published over the past decade, Davidson et al. (92) noted that direct comparison of chemical to mechanical recycling is challenging given the different roles that these technologies play in waste management and the inherent quality differences between polymers recovered from these two types of recycling. Even in cases where mechanical recycling forms the basis of a closed-loop process, quality parameters deteriorate after a sufficient number of cycles, requiring virgin polymer use (93). Similarly, chemical recycling can also lead to deterioration of quality parameters, such as via the build-up of impurities (94). These findings underscore the importance of maintaining a self-consistent comparison of impacts associated with end products.

Techno-Economic Analysis Considerations

The main techno-economic challenge associated with the advancement of any new recycling or upcycling technology is twofold: first, to prove the technical feasibility, and second, to achieve cost competitiveness with virgin polymer production. Technical feasibility entails considerations such as securing a reliable source of reclaimed plastics, obtaining sufficient product yields, and addressing scale-up challenges.

Rigorous TEA requires comparison on a consistent set of financial metrics, including considerations that much of the previous investment in building a petrochemical complex for virgin polymer manufacturing is likely fully amortized, whereas new recycling facilities will require capital investment. Moreover, because the volatility in petroleum and natural gas prices has significant effects on the virgin monomer price in the market, this can often make new recycling methods uncompetitive on an economic basis. Recent analysis has shown that the cost of reclaimed plastic feedstock can contribute to more than 50% of the final monomer price (95). Using a mixed waste plastics stream, which is typically cheaper, will alleviate some of these challenges. As discussed above, this will require approaches that enable the deconstruction and valorization of mixed plastics waste streams.

When coupled, TEA and LCA analysis form a comprehensive assessment of the relationships and trade-offs between economic and environmental impacts. For instance, the most economically promising routes may not always exhibit the most optimal resource use, as is the case in enzymatic recycling of PET, which despite being largely favorable across multiple environmental impact categories leads to increased water usage relative to virgin polymer manufacturing (95).

Life-Cycle Assessment Considerations

There has been considerable discussion in the LCA literature about how to treat end-of-life impacts of systems that involve a recycling phase (96–98). At the heart of this debate is the fundamental LCA concept of allocation—that is, how to apportion the aggregate system-level impacts to specific outputs of that system. The allocation problem is typically formulated as a decision of how to appropriate impacts to multiple coproducts generated from a single manufacturing process. This issue can also arise in chemical recycling when multiple products are generated from a recycling process over time (e.g., a plastic bottle is made from virgin material and then recycled over and over, leading to a new product being formed each cycle). The specific complications of allocation depend on whether the recycling process is open or closed loop, and whether impacts are to be assigned to specific products within the system or to the entire system. In particular, allocation of impacts to specific products, which may be preferable in situations such as product labeling, introduces subjectivity because there are several plausible methods of apportioning total

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impacts to the individual products of a multifunctional system. These allocation methods include economic-based allocation, whereby impacts are assigned to products relative to some measure of their respective values, or physical attribute-based allocation approaches, such as mass- or energy-content allocation (99, 100).

Given the ambiguities introduced by such allocation schemes, the ISO standard 14044 (101) recommends avoiding allocation “wherever possible” and instead suggests a system expansion approach. We note that ISO 14044 was amended in 2020 (ISO 14044:2006/Amd 2:2020) to provide additional guidance on system expansion approaches. In this amendment, the concept of substitution within the multifunctional problem is included in the system expansion definition to subtract the impact of “the environmental burdens associated with the substituted product(s).” In the context of chemical recycling, we define system expansion as explicitly expanding the functional unit to include the multiple functions of the waste polymer. Heijungs et al. (102) provide additional commentary on the discrepancy in defining system expansion. Regardless, this system expansion approach is applicable to both open- and closed-loop chemical recycling, and we describe analysis methods covering both in the following sections.

ANALYSIS FRAMEWORK FOR CLOSED-LOOP RECYCLING

This section describes the analysis framework for closed-loop chemical recycling (**Figure 4b**). Closed-loop chemical recycling is particularly amenable to the system expansion approach for analyzing end-of-life impacts because the product resulting from the recycling stage is identical to what was initially recycled. Therefore, data requirements for characteristics, applications, and recyclability of products are self-contained. This contrasts with an open-loop chemical recycling process, in which system expansion could require consideration of significant additional data stemming from the disparate products generated from the initial recycling process.

Here, we adapt the closed-loop method described by Nicholson et al. (97) to chemical recycling of waste plastics. The framework is constructed as follows:

1. Beginning with the chemical recycling process system, determine the mass ratio a of monomer material that can be recovered from a given starting quantity of reclaimed polymer (for example, 1 kg).
2. If applicable, determine the recovery rate b of the recyclable material from collection, cleaning, sorting, etc.
3. Determine the recycled content mass ratio c of the reclaimed monomer contained in the starting quantity of functionally equivalent secondary polymer product.
4. Assuming that the process of producing, collecting, recycling, and reproducing polymer products proceeds indefinitely over n cycles, calculate the implied aggregate number of product lifetimes L that can be achieved from doing so, including the initial virgin polymer lifetime and given the loss factors identified in steps 1–3, using Equation 1:

$$L = \sum_{n=0}^{\infty} \left(\frac{ab}{c}\right)^n = \frac{c}{c - ab} \quad \text{when } \frac{ab}{c} < 1 \quad 1.$$

An important caveat in Equation 1 is a physical constraint that the amount of monomer recovered from chemical recycling must be less than the amount required to regenerate the equivalent amount of polymer product. In an idealized 100% closed-loop system where no loss occurs, this ratio would approach unity, and the number of lifetimes would approach infinity. In practice, yield and recovery losses will force this ratio to be less than 1, leading to a finite (though not necessarily integral) quantity of aggregate product lifetimes.



- Calculate the normalized combined impact of the entire system (\bar{x}_i) for impact category i by summing one unit of virgin production impact ($x_{v,i}$) and $L - 1$ units of impact from the chemical recycling and recovery phases ($x_{c,i}$) and then dividing the sum by L , shown in Equation 2:

$$\bar{x}_i = \frac{x_{v,i} + (L - 1)x_{c,i}}{L} \quad 2.$$

Note that i in this case could be energy consumption, GHG emissions, or any other life cycle impact category that applies to both the first and subsequent lifetimes of the polymer material.

- Compare this value to the impact from a unit of virgin production (**Figure 4a**).

Singh et al. (95) used this approach to compare impacts for an enzymatically depolymerized PET closed-loop system relative to virgin PET production. In that analysis, the recovery rate for the waste polymer was assumed to be ideal (i.e., $b = 100\%$). In practice (to date), b is considerably lower than 100% for plastics from MSW; in 2018, the recycling rate for PET containers was ~29% in the United States, according to the US Environmental Protection Agency.

ANALYSIS FRAMEWORK FOR OPEN-LOOP RECYCLING AND UPCYCLING

Open-loop recycling yields product(s) that differ from the waste polymer feedstock (**Figure 4c**). Therefore, the n -cycle lifetimes approach described above for closed-loop systems is not applicable, because the output from each open-loop cycle differs from the input. Comparing **Figure 4c** to **Figure 4b** illustrates this difference, showing that the purely open-loop recycling system produces a new product in a single additional cycle (as opposed to the theoretically infinite number of cycles within the closed-loop system ignoring yield and recovery losses).

There are several ways to treat open-loop recycling analyses. One approach is known as the waste value allocation or waste valuation approach, as described by Shen et al. (103) for a PET bottle-to-fiber mechanical recycling process. Waste valuation attempts to allocate some portion of impacts from the first life of the polymer (that which will become the waste feedstock) to the overall impact of the second-life product from the recycling process. This approach, following Shen et al., is detailed as follows:

- An allocation factor AF is calculated using the ratio of recycled plastic values (i.e., market prices) relative to the analogous virgin plastic value, as shown in Equation 3:

$$AF = \frac{\text{Market price of waste polymer}}{\text{Market price of virgin polymer}} \quad 3.$$

- AF is then multiplied by the impact associated with production of the first life of the polymer (X_{1st}), and that quantity is added to the impact associated with the open-loop recycling process itself (X_{OL}), yielding the overall impact for the second-life (recycled or upcycled) product (X_{2nd}):

$$X_{2nd} = X_{OL} + AF * X_{1st}. \quad 4.$$

Note that as with the closed-loop analysis framework, X could represent several different impact types, such as energy consumption, GHG emissions, or others of interest.

Environmental impacts attributed to the upcycled product can then be compared directly to those calculated for a polymer product manufactured from a conventional linear supply chain (**Figure 4a**). Benchmark data on conventional manufacturing supply chains for high-volume (>1 MMT/year global production) polymers have been published recently (8). This analysis



quantified energy consumption and GHG emissions metrics on both an intensity (per-kg) and scaled (by US consumption levels) absolute basis.

The advantage of the waste valuation method relative to a system expansion approach is that environmental impacts are attributed specifically to the upcycled product of interest rather than a combined functional unit of both primary and secondary materials. The disadvantage is that the economic allocation relies on fluctuating polymer market prices, requiring impacts calculated this way to be updated regularly. This waste valuation framework was applied to an open-loop chemical upcycling process converting waste PET bottles to higher-value glass fiber-reinforced composite material as detailed by Rorrer et al. (104).

System expansion is another approach to analyzing impacts of open-loop chemical recycling processes (103). Here, the first- and second-life products (virgin monomers and the valuable upcycled product, respectively) combine to form a single functional unit, which is similar to the approach presented for closed-loop recycling, except that the end-of-life phase impacts require additional consideration in the open-loop context. System boundaries are drawn to distinguish between two systems in which (a) the two components of the functional unit are produced separately and (b) they are linked via the upcycling process. This distinction is illustrated in **Figure 5**.

If a comparison is to be made on an absolute basis (i.e., the difference in magnitude of the impact metric being estimated for the two systems), the portions of the life cycles of the specific products (namely, the waste polymer feedstock and recycled product) that both systems have in

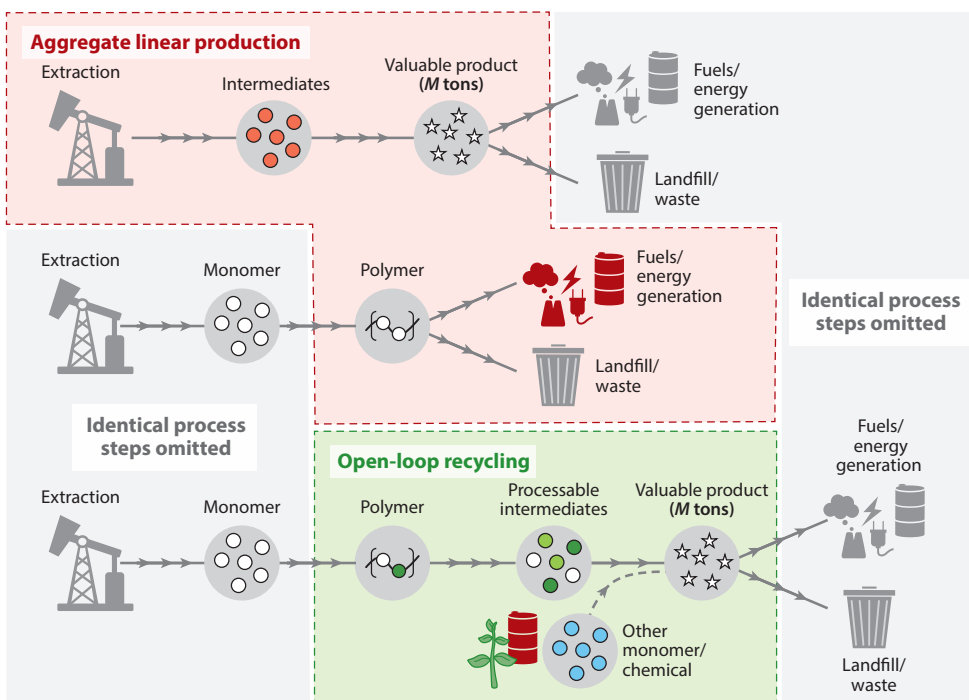


Figure 5

System expansion approach for open-loop recycling. Aggregate linear production of the two products of interest (polymer and valuable product) proceeds independently in the top portion of the figure (*red region*), and production of these same two products is linked through the open-loop recycling approach in the bottom portion (*green region*). Identical steps (*gray regions*) and their corresponding impacts for each scenario are omitted from the analysis.

common can be omitted from the analysis because the interest lies in determining the relative difference between them. This can potentially reduce data requirements necessary to complete the analysis. In contrast, if the estimate is to be made on a relative basis (i.e., a percentage change in the impact metric of interest), no truncation of either system should be made, since omission of impacts from common steps will yield a different percentage difference between the two, which could result in artificially high and thus misleading differences. A comparison of absolute impacts using the system expansion for open-loop upcycling may proceed as follows:

1. Determine the impact X_C of manufacturing a reference amount M of valuable product from conventional methods.
2. Determine the impact X_D from disposal of the quantity of virgin polymer from the conventional linear supply chain such that sufficient waste feedstock could be obtained to complete the upcycling process and yield M amount of valuable product.
3. Determine the impact from producing M quantity of valuable product from the recycling or upcycling process(es). This impact is determined by summing three components:
 - a. X_W : impact from processing (including collection and transport) the waste polymer into molecular intermediates.
 - b. X_A (if needed): impact from the production of other monomers, chemicals, or additives to the process.
 - c. X_U : impact from the production of the valuable product via recycling or upcycling from molecular intermediates and utilizing (if needed) other monomers and chemicals whose impact was determined as X_A .
4. Determine aggregate impacts for each system:
 - a. Aggregate linear production impact = $X_C + X_D$.
 - b. Open-loop recycling impact = $X_W + X_A + X_U$.

The benefit of the system expansion approach is that it avoids potentially unstable allocation assumptions, such as the volatility introduced by an economic waste valuation method that relies on fluctuating market prices. The downsides to this approach are that (a) data requirements are often greater, (b) the analyst must make an assumption about the polymer disposal method, and (c) impacts are not directly attributable to the higher-value product of interest—a critical consideration that may complicate both the interpretation of the results and the comparison with alternative manufacturing systems or substitute products. In either analysis approach for assessing economics and environmental impacts, it is preferable to first develop a robust TEA case for open-loop recycling. If a rigorous TEA is not feasible, but laboratory data are accessible, an estimate of material and energy inputs to the process can be obtained using scaling assumptions (105).

IMPORTANT FEEDSTOCK CONSIDERATIONS AND DATA INPUTS FOR CHEMICAL RECYCLING PROCESS ANALYSIS

Feedstock Cost, Scale, Availability, and Quality

Globally, plastic resin production has been estimated to exceed 360 million tons annually (106). This production eventually leads to a large accumulation of waste plastic. The United States generates the most plastic waste per capita in the world, with totals ranging from 34 to 42 million metric tons per year (4, 107). Most US plastics waste (~75%) is landfilled, whereas the remainder is either incinerated (15.3%), recycled (9.3%), or mismanaged and unaccounted for. The low recycling rate relative to total waste represents an economic opportunity between \$2 and \$4B/year, eligible for several new technologies that can further plastics recycling (108).



All emergent chemical recycling processes that convert mixed waste plastics will require the sourcing and collection of this feedstock and can employ multiple recycling strategies for conversion (**Figure 2**). The simplest plastic waste stream is postindustrial plastic waste, which is often clean and requires minimal sorting (10, 109). Given the high plastics purity, selective targeted chemistries shown in **Figure 2a** are most applicable and viable. However, postindustrial streams can also include multilayer components (e.g., unused packaging components) in which the strategies outlined in **Figure 2b,c** may be more suitable. Despite the applicability of strategies outlined here to postindustrial waste, such waste represents a minute and unaccounted-for fraction of all plastics waste.

Among the most problematic plastic wastes today is mixed postconsumer waste, some of which is processed through MRFs and some of which enters MSW and ultimately is landfilled. At the point at which postconsumer waste enters an MRF, it is not immediately amenable to the processes outlined in **Figure 2** owing to the low volume and comingling of different plastic types. A majority of MRFs in the developed world are referred to as clean MRFs, which rely on consumers to separate recyclable materials from MSW to produce a single stream. An estimated 59% of US households have access to curbside recycling services (6% of which are subscription based), whereas 21% have access only to drop-off programs, and a staggering 20% have no access to recycling services at all (110). Although plastics composition varies, MRFs typically separate their material inputs into bales of old corrugated containers (15%), paper fiber (40%), metals such as aluminum/iron (4%), and glass (15%), with 21% being other residues. Plastics are generally separated into PET and high-density polyethylene (HDPE) (5%), with the remainder being mixed plastic film waste and mixed hard plastic (primarily plastics #3–7). All the commonly found plastic types are exclusively thermoplastic resins and are routinely divided into categories by a resin code identifier (e.g., #1 PET bottles, #2 HDPE containers, #3–7 mixed plastic waste, or PE film). Of these plastic types, PET from soda bottles and HDPE from milk jugs are most the common (mechanically) recycled plastics, comprising roughly 70% of the postconsumer recycling (111). PP (#5) has recently become a focus of separation; however, its market value is volatile and relies heavily on current pricing of the virgin PP (112).

The various stages of MRF separations represent diverse opportunities for different catalytic strategies. The aggregate of the plastics waste prior to sortation may favor the catalytic fractionation processes shown in **Figure 2b** or a universal catalyst for plastics deconstruction shown in **Figure 2c**. Such strategies in **Figure 2b,c** could be applicable for lower bale grades when there is a higher degree of contamination, whereas the strategy outlined in **Figure 2a** would be applicable for higher bale grades or plastics that undergo different sortation steps. Additionally, the price of the sorted, reclaimed resin varies depending on the degree of contamination. The Association of Plastic Recyclers has published guidelines for acceptable contamination levels in packed bales that are largely accepted worldwide. For example, Grade F in PET can contain up to >28% contamination, whereas Grade A is <6% contamination (113). The volume and quality of plastic feedstock are driven by the end market for these materials. In North America, Recycling Markets has data on the weekly price of all recyclable materials and their grades across multiple regions. Additionally, information intelligence companies (often subscription based) such as IHS Markit can be useful to track fossil-derived chemical prices. Plastics News is a free source to track recent prices of both conventional and recycled plastics. Similarly, a recent publication from Chaudhari et al. (114) lists volumes and material flow analysis for MRFs (in the United States), along with virgin resin production, for PET and polyolefins.

Significant variability exists in the prices of reclaimed materials, depending on not only the source of plastic and the degree of contamination but also the market dynamics of supply and demand. The availability of plastics and current infrastructure of MRFs will drive which technologies



are more likely to be developed and adopted at scale, impacting their overall economic viability. As mentioned, plastics that can be recycled mechanically will have a greater demand for their material, and thus the waste plastics purchase price will contribute to the minimum selling price of any conversion products (95). Simultaneously, cheaper or alternative feedstock sources, such as lower-purity bales or textiles, which can potentially be sourced for free, will dramatically lower the feedstock cost. The balance between plastics cost and feedstock purity is greatly affected by the logistics of collection, collected volumes, population education of best practices, region, and operation and final yields through material recovery processes. This is why single-stream recycling, as is prevalent across several US cities, increases the collection volumes; however, it compounds the challenging task of separating different plastics types, which dictate feedstock cost (115). To alleviate these burdens, recyclers have invested in novel separations technology for increased efficiency and higher material recovery (116). Aside from lowering the prices associated with high-purity materials, new technologies may also lead to higher-purity plastic streams beyond PET, HDPE, and PP. Thus, analysis of chemical recycling processes should account for plastic feedstock options that are available today while also considering new plastic waste streams established as a response to markets created by new chemical recycling technologies (81–83).

Match of Feedstock Parameters to Distance for Transport and Scale of Chemical Recycling Facility and Product(s)

Some of the largest risks for any recycling facility (mechanical and chemical) are securing the feedstock (*a*) at relatively affordable price, (*b*) in steady volumes, and (*c*) with consistent quality. In contrast to the fossil-derived plastic industry, many recycling facilities that rely on postconsumer materials, by the nature of collection and transportation logistics, are smaller and decentralized in location. The appropriate collection radius needs to be determined depending on the plant size, but as current recycling facilities are delocalized, the facility may not be able to leverage economies of scale akin to petrochemical manufacture (owing to an existing infrastructure that keeps the virgin polymer prices low). Meeting the demand of postconsumer material, by improving collection volume and quality, will improve the viability of recycling.

A complication related to securing feedstock supply is the reality of time lags between when a polymer is first produced and when it becomes available for recycling. This use-phase residence time can make it difficult to anticipate the availability or consistency of waste feedstock derived from more durable plastic goods. The analysis approaches discussed in this article rely on steady-state assumptions of static and instantaneous supply of feedstock. Consequently, the impacts from such analysis do not convey information about how such impacts could vary when projected out into the future. Although such an approach may be suitable for specific primary and secondary plastic product supply chains, a more robust economy-wide model of polymer recycling may necessitate the inclusion of dynamic intertemporal effects and interactions between the various polymer product life cycles. In such cases, the so-called dynamic LCA approach would be required (117, 118).

CONCLUSIONS

Overall, process assessment tools will be fundamental to understanding new recycling processes and will ultimately enable objective, quantitative comparisons of the incumbent, linear manufacturing technology of today with the emerging, innovative chemical recycling approaches of tomorrow. New chemical recycling approaches, enabled by chemical catalysis, reaction engineering, advanced separations technologies, and rigorous chemical process design, that are both cost effective



and sustainable will be necessary to mitigate the environmental impacts of plastic manufacturing and the global pollution crisis stemming from the accumulation of single-use waste plastics.

SUMMARY POINTS

1. Chemical recycling strategies offer promise for both closed- and open-loop recycling and upcycling for dealing with plastics waste.
2. Rigorous techno-economic analysis and life cycle assessment are the fundamental tools to evaluate candidate chemical recycling processes at any stage of research and development.
3. New chemical recycling technologies should be benchmarked relative to linear, virgin plastics manufacturing processes in terms of economics, energy use, greenhouse gas emissions, and other life cycle inventory metrics.
4. We present and review generalized process frameworks and corresponding process analysis approaches for closed- and open-loop recycling and upcycling, which can be applied for all economic, energy, and life cycle metrics.
5. System boundaries in analysis cases are important for developing meaningful comparisons to tackle the global plastic waste challenge and enable more circular materials flows.
6. The research community should leverage these readily available analysis tools to evaluate new recycling and upcycling process concepts.

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