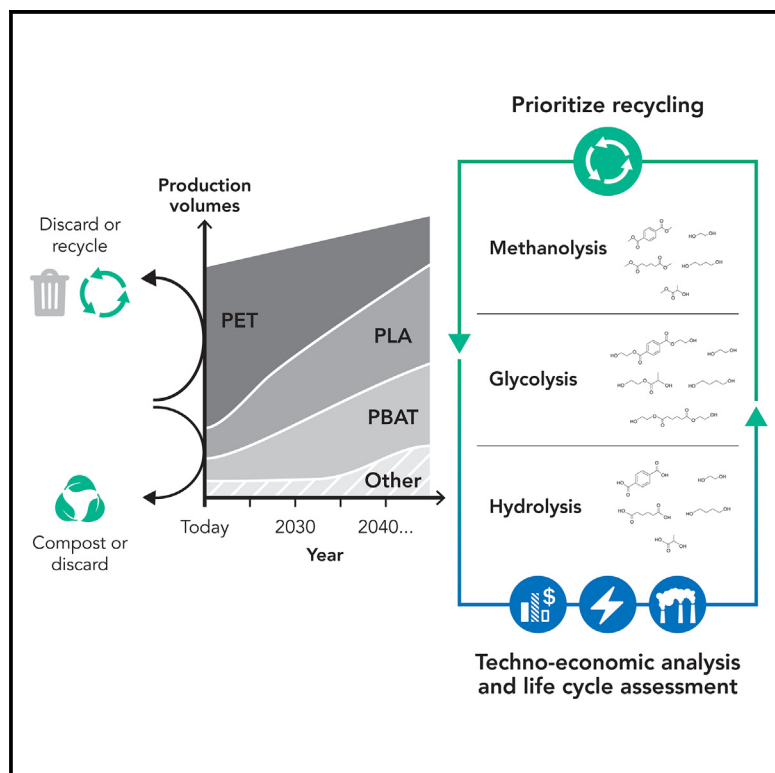# Mixed polyester recycling can enable a circular plastic economy with environmental benefits

Graphical abstract

Highlights

- Chemical recycling can enable a circular economy for mixed polyester plastics

- Methanolysis of PET, PLA, and PBAT outperforms other recycling processes

- Feedstock cost and purity, process yield, and plant scale are key process drivers

- Methanolysis reduces selling price by 31% with lowest overall environmental impacts

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In brief

The heterogeneity of plastic waste necessitates complex separations, often challenging existing recycling technologies. A polyester-based plastic economy could simplify recycling via ester-bond cleavage at end of life. This study evaluates three mixed polyester depolymerization methods— methanolysis, glycolysis, and acid hydrolysis—through techno-economic analysis and life-cycle assessment. Methanolysis is estimated to outperform virgin polyester manufacturing and other recycling strategies on a cost and environmental impact basis, especially when using bio-based feedstocks that may grow in production volume over time.

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Mixed polyester recycling can enable a circular plastic economy with environmental benefits

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SCIENCE FOR SOCIETY Bio-based plastics, derived from renewable feedstocks, present a promising alternative to traditional fossil-fuel-based plastics. However, the diverse chemistries of both bio- and fossil-based plastics complicate waste collection, sorting, and recycling, often leading to end-of-life management that is dominated by landfilling and incineration and results in harmful pollutants and emissions. Chemical recycling methods, including methanolysis, glycolysis, and acid hydrolysis, offer a pathway to address this challenge by depolymerizing mixed polyester waste into bio- and fossil-based monomers. These monomers can be recaptured to make new plastics with required properties such as strength and durability, paving the way for a circular plastic economy. Despite this potential, the economic and environmental performance of these approaches at the life-cycle level remains unclear. Our findings demonstrate that methanolysis can produce high-quality recycled plastics from mixed waste streams at two-thirds the cost while delivering significant environmental benefits. Scaling this approach offers a viable solution to managing plastic waste, advancing the vision of a circular economy.

SUMMARY

The mixed and varied nature of fossil-based and bio-based plastic waste requires complex and costly separations to enable compatibility with recycling technologies. A circular plastic economy based on mixed polyesters through cleaving ester bonds to produce monomers, while re-utilizing bio-based monomers to produce high-quality sustainable plastics, charts an exciting solution. However, the feasibility of such a circular economy solution remains underexplored. Here, we conducted a techno-economic analysis and life-cycle assessment of three polyester depolymerization recycling processes—methanolysis, glycolysis, and acid hydrolysis—for a mixed feedstock (polyethylene terephthalate [PET], polylactic acid [PLA], and polybutylene adipate terephthalate [PBAT]). Methanolysis outperforms glycolysis and hydrolysis economically and environmentally due to more efficient downstream separations, generating products with a 31% decrease in selling price and 21%–46% reduction in acidification, carcinogenic toxicity, fossil-fuel depletion, global warming potential, particulate formation, and smog formation compared to conventional polyester manufacturing. This study highlights the viability of a circular plastic economy for mixed polyesters via a single chemical recycling process.

INTRODUCTION

The reliance on petrochemical feedstocks and failure to mitigate the loss of plastic to landfills and the natural environment have accelerated the depletion of finite resources, resulting in enormous energy and material costs to the global economy.[1–5] The greenhouse gas (GHG) emissions from plastic production are expected to reach 15% of the global carbon budget by 2050.[1] A recent life-cycle assessment (LCA) study from Bardow et al. showed that a net-zero emissions plastics supply chain is

possible when combining biomass feedstocks with high recycling rates.[2] The polyolefin (i.e., polyethylene [PE] and polypropylene [PP]) industry has made substantial strides toward utilizing bio-based feedstocks, with bio-ethanol-derived PE commercially available today. These materials, when recycled via mechanical recycling at high rates, have the potential to be carbon negative and increase circularity. However, due to challenges associated with contamination and degradation, the mechanical recycling rates of PE remain low with limited life cycles. Chemical recycling of polyolefins via pyrolysis is growing in use but remains limited in widespread adoption due to the high energy requirements, and subsequent environmental impacts, needed to cleave carbon-carbon bonds.[6–8] In contrast, polyesters, while currently more energy intensive to produce than polyolefins, contain ester linkages that are prevalent in naturally occurring materials (e.g., cutin, suberin), which enable the use of bio-based feedstocks and more energy-efficient depolymerization into feedstock materials via ester cleavage through known chemical recycling techniques.[9,10] Additionally, previous LCA work has demonstrated reductions in emissions and other negative environmental impacts when recycling polyesters through solvolysis, compared to the pyrolysis or gasification of polyolefins.[11–14]

Polyesters have the potential to direct a future circular plastics system; multiple studies have shown that many bio-based polyesters can meet or exceed the performance of commodity plastics, either individually or in combination, while sequestering biogenic carbon in their backbones.[15–24] The markets for bio-based and partially bio-based commercial polyesters such as polylactic acid (PLA) and polybutylene terephthalate (PBAT) continue to grow.[25,26] However, the end-of-life processing of these polyesters, which are currently marketed as industrially compostable, remains a concern and has limited market adoption.[27] While known to break down under industrial composting conditions, composters often reject these materials due to the high carbon content leading to poor compost health. Additionally, compostable polyesters that enter current mechanical recycling infrastructure are viewed as contaminants to polyethylene terephthalate (PET) recycling streams.[28]

A chemical recycling process that can target the ester linkages in a variable feedstock of both bio-based and non-bio-based polyesters (e.g., PET) could keep valuable carbon in circulation and potentially reduce the environmental impact of plastic production and disposal. Such a polyester-agnostic system would increase the volume of material available for recycling, simplify the sortation process for material recovery facilities (MRFs) (i.e., sort based on common ester bond), and enable a recycling mechanism for existing and emerging compostable polyesters such as polybutylene succinate (PBS), polycaprolactone (PCL), and polyhydroxyalkanoates (PHAs).[25,29,30] Furthermore, the European Union's Single-Use Plastic Directive[31] aims to ban all single-use plastics other than "natural polymers," the definition of which is still under debate but may include bio-based polyesters. Such a transition may lead to strain on agriculture and natural feedstocks that can potentially be mitigated by effective recycling of these materials.

Multiple polyester depolymerization recycling strategies such as methanolysis, glycolysis, aminolysis, and hydrolysis have

been proposed, developed, and, in some cases, scaled up for PET waste management over the past several decades.[6,32,33] The mechanisms to cleave ester linkages will be the same for both PET and bio-based polyesters such as PLA, albeit under different conditions,[34–38] but downstream separation and monomer purification are expected to become increasingly demanding with mixed and variable feedstocks. While comprehensive modeling and analysis has been conducted for individual polyesters,[11,39] this has yet to be reported for mixed polyester feedstocks. It is critical to understand the economic and environmental impacts of a mixed polyester recycling process that could enable the circularity of these materials and reduce reliance on both fossil fuels and agricultural feedstocks.[40]

Here, we report a rigorous process modeling effort comparing chemical recycling processes for deconstructing mixed polyesters into monomers and repolymerizing them into the parent polymers using a representative mixed stream of PET, PLA, and PBAT (Figure 1). The feedstock for this study focuses primarily on packaging applications and was selected based on the criteria of (1) a representative fossil-based polyester (PET), a bio-based and compostable polyester (PLA), and a fossil-based and compostable polyester (PBAT), (2) commercially available and used in packaging applications, and (3) offers a range of properties and target use. We construct detailed process models for three industrially relevant polyester chemical recycling technologies: methanolysis, glycolysis, and acid hydrolysis. We then conduct techno-economic analysis (TEA) and LCA to estimate the minimum selling price (MSP) and environmental impacts of the resulting recycled polymer products. Sensitivity analysis is used to quantify the importance of feedstock composition, operating conditions, downstream separations, and renewable electricity and heat sourcing for process improvement and optimization. Overall, this study benchmarks potential mixed polyester chemical recycling technologies and proposes that amine-catalyzed methanolysis is the most economical pathway with the greatest environmental benefit, generating products with a 31% decrease in selling price and 46% reduction in global warming potential (GWP). Implementing such a recycling strategy could foster circularity for biogenic carbon within polyester materials, simultaneously curbing energy consumption, GHG emissions, waste, and other negative environmental impacts throughout the production and utilization of polyester plastics. These models can have far-reaching implications for emerging ester-based plastic recycling platforms and can provide analysis-driven process guides for expanding feedstocks beyond PET.

RESULTS AND DISCUSSION

Process model development

This study evaluates methanolysis, glycolysis, and acid hydrolysis (Figure 1) because these technologies have been explored extensively and are industrially relevant for PET recycling.[43] Several companies have operated PET methanolysis or glycolysis plants or are pursuing the development of these technologies at scale. Although most industrial activity for hydrolysis is focused on enzymatic or alkaline hydrolysis, we have previously reported on the high environmental impacts associated with base consumption in these processes.[53] As a result, we chose
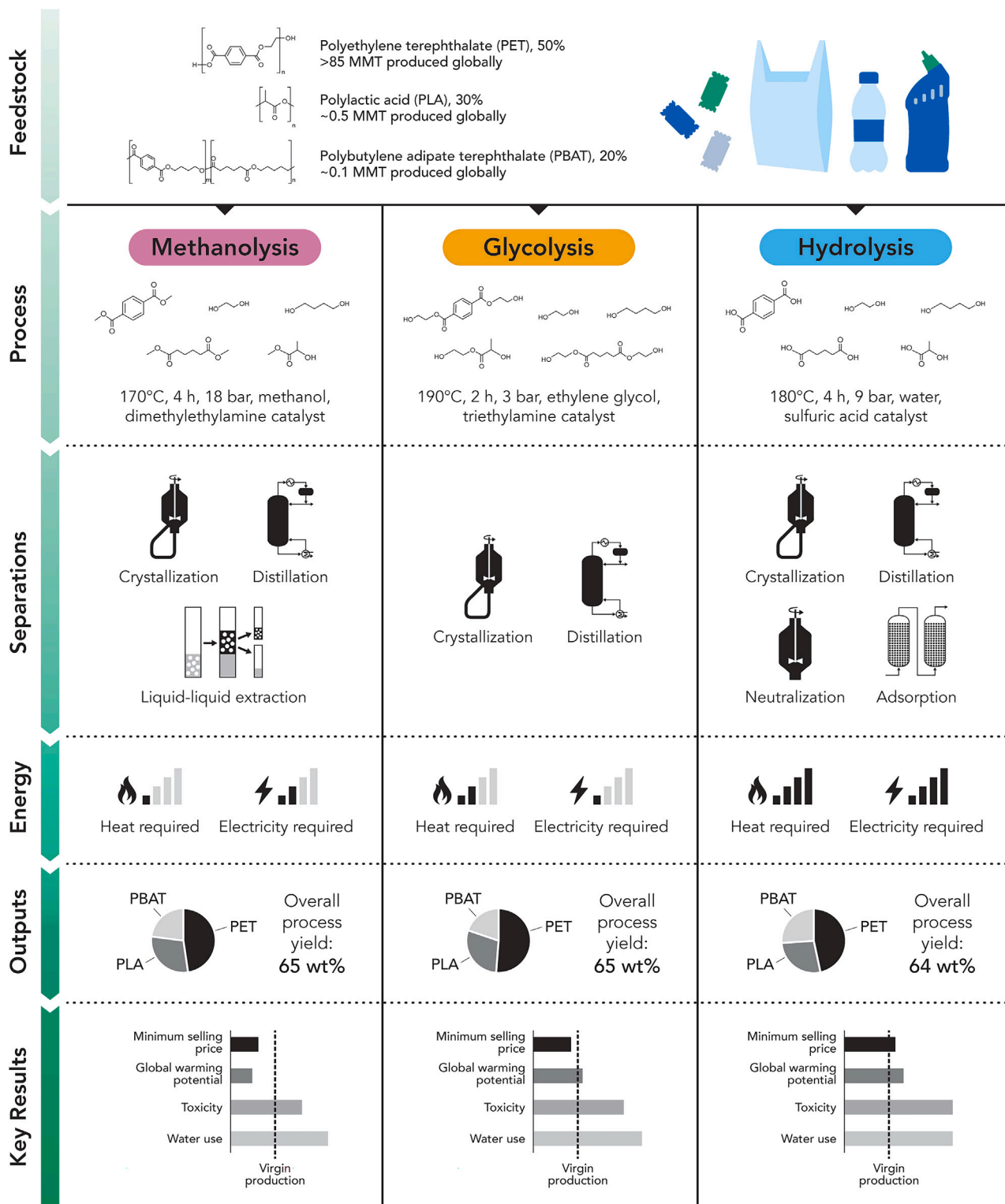
Figure 1. Overview of the mixed polyester chemical recycling technologies explored in this study, including corresponding feedstocks, chemical intermediates generated by each process, high-impact monomer separation operations, energy requirements, outputs, and key economic and environmental results

Overall process yields shown are on a mass basis relative to the total feedstock input and derive from the combined effects of 95% feedstock purity,[41,42] 90% depolymerization yield,[37,43–49] and 75% downstream product recovery.[50–52]
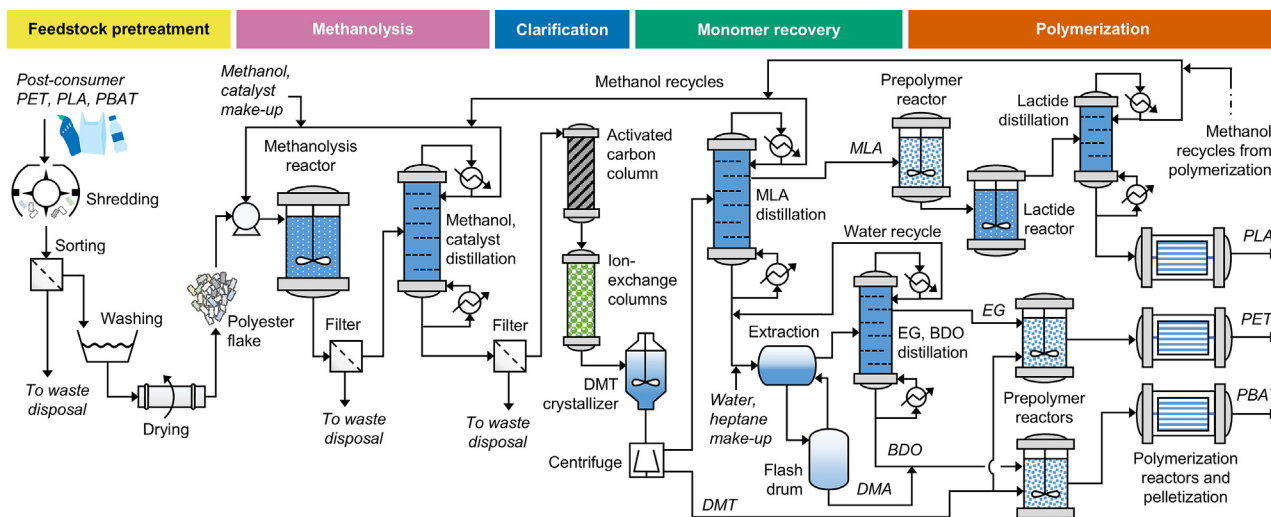
Figure 2. Simplified process flow diagram for the amine-catalyzed methanolysis of PET, PLA, and PBAT shown by process area
Process inputs, intermediates, and outputs are italicized. Detailed process flow diagrams for all sections of the methanolysis process are available in Figures S1–S7.

to explore an acid-catalyzed route that could minimize the need for alkaline reagents to neutralize acidic monomeric products. The chemical recycling feedstock was selected to have an average composition of 50% PET, 30% PLA, and 20% PBAT.[25,54] While this composition ratio does not reflect current market volumes, this study aims to demonstrate a potential future scenario where PLA and PBAT have a larger market share, as currently projected by market reports.[25] PLA and PBAT were selected as additional polyester representatives because they are used primarily for packaging and single-use applications and are, currently, the largest volumes in the compostable polyesters waste stream.[25,26] Other emerging and promising polyesters could also be introduced into the modeled processes as their respective usage grows.[15,18,20,21,23,55,56]

Process models for amine-catalyzed methanolysis, amine-catalyzed glycolysis, and acid-catalyzed hydrolysis were developed and modeled in Aspen Plus V14. When possible, assumptions around reaction conditions and separations were guided by the available literature, and the solubility of reaction products was evaluated experimentally. Due to the exploratory nature of this work, some property method data for compounds were not available and the Aspen property estimation tool was used. Therefore, the results may change as improved property data are reported and incorporated. However, as highlighted through sensitivity analysis and the estimation of error ranges via Monte Carlo analysis, the overall outcomes of the work are not expected to change substantially. Each process is briefly described here with full details and process flow diagrams in the supplemental information (Notes S1–S3 and Figures S1–S21).

In the base-case scenario for all modeled technologies, the facility size was set to process 100 metric tons per day (MTPD), or 36,000 metric tons per year, of mixed polyester waste feedstock. This plant capacity represents 4.5% of the combined 2020 consumption for PET thermoforms and compostable plastics (or, individually, 5% of PET and 44% of compostable plastics con-

sumption) in North America.[26,57] The feedstock was assumed to comprise 95% polyesters with 5% impurities (Table S1) and to be purchased from a MRF or reclaimer at $0.44/kg (Table S2). This price includes the cost of sourcing and sorting the feedstock (assumed here to be similar to the national average of PET thermoform and flexible film bales at $0.16/kg),[41] the cost of pretreatment including washing, flaking, and drying (estimated to be $0.20/kg based on equipment and utility costs), and transport (taken to be $0.08/kg).[58] Impurities include inorganic fillers, glues, paper, and other plastics and align with contamination levels for grade A PET thermoform bales.[41] As average market prices for PLA and PBAT are approximately 1.7–2 times that of PET (Table S2), these polymers could eventually demand higher post-consumer prices. Additionally, certain polyester products may have higher levels of contaminants and metals, such as inorganic fillers in PLA food service items and paper labels in PET thermoforms. To account for this uncertainty, the impact of feedstock cost and purity is explored through sensitivity analysis. The extent of reaction for depolymerization was set to 90% for all technologies[37,43–49] with an overall assumed downstream monomer recovery of 75%.[50–52] Along with the assumed feedstock purity, this results in an overall mass yield of approximately 65% with respect to the total feedstock input. The impact of these recovery and yield assumptions is also further explored through sensitivity analysis. Heat integration was performed in each process to minimize utility consumption.

In the methanolysis process (Figure 2), the polyester feedstock, mixed with methanol, is fed via a slurry pump to a continuous stirred-tank reactor operating at 170°C and 20 bar alongside a dimethylethylamine catalyst with a residence time of 4 h. The catalyst loading is 7 wt % (defined relative to the total feedstock mass) and the solids loading is 30 wt % (defined as the polyester feedstock relative to the total stream).[47,48,59] After the reactor, the mixture is filtered to remove residual solids and distilled to recover the catalyst and some methanol, which is recycled to the reactor. The bottom product is cooled to crystallize
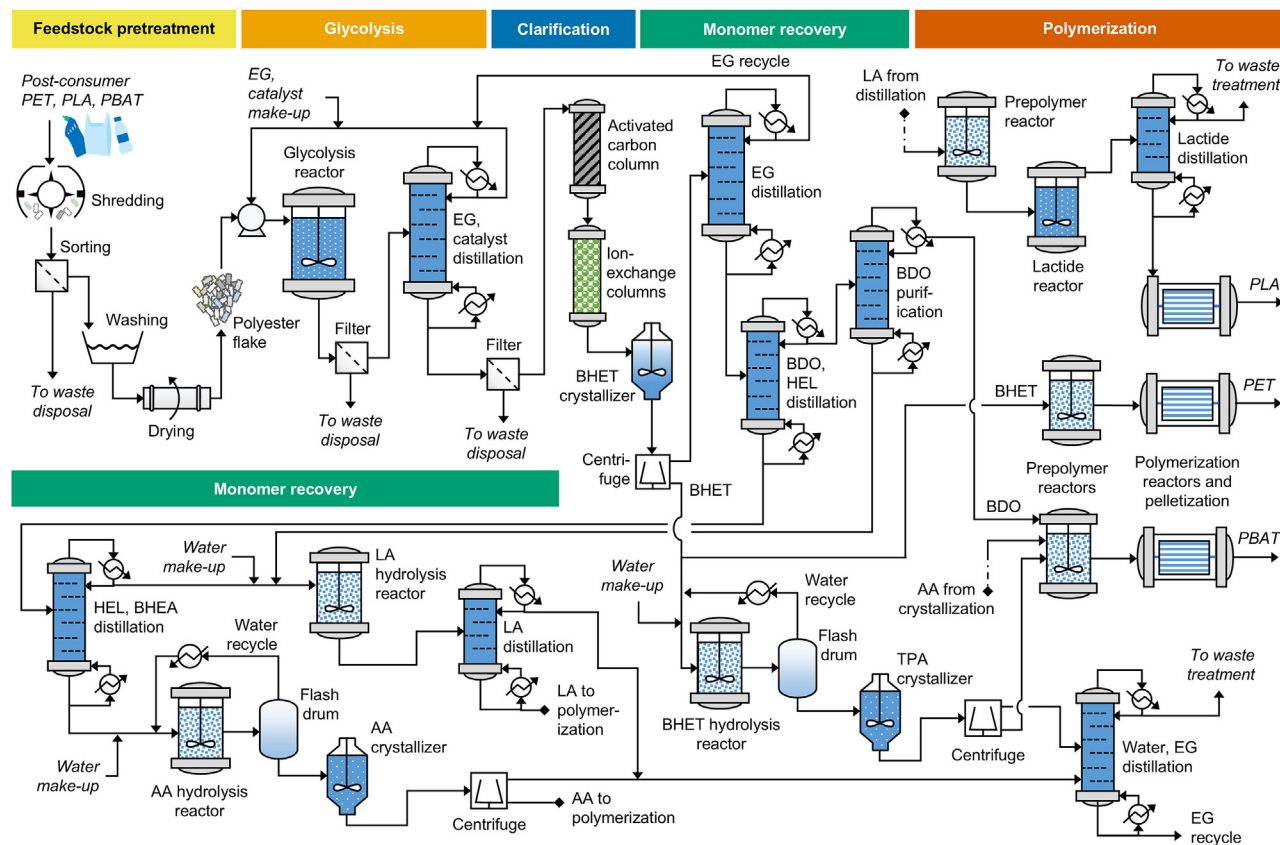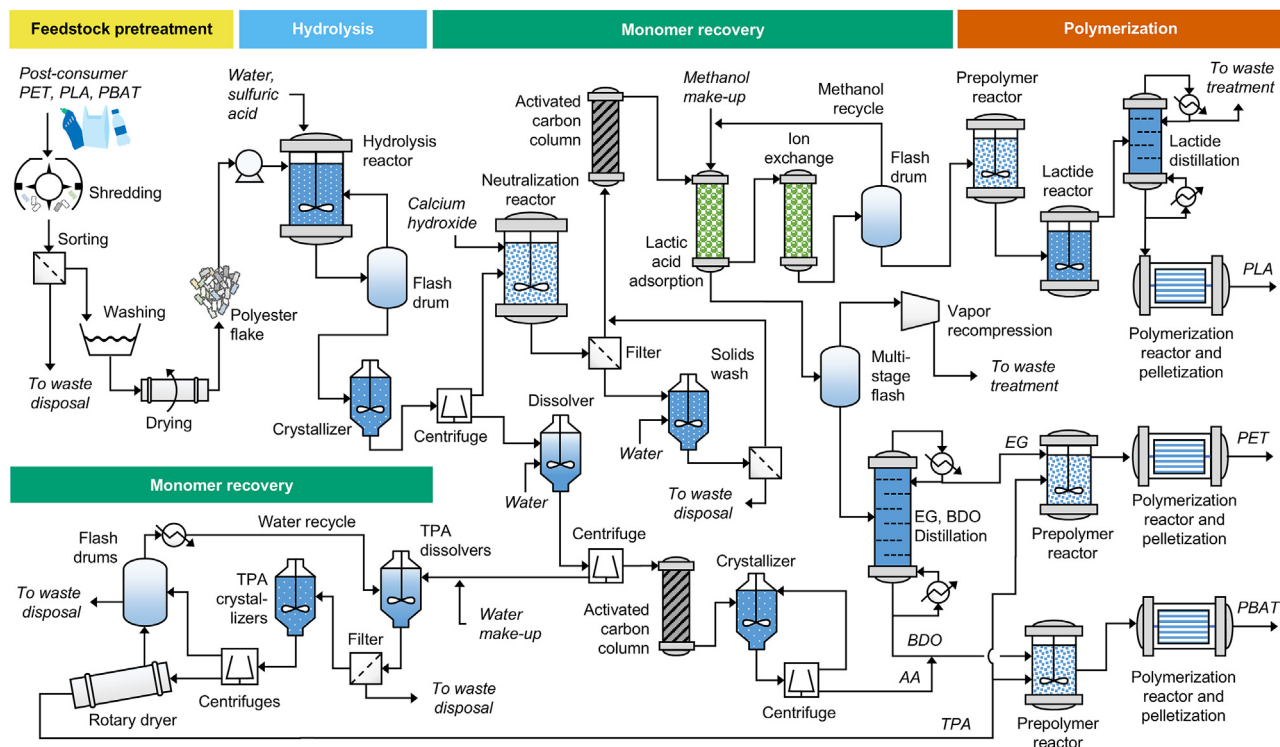
Figure 3. Simplified process flow diagram for the amine-catalyzed glycolysis of PET, PLA, and PBAT shown by process area
Process inputs, intermediates, and outputs are italicized. Detailed process flow diagrams for all sub-sections of the glycolysis process are available in Figures S8–S14.

dimethyl terephthalate (DMT) from solution. The liquid fraction is passed through activated carbon and ion-exchange columns to remove residual colorants and contaminants.[60,61] The treated solution is distilled in a series of columns to recover and separate methyl lactate from methanol and any residual catalyst. Due to an anticipated azeotrope between 1,4-butanediol (BDO) and dimethyl adipate (DMA), the distillation bottoms product containing ethylene glycol (EG), BDO, and DMA is separated using liquid-liquid extraction with water and heptane in a mixer-settler configuration. The organic-rich layer containing DMA is distilled to recover heptane (>99%) and the aqueous layer containing EG and BDO is distilled to recover water and separate the diols. The separated monomers are repolymerized: methyl lactate is converted to lactide, which is polymerized to PLA[62]; DMT and EG are reacted to form bis(2-hydroxyethyl) terephthalate (BHET) and polymerized to PET[63–66]; and DMT, BDO, and DMA are reacted to prepolymer intermediates and polymerized to PBAT.[67–70] Methanol is recovered from the polymerizations (simplified in Figure 2; see Figures S5–S7 for all stream details) and recycled back to the depolymerization reactor.

For amine-catalyzed glycolysis (Figure 3), the polyester feedstock, mixed with EG, is fed via a slurry pump to a continuous stirred-tank reactor operating at 190°C and 3 bar with a triethylamine catalyst and a residence time of 1 h.[37,46,47] The catalyst loading is 7 wt % (defined relative to the total feedstock mass)

and the solids loading is 20 wt % (defined as the polyester feedstock relative to the total stream).[47] The solids loading selected is lower than in methanolysis due to the higher viscosity of the reaction mixture and as guided by the reported ranges in literature. The reaction products are filtered to remove residual solids and distilled to recover the catalyst, which is recycled to the reactor. The bottoms product is passed through activated carbon and ion-exchange columns to remove residual colorants and contaminants.[50,52,60,61,71] The treated solution is cooled and the BHET product is crystallized from solution. The liquid fraction is distilled to recover and purify EG; the bottoms product is further distilled in a series of columns to recover products in the following order: BDO, 2-hydroxyethyl lactate (HEL), and bis(2-hydroxethyl) adipate (BHEA). Before polymerization, HEL, BHEA, and a portion of BHET must first be hydrolyzed to avoid the introduction of EG in PLA and PBAT. The hydrolysis reaction is catalyzed by an acidic ion-exchange resin to form the respective carboxylic acid intermediates (lactic acid [LA], adipic acid [AA], and terephthalic acid [TPA]). LA is recovered through distillation, whereas AA and TPA are recovered through evaporation, crystallization, and drying.[72] EG is recovered from the aqueous solution through distillation and recycled to the polymerization reactor. The separated monomers are sent to polymerization: LA is reacted to lactide and polymerized to PLA[62]; BHET is polymerized to PET[63,64,70]; and TPA, BDO, and AA are reacted to

Figure 4. Simplified process flow diagram for the acid-catalyzed hydrolysis of PET, PLA, and PBAT shown by process area
Process inputs, intermediates, and outputs are italicized. Detailed process flow diagrams for all sub-sections of the hydrolysis process are available in Figures S15–S21.

prepolymer intermediates and polymerized to PBAT.[65,67–70] EG vapors from the PET polymerization are recycled to distillation (not shown in Figure 3, see Figure S13 for all stream details).

In acid-catalyzed hydrolysis (Figure 4), the polyester feedstock is mixed with the aqueous sulfuric acid catalyst and fed via a slurry pump to a continuous stirred-tank reactor operating at 170°C and 3 bar for a residence time of 4 h.[44,45,49] The catalyst concentration is 3 M with a pH of 0. This acid catalyst loading is at the lower end of the 3–17 M range reported in literature[45,60,73] and a longer residence time and higher temperature has therefore been assumed.[45] The reaction solids loading is 20 wt % (defined as the polyester feedstock relative to the total stream),[44,45,49] which is lower than in methanolysis due to the lower solubility of polyesters in water[74] and the formation of solid products in the reactor. The reaction products are flashed to recover a portion of the water, which is directly recycled to the reactor. The remaining mixture is further cooled and then centrifuged to separate solid TPA, AA, and residual solids from the liquid product. The recovered solids are combined with water, heated to dissolve AA, and filtered.[75,76] The filtrate is treated with activated carbon and ion exchange to remove colorant and metal contaminants[77] and then cooled to recrystallize AA; the solids from filtration are further purified through recrystallization in high-temperature water to yield TPA.[78–80] The depolymerization reactor filtrate containing LA, EG, and BDO is neutralized with calcium hydroxide.[81,82] The resulting calcium sulfate precipitate is centrifuged, washed, and disposed of as waste. LA is separated from the filtrate by adsorption on a weak, tertiary

amine resin.[83,84] The LA is eluted from the column using methanol[85] then flashed and distilled to recover and recycle the methanol eluent (96% recovery); the effluent, containing aqueous EG and BDO, is concentrated using reverse osmosis (RO) and separated using distillation.[86–88] The separated monomers are then sent to polymerization: LA is reacted to lactide and polymerized to PLA[62,89]; TPA and EG are reacted to form BHET then polymerized to PET[63,64,66]; TPA, BDO, and AA are reacted to prepolymer intermediates then polymerized to PBAT.[67–70]

Key base-case parameters for each technology are summarized in Table S3. Material and energy balances generated from the Aspen Plus process models were used to size process equipment and estimate expenses. Using a discounted cash-flow analysis with a discount rate of 12% (complete financial parameters provided in Table S4), the overall MSP was calculated for the polymer products (i.e., the selling price of the total PET, PLA, and PBAT mass for which the net present value [NPV] is 0) on a 2020 United States dollar (USD) cost basis. Monte Carlo analysis with 10,000 iterations was run to estimate standard deviations for process MSPs (as described in the experimental procedures).

The environmental impacts of the selected mixed polyester depolymerization technologies were evaluated using life-cycle inventories built from the Aspen Plus process models (Tables S5–S11), the Tool for the Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI 2.1, US 2008)[90] and available water remaining (AWARE)[91] methods, ecoinvent version 3.3 background data,[92] and SimaPro LCA software. All
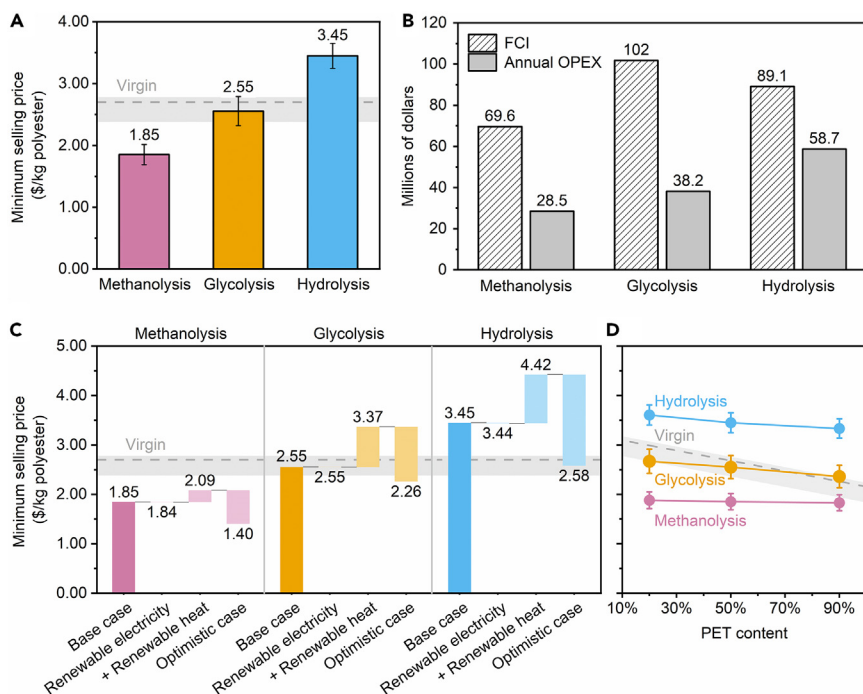
technologies were assessed "cradle to gate," from curbside collection through to repolymerization of the recycled monomers into PET, PLA, and PBAT (Figure S22). A cutoff approach was used in which the mixed polyester waste was assumed to be free of environmental burdens associated with its original production. Recycled polymers were compared to an equivalent mixture of virgin PET (fossil based, ecoinvent), PLA (corn sugar-based, ecoinvent), and PBAT (fossil based; Table S8). The standard deviations of the LCA results were estimated using a Monte Carlo simulation with 1,000 runs. Further details on the LCA goal, scope, and methodology are available in the experimental procedures.

Comparison of chemical recycling technologies

Across the screened processes, methanolysis was estimated to have the lowest MSP at $1.85/kg for the combined polymer products (Figure 5A; Table S12). Glycolysis and hydrolysis were estimated to have MSPs of $2.55/kg and $3.45/kg, respectively, in comparison to the estimated virgin market price of $2.70/kg for an equivalent product mixture. Methanolysis was also estimated to have the lowest annual operating expense and fixed capital investment when compared to glycolysis and hydrolysis (Figure 5B; Table S12). The most impactful aspect of these deconstruction technologies lies in the downstream processing and separations. Even though the methanolysis process has the highest operating pressure and a long residence time, the high recoverability of the methanol and catalyst and the ability to directly repolymerize all monomer products minimize the operational costs and capital expenditure. By contrast, the glycolysis process produces high-boiling monomer products that are mostly separated through distillation and require the hydrolysis of HEL, BHEA, and a portion of the BHET to avoid EG contamination in PBAT and PLA. These intensive steps that

result from the nature of the glycolysis process outweigh the benefits that derive from the easily recoverable triethylamine catalyst and the ability to directly polymerize BHET to PET without requiring an esterification or transesterification step. Similarly, although the acid hydrolysis process yields monomers that can be directly sold or polymerized, it requires relatively complex and energy-intensive separations and purifications (e.g., AA and TPA separation, TPA purification, and LA recovery). When combined with an unrecoverable sulfuric acid catalyst that requires neutralization, the operational costs and capital expenditure of acid hydrolysis are driven up, leading to the highest MSP.

In addition to the base-case scenarios, various decarbonization and optimization scenarios were evaluated (Figure 5C; Table S13). First, a case was considered in which the processes purchase renewable electricity at a price of $0.03/kWh, which is representative of the average purchase price agreement for utility scale solar and wind.[93–96] Across all technologies, this showed a relatively small decrease in MSP of $0.01/kg due to the small contribution of electricity expenses to overall MSP (~1%). Next, a renewable heating case in which renewable natural gas is purchased at $12.40/GJ and used for process heating and steam generation was considered.[97,98] Renewable natural gas refers to upgraded biogas from sources such as landfills, animal manure, and crop residues.[97] Due to the high premium of renewable natural gas relative to its fossil counterpart ($2.70/GJ), all technologies showed increases in MSP, with methanolysis exhibiting the smallest increase in MSP of $0.24/kg due to lower overall process heating requirements. Lastly, an optimistic case including both renewable electricity and heating along with select optimistic process improvements (99% reaction extent, 85% downstream recovery, 99% feedstock purity, 150 MTPD,

Figure 6. LCA screening of mixed polyester chemical recycling strategies

(A) LCA results comparing mixed polyester methanolysis, glycolysis, hydrolysis, and virgin manufacturing. The colored asterisks highlight the process with the lowest environmental impact in each category. Error bars represent standard deviations and were estimated using Monte Carlo analysis with 1,000 iterations.

(B) Comparison of the multi-criteria decision analysis (MCDA) scores (which combine all environmental impact metrics into a single value) of mixed polyester methanolysis, glycolysis, hydrolysis, and virgin manufacturing for decarbonization scenarios including the use of renewable electricity (ReEDS mid-case scenario with 95% decarbonization by 2035), renewable heat (from renewable natural gas), and an optimistic case incorporating additional improvements to process conditions and yields (99% reaction extent, 85% downstream recovery, 99% feedstock purity, 150 MTPD, 30%/40% solids loading).

(C) Comparison of the MCDA scores of mixed polyester methanolysis, glycolysis, hydrolysis, and virgin manufacturing with different ratios of PET content in the feedstock. Raw data are available in Tables S15–S18.

30%/40% solids loading) was modeled. Even with the premium paid for renewable heating, the optimistic case scenarios showed substantial decreases in MSP due to increased yields, lower process heating, and lower material consumption. Under these optimistic case scenario assumptions, all processes were shown to be potentially competitive with the virgin equivalent market price, with glycolysis and hydrolysis showing the largest magnitude in MSP decrease, albeit with final MSPs still higher than methanolysis.

To understand the impact of feedstock composition on process economics, the PET mass fraction in the feedstock was varied while maintaining PLA and PBAT at a mass ratio of 3:2 (Figure 5D; Table S14). Hydrolysis and glycolysis are estimated to exhibit a slight decrease in MSP as the PET fraction increased due to a reduction in methanol and EG consumption, respectively. In contrast, the methanolysis MSP was relatively invariant due to a reduction in the capital recovery charge offsetting an increase in raw material demand for EG makeup in polymerization. As the PET market price is estimated to be less than PLA and PBAT, the reference market price (dashed gray line) is also shown to decrease as PET content increases.

On an environmental basis, methanolysis offered the lowest acidification, carcinogenic toxicity, fossil-fuel depletion, GWP, particulate formation, and smog formation, at 21%–46% lower than virgin manufacturing of an equivalent combination of PET, PLA, and PBAT (Figure 6A; Tables S15–S18). Virgin manufacturing had the lowest impact in the remaining ecotoxicity, eutrophication, non-carcinogenic toxicity, ozone depletion, and water use categories (17%–59% lower than methanolysis). Glycolysis offered the second-best performance across the recycling technologies, with impacts 1.2–4.2 times higher than methanolysis and 1.0–10.2 times higher than virgin manufacturing. Hydrolysis exhibited life-cycle impacts 1.3–3.1 and 1.3–6.2 times higher than methanolysis and virgin polyester,

respectively. Methanolysis tends to have the lowest impacts of the three assessed recycling technologies due to its streamlined downstream separations and production of monomers that are more efficient to polymerize. This results in lower steam (5.4 kg/kg) and natural gas (1.4 MJ/kg) consumption than glycolysis (18.6 kg/kg and 2.5 MJ/kg) or hydrolysis (18.8 kg/kg and 18.5 MJ/kg). Furthermore, methanolysis generates less waste for disposal (0.25 kg/kg) than glycolysis (0.71 kg/kg) or hydrolysis (2.62 kg/kg), contributing to its lower impacts. Glycolysis produces more organic waste due to EG losses (treated as hazardous waste by incineration with energy recovery), while hydrolysis generates more solid waste due to the formation of a calcium sulfate byproduct (treated as inert waste in a sanitary landfill). If the calcium sulfate could be sold as a co-product for applications such as plaster or fertilizer, the quantity of waste generated by hydrolysis would decrease 86% to 0.36 kg/kg.

The LCA system boundary can also be expanded from cradle to gate (Figure 6A) to cradle to grave (Figure S22). This enables comparison between a business-as-usual scenario (virgin polyester synthesis, manufacturing into 50% bottles and 50% film, and disposal by landfilling, incineration, or mechanical recycling according to 2019 US disposal data[5]) and a recycling scenario (virgin polyester synthesis, manufacturing into 50% bottles and 50% film, and disposal by chemical recycling, all normalized over the multiple lifetimes that can be achieved by repeated recycling[40]) (Figure S22). See the experimental procedures for further details on the life-cycle normalization process. Under this expanded system boundary, methanolysis retained lower environmental impacts than virgin polyester across all metrics except ozone depletion and water use. Glycolysis also became more competitive under the expanded system boundary, with impacts in many cases statistically equivalent to methanolysis or virgin manufacturing. This performance improvement is primarily linked to the higher PET yield of glycolysis (70%) than

methanolysis (65%), which means that less supplemental virgin PET is required to re-manufacture 1 kg of mixed polyester.

Each chemical recycling technology also has the potential to improve with future innovations and market changes. To explore this, we conducted multi-criteria decision analysis (MCDA) by normalizing each environmental impact metric by the highest value and summing the results into a single score (see the supplemental information for details). This systematic technique enables the evaluation and ranking of options across multiple, often conflicting, criteria.[99] A lower MCDA score indicates a "better" outcome. Switching to a renewable electricity grid enabled reductions in MCDA score of 23% for methanolysis, 23% for glycolysis, 14% for hydrolysis, and 9% for virgin manufacturing (Figure 6B; Tables S15–S18). Adding renewable natural gas heating in addition to renewable electricity allowed all recycling options to exhibit lower MCDA scores than virgin polyesters, showcasing the compatibility of a circular polyester economy with decarbonization strategies. The effects of renewable electricity and heating on virgin polyester manufacturing were minimal as most life-cycle impacts are associated with fossil-fuel extraction and refining into monomers. Incorporating potential recycling yield improvements as mentioned above (optimistic case) resulted in MCDA scores of 2.6, 3.5, and 4.7 for methanolysis, glycolysis, and hydrolysis, respectively, in comparison to virgin manufacturing at 4.8. While these results suggest holistic benefits, it should be noted that the recycling technologies still exhibit tradeoffs, including higher ecotoxicity, non-carcinogenics, ozone depletion, and water use than virgin manufacturing with renewable electricity and heat. Additionally, virgin polyester manufacturing could be further decarbonized through biogenic carbon sequestration when using a fully bio-based PBAT or PET in contrast to the fossil-fuel-based PBAT and PET modeled here.[1,100] Such an approach could make biodegradable polyesters more environmentally competitive with the PE films that are standard today (1.93–2.18 kg CO_2 eq/kg) but could also reduce the relative benefits of chemical recycling.

If PET is gradually replaced with biodegradable polyesters such as PLA and PBAT, the GWP of recycling will alter due to changes in yields and monomer separation requirements (Figure 6C; Tables S15–S18). The GWPs of both hydrolysis and glycolysis increased with decreasing PET content. At lower PET loadings, glycolysis is anticipated to experience higher EG losses during monomer separation, resulting in higher organic waste generation. Hydrolysis will require higher methanol makeup and disposal for LA processing, and correspondingly higher steam consumption for methanol recovery. In contrast, the GWP of methanolysis decreased by 3% relative to the base case, resulting in an impact 2.5 times lower than a virgin polyester mixture containing 20% PET. At lower PET loadings, methanolysis will require less EG makeup and natural gas for PET polymerization, as well as lower distillation energy requirements to separate EG from BDO.
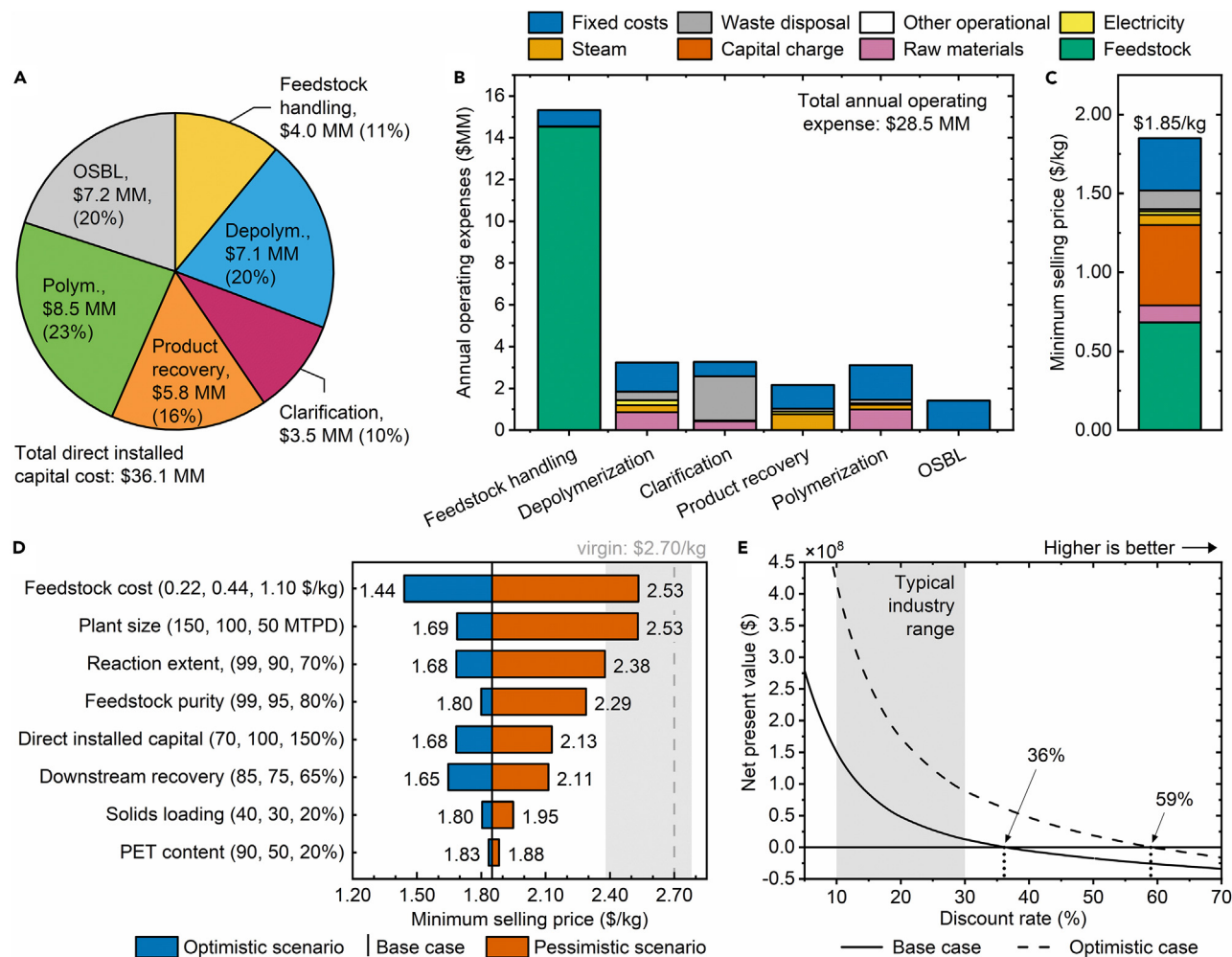
Detailed analysis of mixed polyester methanolysis
Based on the economic and environmental results for the recycling techniques under both base-case assumptions and potential future scenarios, we down-selected methanolysis for further characterization and optimization for mixed polyester recycling. In the base-case scenario for methanolysis, the total direct

installed cost was estimated to be $36.1 million (MM) (Figure 7A; Table S19). The largest contributions came from repolymerization of monomers and the assumed outside battery limit (OSBL) contribution for plant utility integration. The polymerization section accounted for the largest cost at $8.5 MM due to the separate polymerization lines required for each polymer. This highlights that the co-location of the methanolysis plant with existing polymerization facilities could substantially reduce capital costs. Product recovery and depolymerization were the next highest contributors at $6–7 MM each, primarily due to reactor and distillation column costs. Minor contributors included feedstock handling and clarification sections, which accounted for approximately $4 MM each. The total annual operating expense was estimated to be $28.5 MM with feedstock costs dominating (Figure 7B; Table S20). Fixed costs also exhibited a high contribution to operating expenses due to the number of operators required for the many unit operations in the process. The MSP for methanolysis was $1.85/kg (Figure 7C; Table S21), with the two largest contributions coming from the feedstock (37% of overall MSP) and the capital charge (28% of overall MSP). Fixed costs also contributed 18% to the overall MSP with smaller contributions coming from waste disposal, raw material consumption, and steam.

Univariate sensitivity analysis was conducted to understand the impact of key process variables on the MSP of methanolysis (Figure 7D; Table S22). Feedstock cost showed the largest impact on overall MSP due to its high contribution to MSP and the wide range of the bounds explored. The lower bound of $0.22/kg represents a cost scenario in which only the expenses for washing, drying, and flaking are included, whereas the upper bound of $1.10/kg represents a high-feedstock-cost scenario and is derived from historical PET bottle flake costs. Importantly, the pessimistic feedstock cost scenario of $1.10/kg is still expected to result in an MSP lower than the virgin market price for methanolysis. Other process variables, including reaction extent, feedstock purity, and downstream recovery, showed a high impact on process economics as they are linked to the overall process yield. Additionally, due to the high contribution of capital recovery and fixed costs to the MSP, plant size was shown to be the second most impactful variable, emphasizing the importance of economies of scale. Lastly, the variables explored with minor impacts on economics included solids loading and feedstock PET content. As with other recycling technologies,[11–14,101–103] these insights emphasize the importance of securing feedstock in sufficient volumes and at low, reliable cost points to maximize process profitability.

Since the methanolysis process is assumed to produce polymer products on par with virgin quality, an economic scenario was considered where the overall product selling price was set equal to the representative virgin market price of $2.70/kg. The results for the NPV of the plant across a range of discount rates are shown in Figure 7E (Table S23). The base-case scenario was shown to have a break-even discount rate of 36% (i.e., where the NPV is equal to zero), which is more profitable than the typical discount rate range for industrial processes of 10%–30% (the shaded region in Figure 7E). As unproven technologies typically carry greater financial risk, a higher discount rate is desirable and highlights the economic potential of the methanolysis process. The optimistic case shows that process improvements could
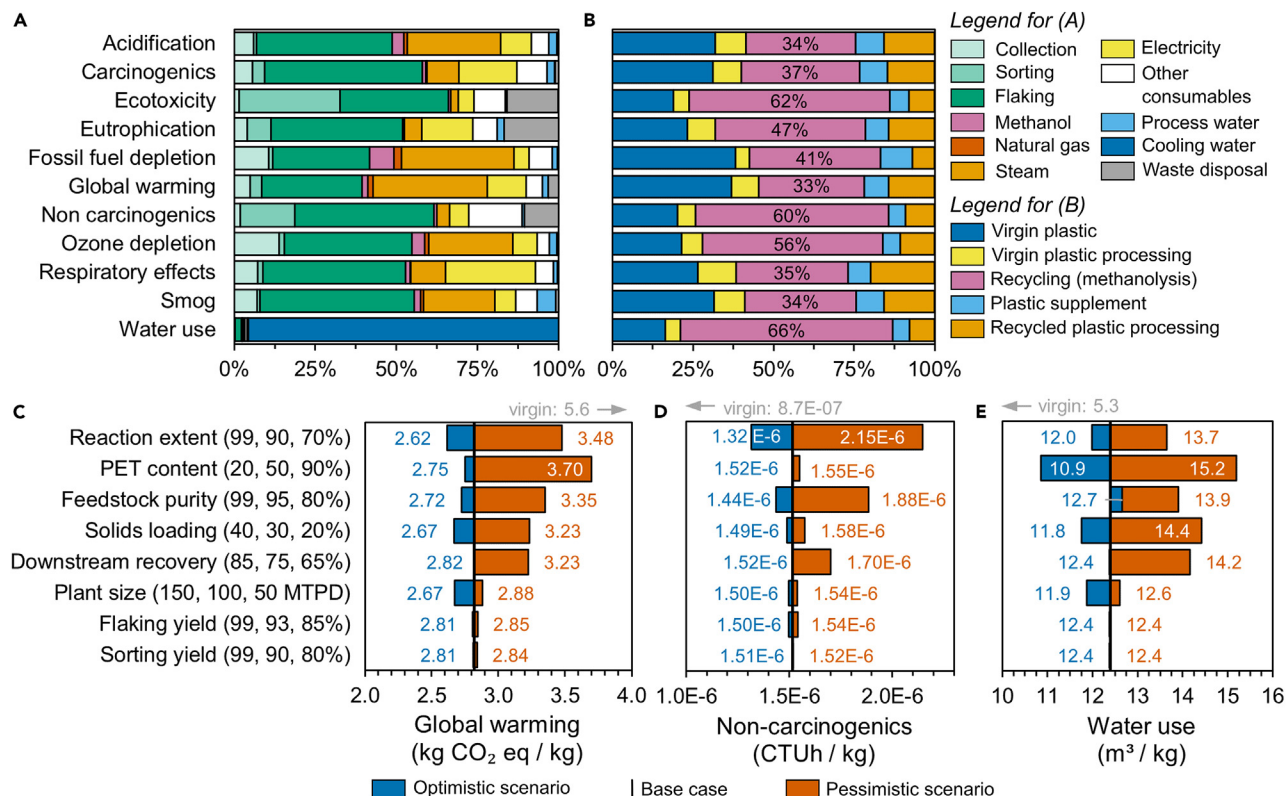
Figure 7. In-depth TEA of mixed polyester methanolysis

(A) Direct installed capital costs in $MM by process area for the base case.

(B) Annual plant operating expenses in $MM for each process area divided into key cost categories.

(C) MSP of the mixed polyester product for the base case divided into key cost categories.

(D) Univariate sensitivity analysis results for the MSP of the polyester products. The numbers listed in parentheses on the y axes correspond to the left (blue, optimistic), middle (black, base case), and right (orange, pessimistic) points of the graph. The virgin market price range ($2.38–2.78/kg) for an equivalent product mix is shaded in gray with the average value of $2.70/kg shown as a dashed gray line.

(E) Net present value (NPV) curves for the base case and optimistic case scenarios for a product selling price equal to the virgin market value of $2.70/kg. Drop lines are shown at break-even discount rates where the NPV is equal to 0. The typical range for a feasible discount rate is shaded in gray. See the supplemental information for corresponding data (Tables S2 and S19–S23). Depolym., depolymerization; Polym., polymerization; OSBL, outside battery limits; MTPD, metric tons per day.

greatly increase the break-even discount rate for the process up to 59%. The corresponding capital and operating expenses, MSP breakdowns, univariate sensitivity analyses, and NPV calculations for glycolysis and hydrolysis are available in the supplemental information (Figures S23–S24; Tables S24–S33).

Most of the environmental impacts of methanolysis, except water use, could be linked to feedstock preparation (33%–66% contribution to impacts), steam (2%–35%), electricity (5%–28%), and other consumables encompassing EG, heptane, and additional organic and inorganic chemicals (4%–16%) (Figure 8A; Table S34). The impacts of feedstock preparation are related to electricity use for sorting and shredding equipment (0.35 kWh/kg), landfilling of feedstock losses and contaminants

(0.2 kg/kg), and transportation of the feedstock by diesel-powered truck between collection, sorting, and recycling facilities (total of 700 km).[104] Steam in the ecoinvent database is assumed to be generated primarily from natural gas (>60%), as well as from coal and fuel oil, which drive the overall impacts of steam use.[92] For example, natural gas venting during extraction and refining contributes strongly to climate change,[105] while blasting during coal mining releases a variety of air emissions that lead to acidification.[106] The life-cycle impacts of electricity, which in the US is still generated primarily from natural gas and coal,[107] are similarly affected by the extraction and combustion of these fossil fuels. Furthermore, ecotoxicity, eutrophication, and non-carcinogenics are linked to waste disposal (10%–17%), particularly

Figure 8. In-depth LCA of mixed polyester methanolysis

(A) Contribution of various process components to the life-cycle impacts of mixed polyester methanolysis.

(B) Contribution of life-cycle stages to the life-cycle impacts of mixed polyester methanolysis when the system boundary is expanded to cradle to cradle (virgin polyester production through to recycling and processing back into packaging products).

(C–E) Effect of sensitivity cases on (C) global-warming potential (GWP), (D) non-carcinogenic toxicity, and (E) water use. The numbers listed in parentheses on the y axes correspond to the left (blue, optimistic), middle (black, base case), and right (orange, pessimistic) points of the graph. See the supplemental information for corresponding data (Tables S15 and S34).

landfilling of the unreacted plastic feedstock mixture because non-plastic contaminants such as metals are assumed to seep into the landfill leachate.[108] Methanol also contributes to acidification, fossil-fuel depletion, and ozone depletion (4%–8%) due to its use of a synthesis gas feedstock derived from natural gas,[109] while cooling water accounts for 96% of water use.

If we consider the entire cradle-to-cradle life cycle of mixed polyester from virgin production and manufacturing into bottles and films through to methanolysis and re-manufacturing, the recycling step accounts for 34%–66% of all impacts, followed by virgin polyester synthesis at 16%–37% (Figure 8B; Table S34). In contrast, for a conventional cradle-to-grave life cycle in which mixed polyester is sent to landfill and incineration, virgin synthesis would account for 34%–84% of all impacts while end-of-life management would contribute 0.2%–54%. Displacing virgin manufacturing with methanolysis could reduce virgin material demand and thereby lower the overall environmental impacts of the polyester sector, especially when combined with the decarbonization opportunities discussed in Figure 8B. Cycling polyesters through methanolysis multiple times could further reduce the environmental impacts. Increasing the recycling rate from the 54% assumed in the base case to 99%—including all sorting (90% increases to 100% yield), flaking (93% increases

to 100% yield), and methanolysis (65% increases to 99% yield) steps—could enable 1 kg of virgin polyester to undergo 100 lifetimes and reduce the overall GWP of the system by 25% (Figure S22B).

The effects of univariate sensitivity cases on the environmental performance of methanolysis are explored for global warming, non-carcinogenic toxicity, and water use in the main text (Figures 8C–8E) and for all other impact categories in the supplemental information (Figure S25; Table S15). Of the variables investigated in the methanolysis sensitivity analysis, depolymerization reaction extent was the most impactful parameter for ecotoxicity, eutrophication, carcinogenic toxicity, fossil-fuel depletion, non-carcinogenic toxicity, ozone depletion, particulates formation, and smog formation. As yields increase, less mixed polyester flake input will be needed per unit of output polyester: 1.40 kg_{in}/kg_{out} in the optimistic case versus 1.54 kg_{in}/kg_{out} for the base case and 1.99 kg_{in}/kg_{out} for the pessimistic case. Electricity and some consumable requirements also vary slightly between scenarios, although these alterations are expected to have less of an impact than that of feedstock requirements given that most assessed life-cycle impacts are dominated by feedstock collection, sorting, and pretreatment into flake. For GWP and water use, PET content was the most

Feedstock pretreatment	Depolymerization	Clarification	Monomer recovery	Polymerization
Improve collection and sorting to maximize polyester recovery.	Optimize conditions to maximize depolymerization yield. Increase solids loading to decrease solvent recovery demands.	Minimize monomer losses.	Explore alternative monomer separation technologies with lower energy use than distillation. Use easily recoverable catalysts.	Enable compatibility with lower purity monomer streams or explore copolymers that do not need intensive separations.

Economy wide: Utilize electricity and heating from renewable sources. Standardize polyester monomers.

Figure 9. Suggested process improvements by process section for the mixed polyester deconstruction technologies explored in this work

impactful parameter. Natural gas, steam, electricity, and cooling water consumption are anticipated to decrease with lower PET content because downstream separation and polymerization of the PLA and PBAT monomers are less energy intensive than those of DMT, as discussed above. Increasing the efficiency of upstream feedstock processing (sorting and flaking yields) or adjusting the plant size are expected to have the least impact on all LCA scores. The environmental impact breakdowns and sensitivity analysis for glycolysis and hydrolysis are available in the supplemental information (Figures S26–S28; Tables S16, S17, S35, and S36).

Opportunities for further process improvements and limitations of this analysis

Based on this TEA and LCA, we propose a series of research targets to refine the feasibility of deconstruction technologies for mixed polyester waste (Figure 9). First, all technologies would benefit from the use of a high-purity feedstock (i.e., high polyester content, low contaminant content). Such a feedstock could potentially be sourced from MRFs equipped with suitable near-infrared spectroscopy separations or from packaging drop-off sites.[110] However, a high-purity feedstock often comes with a price premium, which contradicts the low feedstock cost identified as important in the MSP sensitivity analysis. It will therefore be crucial to identify a robust waste supply chain early in the technological scaling process. Furthermore, it would be beneficial to explore whether methanolysis can operate efficiently on bulk plastic rather than polyester flakes to minimize the energy requirements associated with feedstock pretreatment.

For all screened technologies, the deconstruction processes themselves could benefit from overall yield optimization. For the methanolysis process, we estimate that a depolymerization reaction extent of at least 80% should be sufficient for the MSP and environmental impacts to be competitive with virgin polyester production. Increasing the solids loading from the base-case values could also help minimize solvent recovery requirements, reducing costs and environmental impacts. Furthermore, downstream recovery in the proposed mixed polyester chemical recycling processes is currently underexplored. A key research area will likely be to maximize monomer recovery while using lower-energy separation technologies. One example in the methanolysis process is the separation and purification of EG and BDO via distillation, which accounts for 41% of the overall steam consumption. Replacing this step with azeotropic distillation,[111,112] reactive extraction and distillation,[113] or melt crystallization,[114,115] or changing the upstream liquid-liquid extraction

solvent system, could greatly reduce the overall steam consumption. All or some of the purified monomers could also be sold directly to existing polymerization plants to reduce the staffing and capital costs associated with polymerization.

While the analysis results indicate that methanolysis has potential as a flexible, polyester-agnostic recycling technology, experimental work will be necessary to validate and improve upon the process design presented here. Furthermore, this analysis is highly dependent on the proposed process designs and underlying assumptions. As a result, glycolysis, hydrolysis, and other technologies should not be discounted for application to mixed polyesters but instead modified when useful. For example, in-depth LCA characterization of glycolysis suggested that increasing depolymerization reaction extent, feedstock purity, and downstream recovery yield could reduce the consumption of impactful components such as steam and waste disposal (Figure S25). The adoption of copolymers such as PET-PBT,[116] PET-PLA,[117] or poly(butylene adipate-co-ethylene terephthalate)[118] could also make glycolysis more competitive by reducing purification requirements and eliminating the need for energy-intensive monomer hydrolysis prior to polymerization. These copolymers could be used in direct applications such as polyurethane foams.[119,120] Hydrolysis environmental impacts, meanwhile, were dominated by sulfuric acid and steam consumption, which could be minimized by using a recoverable acid catalyst[49,121] or by increasing solids loading, depolymerization reaction extent, and downstream recovery yield (Figure S26).

Due to the scope and exploratory nature of this work, not all innovations, scenarios, behaviors, or impacts were assessed. Further work could focus on understanding the effect of real-world post-consumer feedstocks on chemical recycling strategies, such as characterizing problematic contaminants or the performance of compatibilized blends. Process modifications may also be necessary to ensure compatibility with other polyesters, including PBS and PHAs. Many of these contamination, compatibility, and availability issues for post-consumer plastic feedstocks are linked to access to curbside collection programs, which are already minimal for polymer composting and expected to be a major barrier to sourcing a mixed polyester feedstock for chemical recycling.[122] Current MRF infrastructure could be adapted to include additional near-infrared sortation for bio-based polyesters but may also present challenges when trying to achieve single streams of polyesters, like bottle grade PET,[123] which can be efficiently processed by mechanical recycling.[11] However, if a recycling process could accommodate mixed polyesters, the common ester bonds would allow for an

easier "one-shot" sortation of all polyesters, including PET, into a single stream at an MRF.

Conclusions

In this work, we compared the process economics and environmental performance of selective depolymerization via methanolysis, glycolysis, and hydrolysis for the recycling of a mixed polyester stream containing PET, PLA, and PBAT. The results of the analysis highlight the potential benefits of a system that harmonizes recycling with mixed and variable polyesters, including bio-based materials, to keep valuable carbon molecules in circulation rather than permit them to degrade. Another advantage of chemically recycling mixed polyesters is the ability to process a wider range of form factors beyond packaging. This includes other emission-intensive waste streams such as textiles, electronics, and building and construction waste. Expanding the scope of acceptable materials enhances the potential for waste reduction and promotes a more comprehensive approach to sustainability.[124,125]

Methanolysis was found to have the most advantageous overall performance for polyester recycling with an MSP of $1.85/kg in the base-case scenario, which represents a 31% decrease relative to the estimated market value of an equivalent mixture of PET, PLA, and PBAT. Methanolysis also showed life-cycle environmental benefits including a 46% reduction in GWP and a 29% reduction in carcinogenic toxicity relative to virgin production, with all other life-cycle impact metrics lower than or statistically equivalent to virgin production. Recycling via glycolysis or acid hydrolysis was found to have higher costs and environmental impacts in the base-case scenario but has the potential to be competitive with virgin production under process optimization and decarbonization conditions.

This work demonstrates that, with a surplus of potential technologies to choose from, process modeling alongside TEA and LCA can help guide the direction of early-stage research and down-select optimum recycling pathways for select waste streams. As the market and demand for bio-based polyesters grows, a flexible chemical recycling process will be crucial for enabling an effective and sustainable circular economy.

EXPERIMENTAL PROCEDURES

TEA

Goal and scope

The goal of this work was to determine the economic and environmental feasibility of a chemical deconstruction approach to mixed polyester recycling. To that end, three process models were developed to represent key industry technologies of interest: methanolysis, glycolysis, and hydrolysis. Process models for representative processes were developed in Aspen Plus V14 guided by available literature including publications, patents, and technology reports. The POLYNRTL model package was used for methanolysis and glycolysis and the EP-NRTL package was used for hydrolysis.

Some property method data for compounds were not available and the Aspen property-estimation tool was employed where necessary. Complete property estimation was required for the glycolysis products HEL and BHEA, which may result in particularly high uncertainty for distillation operations involving these components. Where important, compound behavior was determined experimentally; this included validating the proposed deconstruction technologies on mixed polyester substrates, confirming compound miscibility and solubilities, and testing the proposed AA and TPA crystallization separation under highly acidic conditions in hydrolysis. Data for these experiments are not included in this work.

At this level of modeling and with the underlying assumptions, there are aspects of the modeled processes that may not be fully accounted for including unpredictable equilibrium or thermodynamic behavior (i.e., azeotropes, phase separation, etc.) and application of unique separation approaches (surfactants, membrane separations, etc.). Therefore, it will be necessary to re-evaluate the designs and underlying assumptions if these technologies are further developed.

Full process descriptions are provided in Notes S1–S3 with detailed process flow diagrams provided in Figures S1–S21. Some equipment that was accounted for in the economic analysis is not shown in these diagrams due to how the items were costed or for simplicity. This includes items such as spare pumps or storage and surge tanks.

For all modeled processes, mixed polyester flakes are blended with the respective solvent and fed continuously into the depolymerization reactor via a slurry. While many PET depolymerization technologies use melt extrusion coupled with backflush filtration to continuously remove solid contaminants and feed the plastic into a reactor,[126] this method becomes more challenging at lower reaction temperatures and with mixed feedstocks having different melt temperatures. Instead, we adopted the slurry method for continuous feeding and placed solids removal filtration after the depolymerization reaction step in the modeled process.

n^{th}-plant assumptions

The analysis performed in this work assumes n^{th}-plant assumptions, meaning that many of the economic and technological assumptions used (e.g., depolymerization extents, on-stream time, financing amounts) represent a mature technology and not a pioneer plant. While the process models developed here are theoretical and unproven at a high technology readiness level, n^{th}-plant assumptions are employed to better understand the potential for the technologies and avoid overshadowing of performance especially when comparing to incumbent technologies. More details on these assumptions can be found in the National Renewable Energy Laboratory (NREL) design reports.[127]

Discounted cash-flow analysis and the MSP

This section summarizes the approach behind the discounted cash-flow economic analysis conducted. The description is adapted from a 2011 design report by Davis et al.[128]

After estimating the total capital investment, variable operating costs, and fixed operating costs, a discounted cash-flow analysis was used to determine the MSP per kilogram of overall polymer product produced. This is performed by iterating the selling cost of the product until the NPV of the plant is zero. This discounted cash-flow analysis requires that the discount rate, depreciation method, income tax rates, plant life, and construction start-up duration be specified. Because this plant is assumed to be equity financed, this also requires assumptions around the loan terms. See Table S4 for a list of the parameters used in the base-case scenarios for the deconstruction technologies.

Total capital investment

The capital costs for equipment were calculated using a combination of quotes from previous NREL design reports and Aspen Process Economic Analyzer V14. When necessary, these costs were scaled by a factored approach with corresponding installation factors as described in Peters and Timmerhaus.[129] Indirect costs such as piping and facilities and the assumed contributions for utility and waste integration from the OSBLs were based on the direct installed costs. The employed factors are summarized in Table S4.

Discount rate

In the base-case scenarios, the discount rate was set to 12% and the plant lifetime was set to 30 years. A discount rate of 10% was previously used in design reports and was based on the recommendation in Short et al.,[128] but we use the higher discount rate of 12% based on feedback from industry partners.

Equity financing

It was assumed that the chemical recycling plants modeled here would be 40% equity finance with 8% interest paid back across a 10-year period. The principal is taken out in stages over the 3-year construction period (see Table S4). Interest on the loan is paid during this period, but principal is not paid back in alignment with the nth-plant assumptions used in this work.

Depreciation

The Internal Revenue Service (IRS) Modified Accelerated Cost Recovery System (MACRS) was used to determine the amount of capital depreciation to calculate the amount of federal taxes to be paid. This is in alignment with

previous design reports from NREL.[130] As described in IRS publication 946,[131] a recycling plant falls under Asset Class 49.5, "Waste Reduction and Resource Recovery Plants." This class uses a 7-year recovery period.

Taxes

The federal corporate tax rate used in our analysis is 21% as stated by IRS publication 542 for corporations.[132] Income tax is averaged over the plant life and that average is calculated on a per-kilogram basis. This amount of tax to be paid varies annually due to changes in the volume of polymer product produced and plant depreciation. In some cases, no income is paid in the first few years of operation if the depreciation and loan interest deductions are greater than the net income. State taxes are not considered in this economic analysis, primarily because the location of the plant has not been determined and rates can vary from 0%–19%.

Construction time

The construction time for this analysis is assumed to occur over 2 years with an added 12 months for planning and engineering design as summarized in Table S4. This assumption is important to the cash-flow analysis because large amounts of capital are being spent but no income is generated. As noted in previous design reports from NREL,[128] this construction period falls within the ranges for smaller refineries outlined by Perry and Green[133] and those for large refineries.[134]

Start-up time

Perry and Green[133] indicate that, for a moderately complex plant, start-up should be about 25% of the construction time, or 6 months in this case. Considering that this design is for the nth operating plant, we assumed a start-up time of 3 months. The start-up period is not completely wasted, however. We assume that an average of 50% production could be achieved during that period while incurring 75% of variable expenses and 100% of fixed expenses (see Table S4).

Working capital

Peters and Timmerhaus[129] define working capital as money available to cover (1) raw materials and supplies in inventory, (2) finished product in storage, (3) accounts receivable, (4) cash on hand for monthly payments such as wages and maintenance supplies, (5) accounts payable, and (6) taxes payable. They note that working capital can fall between 10% and 20% of the fixed capital investment. This money is spent during the start-up phase and is carried through the life of the plant to purchase materials and supplies. Garrett[135] suggests that using a fraction of the yearly operating cost, typically 10%–35%, is more relevant. As noted by Seider,[136] the working capital should ultimately be recalculated based on the annual operating and installed capital costs once they are known. When performing the calculations suggested by Seider,[136] the working capital amounts to 10%–12% across the technology base cases. This percentage aligns well with the initial estimate strategies outlined above from both Peters and Timmerhaus and Garrett. As a result, we chose a working capital of 12% of the FCI across all base cases in this work. Table S4 summarizes the parameters used in the discounted cash-flow analysis.

Uncertainty analysis

Uncertainty analysis was applied for the MSP of the processes. Historical market prices within a 5-year time period (2016–2020) were used to bound the prices. Where market data were unavailable or unreliable, lower bounds and upper bounds were assumed to be 80% and 120% of the averages, respectively. Monte Carlo analysis was performed using a triangular distribution with 10,000 iterations, giving mean and σ values.

Sensitivity analysis

Sensitivity analysis was conducted in a univariate manner, meaning that only one variable was changed relative to the base case to understand its impact. Bounds for these variables were guided by similar technologies for PET or polyester deconstruction or by engineering intuition where not available. Although the sensitivities explored were univariate, each sensitivity case can likely benefit from optimization of the model under those specific conditions.

LCA

Goal and scope

The goal of this work was to compare the environmental impacts of three chemical recycling strategies for mixed polyesters relative to virgin manufacturing of those same polyesters. This LCA also aimed to identify key areas for innovation and potential challenges and opportunities that may arise with future market changes. All results reported in the main text use a cradle-to-gate system boundary and a cutoff approach in which post-consumer plastic waste is assumed to be free of environmental burdens. For the recycling strategies, cradle-to-grave includes post-consumer mixed polyester collection, sorting at an MRF with a 10% mass loss, processing into flake with a 7% mass loss (final purity = 95% target polyesters), recycling to monomers, and separation and repolymerization of the monomers into plastics. For virgin manufacturing, cradle to grave includes resource extraction, fossil-fuel refining into chemicals, and polymerization of the chemicals into plastics. Manufacturing into final products (e.g., bottles or films) and the product-use phase are not included. Results are reported per kilogram of output mixed polyester.

To consider the effect of chemically recycling polyesters multiple times through the reported strategies, normalized life-cycle impacts were also calculated and are reported in the supplemental information according to a system-expansion approach.[40] The number of product lifetimes (L) that could be obtained from recycled polyesters were calculated with Equation 1:

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

where a = mass yield of the recycling process; b = mass yield of pre-recycling steps including collection, sorting, and flaking; c = mass ratio of recycled monomers contained in 1 kg of secondary polyester; and n = number of recycling cycles. For all base cases, a = 0.65 for methanolysis, 0.65 for glycolysis, and 0.64 for hydrolysis; b = 0.84 (90% sorting yield and 93% bale-to-flake yield); and c = 0.87 for methanolysis, 0.98 for glycolysis, and 0.76 for hydrolysis. Note that b does not include losses from the collection phase; incorporating this factor would substantially change L and thus the normalized environmental impacts.

The normalized impact of the entire system ($\overline{x_i}$) for impact category i was then calculated with Equation 2:

$$\overline{x_i} = \frac{x_{v,i}+(L-1)x_{c,i}}{L} \qquad \text{(Equation 2)}$$

where $x_{v,i}$ = impacts of one unit of virgin polyester production and $x_{c,i}$ = impacts of one unit of recycled polyester from the selected chemical recycling process. The resulting value was then compared to the impact from one unit of virgin polyester (50% PET, 30% PLA, and 20% PBAT) production and disposal. Disposal was assumed to be 76% sanitary landfill, 9% incineration with energy recovery, and 15% mechanical recycling for PET, and 90% sanitary landfill and 10% incineration with energy recovery for PLA and PBAT, according to 2019 US data.[5] Both virgin and recycled polyester are manufactured into 50% bottles by stretch blow molding and 50% film by extrusion. It is assumed that the recycled polyester has the same material quality as virgin polyester and therefore can be directly substituted into the manufacturing stream.

Inventory analysis

Background data were sourced from ecoinvent version 3.3 (allocation, cutoff by classification—unit).[92] US-specific inventories were used when available; if unavailable, global average data were used instead. Additional inventories were obtained from the literature: polyester collection (based on PET collection data; Table S5), polyester sorting (based on PET sorting data; Table S6), polyester flaking (based on PET bottle flaking data; Table S7), and virgin PBAT production (Table S8). The renewable electricity inventory was prepared using the grid mix reported in the Regional Energy Deployment System (ReEDS) mid-case scenario with 95% decarbonization by 2035 (43% wind, 32% photovoltaics, 12% nuclear, 5% hydropower, 5% natural gas, 1% geothermal, and 2% other).[137] The renewable heat inventory was supplied by ecoinvent (market for heat, future[138]) and assumes biogas production and upgrading from a combination of landfill gas, sewage sludge anaerobic digestion, and grass digestion.

Impact assessment

The LCA was conducted using SimaPro software and the TRACI 2.1 US 2008[90] and AWARE[91] methods. TRACI is a US-oriented method developed by the US Environmental Protection Agency that uses a midpoint approach to quantify acidification (kg SO_2 equiv), carcinogenics (comparative toxic unit for human

[CTUh]), ecotoxicity (comparative toxic unit for aquatic ecotoxicity [CTUe]), eutrophication (kg N equiv), fossil-fuel depletion (MJ surplus energy), global warming (kg CO_2 equiv), non-carcinogenics (CTUh), ozone depletion (kg trichloro-fluoromethane equiv [kg CFC-11 equiv]), particulates exposure (kg fine particulate matter equiv [kg PM2.5 equiv]), and smog formation (kg ozone equiv [kg O_3 equiv]). AWARE is a midpoint method for determining water use (m^3) and considers the potential for water depletion averaged over 1 year.

Uncertainty analysis

The uncertainty of the methanolysis, glycolysis, and hydrolysis inventories was estimated using a semi-quantitative pedigree approach. This method enables verification of the reliability (or unreliability) of point estimates. Each item in the life-cycle inventory was given reliability, completeness, temporal correlation, geographical correlation, and further technological correlation scores (scale of 1–5) according to the rubric previously published in the electronic supplementary information (Table S8) of Uekert et al.[53] The sum of these scores were assigned a certain standard deviation (σ): scores of 5–9 were varied by ±5%, 10–14 by ±10%, 15–19 by ±15%, 20–24 by ±20%, and 25 by ±25%. Most material, energy, and emission flows in this work fell within the ±20% category. The uncertainties of background processes were provided by log-normal distributions in the ecoinvent database. Using these distributions, Monte Carlo analysis was performed with 1,000 iterations, giving mean and σ values. Error propagation was applied when needed.

MCDA

MCDA was conducted by dividing the results for a given metric (x_n) for all selected scenarios (e.g., decarbonization scenarios or PET content scenarios) by the maximum value for that metric (x_{max}) according to Equation 3.

$$\overline{x} = \frac{x_n}{x_{max}} \qquad \text{(Equation 3)}$$

The normalized values ($\overline{x}$) were then summed (no weighting applied) into a single MCDA score. Here, a lower score indicates a better outcome.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and materials should be directed to and will be fulfilled by the lead contact, Katrina M. Knauer (katrina.knauer@nrel.gov).

Material availability

This study did not generate new unique materials.

Data and code availability

The methods and resulting data used in this article are provided in full in the supplemental information and deposited via Zenodo: https://doi.org/10.5281/zenodo.14193593. Processes were modeled in Aspen Plus V14, economic calculations were performed in Microsoft Excel, and LCA was conducted in SimaPro. Please contact authors for questions or requests related to the models used for this analysis.

AUTHOR CONTRIBUTIONS

G.T.B., A.J.J., and K.M.K. contributed to the initial conceptualization. J.S.D. developed the process and economic models. J.S.D., J.B.C., H.C., Y.L., A.S., A.J.J., O.D.M., and K.M.K. contributed to the process design and analysis. J.B.C., H.C., and Y.L. conducted experiments to validate certain assumptions. T.U. conducted the environmental analysis. J.S.D., T.U., and K.M.K. wrote the manuscript with contributions from all authors.

DECLARATION OF INTERESTS

J.S.D., J.B.C., H.C., Y.L., O.D.M., G.T.B., A.J.J., and K.M.K. have submitted patent applications on the amine-catalyzed methanolysis of mixed polyesters and the downstream recovery of monomers.

REFERENCES

1. Zheng, J., and Suh, S. (2019). Strategies to reduce the global carbon footprint of plastics. Nat. Clim. Change 9, 374–378. https://doi.org/10.1038/s41558-019-0459-z.

2. Meys, R., Kätelhön, A., Bachmann, M., Winter, B., Zibunas, C., Suh, S., and Bardow, A. (2021). Achieving net-zero greenhouse gas emission plastics by a circular carbon economy. Science 374, 71–76. https://doi.org/10.1126/science.abg9853.

3. Nicholson, S.R., Rorrer, N.A., Carpenter, A.C., and Beckham, G.T. (2021). Manufacturing energy and greenhouse gas emissions associated with plastics consumption. Joule 5, 673–686.

4. Bachmann, M., Zibunas, C., Hartmann, J., Tulus, V., Suh, S., Guillén-Gosálbez, G., and Bardow, A. (2023). Towards circular plastics within planetary boundaries. Nat. Sustain. 6, 599–610. https://doi.org/10.1038/s41893-022-01054-9.

5. Milbrandt, A., Coney, K., Badgett, A., and Beckham, G.T. (2022). Quantification and evaluation of plastic waste in the United States. Resour. Conserv. Recycl. 183, 106363. https://doi.org/10.1016/j.resconrec.2022.106363.

6. Rahimi, A., and García, J.M. (2017). Chemical recycling of waste plastics for new materials production. Nat. Rev. Chem 1, 1–11.

7. Ellis, L.D., Rorrer, N.A., Sullivan, K.P., Otto, M., McGeehan, J.E., Román-Leshkov, Y., Wierckx, N., and Beckham, G.T. (2021). Chemical and biological catalysis for plastics recycling and upcycling. Nat. Catal. 4, 539–556. https://doi.org/10.1038/s41929-021-00648-4.

8. Martín, A.J., Mondelli, C., Jaydev, S.D., and Pérez-Ramírez, J. (2021). Catalytic processing of plastic waste on the rise. Chem 7, 1487–1533. https://doi.org/10.1016/j.chempr.2020.12.006.

9. Coates, G.W., and Getzler, Y.D.Y.L. (2020). Chemical recycling to monomer for an ideal, circular polymer economy. Nat. Rev. Mater. 5, 501–516. https://doi.org/10.1038/s41578-020-0190-4.

10. Tournier, V., Duquesne, S., Guillamot, F., Cramail, H., Taton, D., Marty, A., and André, I. (2023). Enzymes' Power for Plastics Degradation. Chem. Rev. 123, 5612–5701. https://doi.org/10.1021/acs.chemrev.2c00644.

11. Uekert, T., Singh, A., DesVeaux, J.S., Ghosh, T., Bhatt, A., Yadav, G., Afzal, S., Walzberg, J., Knauer, K.M., Nicholson, S.R., et al. (2023). Technical, Economic, and Environmental Comparison of Closed-Loop Recycling Technologies for Common Plastics. ACS Sustainable Chem. Eng. 11, 965–978. https://doi.org/10.1021/acssuschemeng.2c05497.

12. Volk, R., Stallkamp, C., Steins, J.J., Yogish, S.P., Müller, R.C., Stapf, D., and Schultmann, F. (2021). Techno-economic assessment and comparison of different plastic recycling pathways: A German case study. J. Ind. Ecol. 25, 1318–1337. https://doi.org/10.1111/jiec.13145.

13. Afzal, S., Singh, A., Nicholson, S.R., Uekert, T., DesVeaux, J.S., Tan, E.C.D., Dutta, A., Carpenter, A.C., Baldwin, R.M., and Beckham, G.T. (2023). Techno-economic analysis and life cycle assessment of mixed plastic waste gasification for production of methanol and hydrogen. Green Chem. 25, 5068–5085. https://doi.org/10.1039/d3gc00679d.

14. Yadav, G., Singh, A., Dutta, A., Uekert, T., DesVeaux, J.S., Nicholson, S.R., Tan, E.C., Mukarakate, C., Schaidle, J.A., Wrasman, C.J., et al. (2023). Techno-economic analysis and life cycle assessment for catalytic fast pyrolysis of mixed plastic waste. Energy Environ. Sci. 16, 3638–3653. https://doi.org/10.1039/d3ee00749a.

15. Stempfle, F., Ortmann, P., and Mecking, S. (2016). Long-Chain Aliphatic Polymers To Bridge the Gap between Semicrystalline Polyolefins and Traditional Polycondensates. Chem. Rev. 116, 4597–4641. https://doi.org/10.1021/acs.chemrev.5b00705.

16. Schneiderman, D.K., and Hillmyer, M.A. (2017). 50th Anniversary Perspective: There Is a Great Future in Sustainable Polymers. Macromolecules 50, 3733–3749. https://doi.org/10.1021/acs.macromol.7b00293.

17. Jehanno, C., Pérez-Madrigal, M.M., Demarteau, J., Sardon, H., and Dove, A.P. (2019). Organocatalysis for depolymerisation. Polym. Chem. 10, 172–186. https://doi.org/10.1039/C8PY01284A.

18. Hatti-Kaul, R., Nilsson, L.J., Zhang, B., Rehnberg, N., and Lundmark, S. (2020). Designing Biobased Recyclable Polymers for Plastics. Trends Biotechnol. 38, 50–67. https://doi.org/10.1016/j.tibtech.2019.04.011.

19. Häußler, M., Eck, M., Rothauer, D., and Mecking, S. (2021). Closed-loop recycling of polyethylene-like materials. Nature 590, 423–427. https://doi.org/10.1038/s41586-020-03149-9.

20. Cywar, R.M., Rorrer, N.A., Hoyt, C.B., Beckham, G.T., and Chen, E.Y.X. (2021). Bio-based polymers with performance-advantaged properties. Nat. Rev. Mater. 7, 83–103. https://doi.org/10.1038/s41578-021-00363-3.

21. Cederholm, L., Olsén, P., Hakkarainen, M., and Odelius, K. (2023). Design for Recycling: Polyester- and Polycarbonate-Based A–B–A Block Copolymers and Their Recyclability Back to Monomers. Macromolecules 56, 3641–3649. https://doi.org/10.1021/acs.macromol.3c00274.

22. Quinn, E.C., Knauer, K.M., Beckham, G.T., and Chen, E.Y.X. (2023). Mono-material product design with bio-based, circular, and biodegradable polymers. One Earth 6, 582–586. https://doi.org/10.1016/j.oneear.2023.05.019.

23. Zhou, L., Zhang, Z., Shi, C., Scoti, M., Barange, D.K., Gowda, R.R., and Chen, E.Y.-X. (2023). Chemically circular, mechanically tough, and melt-processable polyhydroxyalkanoates. Science 380, 64–69. https://doi.org/10.1126/science.adg4520.

24. Manker, L.P., Dick, G.R., Demongeot, A., Hedou, M.A., Rayroud, C., Rambert, T., Jones, M.J., Sulaeva, I., Vieli, M., Leterrier, Y., et al. (2022). Sustainable polyesters via direct functionalization of lignocellulosic sugars. Nat. Chem. 14, 976–984. https://doi.org/10.1038/s41557-022-00974-5.

25. European Bioplastics (2020). Bioplastics market update 2020. https://www.european-bioplastics.org/market-update-2020-bioplastics-continue-to-become-mainstream-as-the-global-bioplastics-market-is-set-to-grow-by-36-percent-over-the-next-5-years/.

26. Hackett, M., Zeng, L., and Masuda, T. (2021). Biodegradable Polymers (IHS Markit).

27. Rosenboom, J.-G., Langer, R., and Traverso, G. (2022). Bioplastics for a circular economy. Nat. Rev. Mater. 7, 117–137. https://doi.org/10.1038/s41578-021-00407-8.

28. Aldas, M., Pavon, C., De La Rosa-Ramírez, H., Ferri, J.M., Bertomeu, D., Samper, M.D., and López-Martínez, J. (2021). The Impact of Biodegradable Plastics in the Properties of Recycled Polyethylene Terephthalate. J. Polym. Environ. 29, 2686–2700. https://doi.org/10.1007/s10924-021-02073-x.

29. Chen, G.-Q., and Patel, M.K. (2012). Plastics Derived from Biological Sources: Present and Future: A Technical and Environmental Review. Chem. Rev. 112, 2082–2099. https://doi.org/10.1021/cr200162d.

30. European Commission; Directorate-General for Environment (2022). Biobased Plastic – Sustainable Sourcing and Content – Final Report (Publications Office of the European Union)). https://doi.org/10.2779/668096.

31. European Parliament and the Council of the European Union (2019). Directive (EU) 2019/904 of the European Parliament and of the Council of 5 June 2019 on the reduction of the impact of certain plastic products on the environment. http://data.europa.eu/eli/dir/2019/904/oj.

32. Sinha, V., Patel, M.R., and Patel, J.V. (2010). PET waste management by chemical recycling: a review. J. Polym. Environ. 18, 8–25.

33. Bartolome, L., Imran, M., Cho, B.G., Al-Masry, W.A., and Kim, D.H. (2012). Recent Developments in the Chemical Recycling of PET. In Material Recycling: Trends and Perspectives, D. Achilllas, ed. (IntechOpen).

34. Brake, L.D. (1993). Preparation of alkyl esters by depolymerization. US patent 5264617A.

35. Carné Sánchez, A., and Collinson, S.R. (2011). The selective recycling of mixed plastic waste of polylactic acid and polyethylene terephthalate by control of process conditions. Eur. Polym. J. 47, 1970–1976. https://doi.org/10.1016/j.eurpolymj.2011.07.013.

36. Yang, R., Xu, G., Dong, B., Guo, X., and Wang, Q. (2022). Selective, Sequential, and "One-Pot" Depolymerization Strategies for Chemical Recycling of Commercial Plastics and Mixed Plastics. ACS Sustainable Chem. Eng. 10, 9860–9871. https://doi.org/10.1021/acssuschemeng.2c01708.

37. Grause, G. (2022). Depolymerisation of Fossil Fuel and Biomass-derived Polyesters. In Production of Biofuels and Chemicals from Sustainable Recycling of Organic Solid Waste, Z. Fang, R.L. Smith, Jr, and L. Xu, eds. (Springer Nature Singapore), pp. 283–316. https://doi.org/10.1007/978-981-16-6162-4_9.

38. Spicer, A.J., Brandolese, A., and Dove, A.P. (2024). Selective and Sequential Catalytic Chemical Depolymerization and Upcycling of Mixed Plastics. ACS Macro Lett. 13, 189–194. https://doi.org/10.1021/acsmacrolett.3c00751.

39. Clark, R.A., and Shaver, M.P. (2024). Depolymerization within a Circular Plastics System. Chem. Rev. 124, 2617–2650. https://doi.org/10.1021/acs.chemrev.3c00739.

40. Nicholson, S.R., Rorrer, J.E., Singh, A., Konev, M.O., Rorrer, N.A., Carpenter, A.C., Jacobsen, A.J., Román-Leshkov, Y., and Beckham, G.T. (2022). The Critical Role of Process Analysis in Chemical Recycling and Upcycling of Waste Plastics. Annu. Rev. Chem. Biomol. Eng. 13, 301–324. https://doi.org/10.1146/annurev-chem-bioeng-100521-085846.

41. Recycling Markets - Secondary Materials Pricing. https://www.recyclingmarkets.net/secondarymaterials/index.html.

42. Association of. Plastic Recyclers (APR). PET Resin Specifications. https://plasticsrecycling.org/tools-and-resources/recycler-resources/model-bale-specifications/.

43. Li, H., Aguirre-Villegas, H.A., Allen, R.D., Bai, X., Benson, C.H., Beckham, G.T., Bradshaw, S.L., Brown, J.L., Brown, R.C., Cecon, V.S., et al. (2022). Expanding plastics recycling technologies: chemical aspects, technology status and challenges. Green Chem. 24, 8899–9002. https://doi.org/10.1039/D2GC02588D.

44. Tustin, G.C., Thomas M. Pell, J., Jenkins, D.A., and Jernigan, M.T. Process for the Recovery of Terephthalic Acid and Ethylene Glycol from Poly(ethylene Terephthalate). US patent 5,413,681.

45. Yoshioka, T., Motoki, T., and Okuwaki, A. (2001). Kinetics of Hydrolysis of Poly(ethylene terephthalate) Powder in Sulfuric Acid by a Modified

Shrinking-Core Model. Ind. Eng. Chem. Res. 40, 75–79. https://doi.org/10.1021/ie000592u.

46. Khoonkari, M., Haghighi, A.H., Sefidbakht, Y., Shekoohi, K., and Ghaderian, A. (2015). Chemical Recycling of PET Wastes with Different Catalysts. International Journal of Polymer Science. https://doi.org/10.1155/2015/124524.

47. Allen, R.D., Bajjuri, K.M., Hedrick, J.L., Breyta, G., and Larson, C.E. (2016). Methods and materials for depolymerizing polyesters. US patent 9255194B2.

48. Essaddam, H. (2017). Polyethylene terephthalate depolymerization. US patent US9550713B1.

49. Yang, W., Wang, J., Jiao, L., Song, Y., Li, C., and Hu, C. (2022). Easily recoverable and reusable p-toluenesulfonic acid for faster hydrolysis of waste polyethylene terephthalate. Green Chem. 24, 1362–1372. https://doi.org/10.1039/D1GC04567A.

50. Inada, S., and Sato, K. (2000). Bis-β-hydroxyethyl terephthalate. US patent 7030264B1.

51. Essaddam, A., and Essaddam, F. (2019). Terephthalic acid esters formation. US patent 10252976B1.

52. Zhang, Q., Huang, R., Yao, H., Lu, X., Yan, D., and Xin, J. (2021). Removal of Zn2+ from polyethylene terephthalate (PET) glycolytic monomers by sulfonic acid cation exchange resin. J. Environ. Chem. Eng. 9, 105326. https://doi.org/10.1016/j.jece.2021.105326.

53. Uekert, T., DesVeaux, J.S., Singh, A., Nicholson, S.R., Lamers, P., Ghosh, T., McGeehan, J.E., Carpenter, A.C., and Beckham, G.T. (2022). Life cycle assessment of enzymatic poly(ethylene terephthalate) recycling. Green Chem. 24, 6531–6543. https://doi.org/10.1039/d2gc02162e.

54. Zhao, X., Cornish, K., and Vodovotz, Y. (2020). Narrowing the Gap for Bioplastic Use in Food Packaging: An Update. Environ. Sci. Technol. 54, 4712–4732. https://doi.org/10.1021/acs.est.9b03755.

55. Cywar, R.M., Ling, C., Clarke, R.W., Kim, D.H., Kneucker, C.M., Salvachúa, D., Addison, B., Hesse, S.A., Takacs, C.J., Xu, S., et al. (2023). Elastomeric vitrimers from designer polyhydroxyalkanoates with recyclability and biodegradability. Sci. Adv. 9, eadi1735. https://doi.org/10.1126/sciadv.adi1735.

56. Li, X.-L., Clarke, R.W., An, H.-Y., Gowda, R.R., Jiang, J.-Y., Xu, T.-Q., and Chen, E.Y.-X. (2023). Dual Recycling of Depolymerization Catalyst and Biodegradable Polyester that Markedly Outperforms Polyolefins. Angew. Chem., Int. Ed. Engl. 62, e202303791. https://doi.org/10.1002/anie.202303791.

57. National Association for PET Container Resources (NAPCOR) (2021). 2020 PET Thermoform Recycling: A Progress Report. https://napcor.com/wp-content/uploads/2020/10/2020-09_NAPCOR-thermoform-progress-report-Update_FINAL.pdf.

58. Grousset, R., Cordle, M., Carhart, J., Harrington-Smith, C., and Edwards, S. (2024). How to Scale the Recycling of Flexible Film Packaging: Modeling Pyrolysis' Role in Collection. Quantity and Costs of a Comprehensive Solution (Eunomia Research & Consulting, APR). https://eunomia.eco/reports/how-to-scale-the-recycling-of-flexible-film-packaging-modeling-pyrolysis-role-in-collection-quantity-and-costs-of-a-comprehensive-solution/.

59. Tustin, G.C., Jr, T.M.P., Jenkins, D.A., and Jernigan, M.T. (1995). Process for the recovery of terephthalic acid and ethylene glycol from poly(ethylene terephthalate). US patent 5413681A.

60. Jr, G.E.B., and O'Brien, R.C. (1976). Method for recovering terephthalic acid and ethylene glycol from polyester materials. US patent 3952053A.

61. Li, M., Lu, J., Li, X., Ge, M., and Li, Y. (2020). Removal of disperse dye from alcoholysis products of waste PET fabrics by nitric acid-modified activated carbon as an adsorbent: Kinetic and thermodynamic studies. Textil. Res. J. 90, 2058–2069. https://doi.org/10.1177/0040517520909510.

62. Gruber, P.R., Hall, E.S., Kolstad, J.J., Iwen, M.L., Benson, R.D., and Borchardt, R.L. (1993). Continuous process for the manufacture of a purified lactide from esters of lactic acid. US patent 5247059A.

63. Environmental Protection Agency (EPA) (1991). Poly(ethylene terephthalate). https://www3.epa.gov/ttnchie1/ap42/ch06/index.html.

64. Seavey, K.C., and Liu, Y.A. (2008). Poly(Ethylene Terephthalate) Melt Process Simulation in Polymers Plus. In Step-Growth Polymerization Process Modeling and Product Design (John Wiley & Sons, Inc.), pp. 507–539. https://doi.org/10.1002/9780470292488.

65. Bell, S. (2017). Polyethylene Terephthalate - PEP Report 18D (IHS Markit).

66. Endert, E.S.V., Hagen, R., Hille, T., Atlas, C., and Thiele, U. (2006). Method for the continuous production of high-molecular polyester and device for carrying out the method. US patent 7115701B2.

67. Buchanan C.M., Gardner R.M., Wood M.D., White A.W., Gedon S.C., Barlow Jr F.D. Aliphatic aromatic copolyesters. US patent US6342304B1 2002.

68. Yang, X., Auffermann, J., Sinkel, C., Lohmann, J., Loos, R., Skupin, G., Künkel, A., and Börger, L. (2013). Biodegradable polyester mixture. US patent 10526461B2.

69. Kang, G.D., Yun, K.C., Kim, S.Y., Ryum, J., Kim, B.S., Byun, K.S., Kim, S.H., and Park, S.B. (2016). Method for continuously preparing biodegradable aliphatic/aromatic polyester copolymer. US patent 9334359B2.

70. Nakamoto, H., Harada, S., Oda, C., Sase, Y., and Suzuki, M. (2008). Process and apparatus for continuous polycondensation. US patent 7431893B1.

71. Cudmore, W.J. (1986). Polyethylene terephthalate saponification process. US patent 4578502A.

72. Berrod, G., Grillon, E., and Klinger, F. (1994). Hydrolysis of Alkyl Dicarboxylates. US patent 5312981.

73. Pusztaszeri, S.F. (1982). Method for recovery of terephthalic acid from polyester scrap. US patent 4355175A.

74. Karim, S.S., Farrukh, S., Matsuura, T., Ahsan, M., Hussain, A., Shakir, S., Chuah, L.F., Hasan, M., and Bokhari, A. (2022). Model analysis on effect of temperature on the solubility of recycling of Polyethylene Terephthalate (PET) plastic. Chemosphere 307, 136050. https://doi.org/10.1016/j.chemosphere.2022.136050.

75. Lesage, G., Peñate, I.Q., Franceschi, S., Perez, E., Garrigues, J.-C., Poux, M., and Cognet, P. (2020). Sustainable process for adipic acid production from cyclohexene in microemulsion. Catal. Today 346, 40–45. https://doi.org/10.1016/j.cattod.2019.02.065.

76. Shen, C., Zhao, X., Long, Y., An, W., Zhou, X., Liu, X., Xu, S., and Wang, Y.-Z. (2023). Approach for the Low Carbon Footprint of Biodegradable Plastic PBAT: Complete Recovery of Its Every Monomer via High-Efficiency Hydrolysis and Separation. ACS Sustainable Chem. Eng. 11, 2005–2013. https://doi.org/10.1021/acssuschemeng.2c07413.

77. Tournier, V., Texier, H., Desrousseaux, M.-L., Topham, C., Andre, I., Barbe, S., Duquesne, S., and Marty, A. (2018). Novel Esterases and Uses Thereof. International patent WO2018011281.

78. Meyer, D.H. Process for purifying terephthalic acid. US patent 3288849A.

79. Sheehan, R.J. (2011). Terephthalic Acid, Dimethyl Terephthalate, and Isophthalic Acid. Ullmann's Encyclopedia of Industrial Chemistry. https://doi.org/10.1002/14356007.a26_193.pub2.

80. Cesar, M.A. Terephthalic acid - PEP Report 9F. SRI Consulting. https://www.spglobal.com/pdf/RP009F_toc_174145110917062932.pdf .

81. Komesu, A., Wolf Maciel, M.R., Rocha de Oliveira, J.A., da Silva Martins, L.H., and Maciel Filho, R. (2016). Purification of Lactic Acid Produced by Fermentation: Focus on Non-traditional Distillation Processes. Separ. Purif. Rev. 46, 241–254. https://doi.org/10.1080/15422119.2016.1260034.

82. Komesu, A., Wolf Maciel, M.R., and Maciel Filho, R. (2017). Separation and Purification Technologies for Lactic Acid – A Brief Review. Bioresources 12, 6885–6901. https://doi.org/10.15376/biores.12.3.6885-6901.

83. Bayazit, Ş.S., İnci, I., and Uslu, H. (2011). Adsorption of Lactic Acid from Model Fermentation Broth onto Activated Carbon and Amberlite IRA-67. J. Chem. Eng. Data 56, 1751–1754. https://doi.org/10.1021/je1006345.

84. Din, N.A.S., Lim, S.J., Maskat, M.Y., Mutalib, S.A., and Zaini, N.A.M. (2021). Lactic acid separation and recovery from fermentation broth by ion-exchange resin: A review. Bioresour. Bioprocess. 8, 31. https://doi.org/10.1186/s40643-021-00384-4.

85. Delgado, J.A., Águeda, V.I., Uguina, M.Á., García, Á., Matarredona, J., and Moral, R. (2018). Modeling of the separation of lactic acid from an aqueous mixture by adsorption on polyvinylpyridine resin and desorption with methanol. Separation and Purification Technology 200, 307–317. https://doi.org/10.1016/j.seppur.2018.02.047.

86. Jehle, W., Staneff, T., Wagner, B., and Steinwandel, J. (1995). Separation of glycol and water from coolant liquids by evaporation, reverse osmosis and pervaporation. J. Membr. Sci. 102, 9–19. https://doi.org/10.1016/0376-7388(94)00202-a.

87. Biancari, A., Palma, L.D., Ferrantelli, P., and Merli, C. (2003). Ethylene Glycol Recovery from Dilute Aqueous Solution. Environ. Eng. Sci. 20, 103–110. https://doi.org/10.1089/109287503763336539.

88. Davis, R.E., Grundl, N.J., Tao, L., Biddy, M.J., Tan, E.C., Beckham, G.T., Humbird, D., Thompson, D.N., and Roni, M.S. (2018). Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels and Coproducts: 2018 Biochemical Design Case Update. In Biochemical Deconstruction and Conversion of Biomass to Fuels and Products via Integrated Biorefinery Pathways (National Renewable Energy Lab. (NREL)). 2018/11/19/, NREL/TP-5100-71949.

89. Bell, S. Bio-Based Polymers, PEP Report 265B. IHS Markit. https://www.spglobal.com/commodityinsights/en/ci/products/chemical-technology-pep-265b-bio-based-polymers.html.

90. Bare, J. (2011). TRACI 2.0: the tool for the reduction and assessment of chemical and other environmental impacts 2.0. Clean Technol. Environ. Policy 13, 687–696. https://doi.org/10.1007/s10098-010-0338-9.

91. Boulay, A.-M., Bare, J., Benini, L., Berger, M., Lathuillière, M.J., Manzardo, A., Margni, M., Motoshita, M., Núñez, M., Pastor, A.V., et al. (2017). The WULCA consensus characterization model for water scarcity footprints: assessing impacts of water consumption based on available water remaining (AWARE). Int. J. Life Cycle Assess. 23, 368–378. https://doi.org/10.1007/s11367-017-1333-8.

92. Wernet, G., Bauer, C., Steubing, B., Reinhard, J., Moreno-Ruiz, E., and Weidema, B. (2016). The ecoinvent database version 3 (part I): overview and methodology. Int. J. Life Cycle Assess. 21, 1218–1230. https://doi.org/10.1007/s11367-016-1087-8.

93. Bolinger, M., Wiser, R., and O'Shaughnessy, E. (2022). Levelized cost-based learning analysis of utility-scale wind and solar in the United States. iScience 25, 104378. https://doi.org/10.1016/j.isci.2022.104378.

94. U.S. Energy Information Administration (EIA) (2022). Cost and Performance Characteristics of New Generating Technologies. In Annual Energy Outlook 2022 https://www.eia.gov/outlooks/aeo/assumptions/pdf/elec_cost_perf.pdf.

95. Lawrence Berkeley National Laboratory (2023). Utility-Scale Solar, 2023 Edition. https://emp.lbl.gov/utility-scale-solar.

96. Lawrence Berkeley National Laboratory (2024). Land-Based Wind Market Report, 2024 Edition. https://emp.lbl.gov/sites/default/files/2024-08/Land-Based%20Wind%20Market%20Report_2024%20Edition.pdf.

97. Milbrandt, A., Bush, B., and Melaina, M. (2016). Biogas and Hydrogen Systems Market Assessment (National Renewable Energy Laboratory (NREL)). https://www.nrel.gov/docs/fy16osti/63596.pdf.

98. ICF Resources (2020). Study on the Use of Biofuels (Renewable Natural Gas) in the Greater Washington, D.C. Metropolitan Area. https://www.worldbiogasassociation.org/wpcontent/uploads/2020/03/200316-WGL-RNG-Report-FINAL-1.pdf.

99. Ishizaka, A., and Nemery, P. (2013). Multi-Criteria Decision Analysis. https://doi.org/10.1002/9781118644898.

100. Tachibana, Y., Kimura, S., and Kasuya, K.-i. (2015). Synthesis and Verification of Biobased Terephthalic Acid from Furfural. Sci. Rep. 5, 8249. https://doi.org/10.1038/srep08249.

101. Larrain, M., Van Passel, S., Thomassen, G., Van Gorp, B., Nhu, T.T., Huysveld, S., Van Geem, K.M., De Meester, S., and Billen, P. (2021). Techno-economic assessment of mechanical recycling of challenging post-consumer plastic packaging waste. Resour. Conserv. Recycl. 170, 105607. https://doi.org/10.1016/j.resconrec.2021.105607.

102. Singh, A., Rorrer, N.A., Nicholson, S.R., Erickson, E., DesVeaux, J.S., Avelino, A.F., Lamers, P., Bhatt, A., Zhang, Y., Avery, G., et al. (2021). Techno-economic, life-cycle, and socioeconomic impact analysis of enzymatic recycling of poly(ethylene terephthalate). Joule 5, 2479–2503. https://doi.org/10.1016/j.joule.2021.06.015.

103. Lin, R., and Sharpe, R.J. (2020). Method for producing dimethyl terephthalate from polyester methanolysis depolymerization systems. Patent. WO2021126939A1.

104. Ghosh, T., Avery, G., Bhatt, A., Uekert, T., Walzberg, J., and Carpenter, A. (2023). Towards a circular economy for PET bottle resin using a system dynamics inspired material flow model. J. Clean. Prod. 383, 135208. https://doi.org/10.1016/j.jclepro.2022.135208.

105. Timothy, J.S., Cooney, G., Jamieson, M., Littlefield, J., and Marriott, J. (2014). Life Cycle Greenhouse Gas Perspective on Exporting Liquefied Natural Gas from the United States. https://www.energy.gov/fecm/articles/life-cycle-greenhouse-gas-perspective-exporting-liquefied-natural-gas-united-states.

106. Burchart-Korol, D., Fugiel, A., Czaplicka-Kolarz, K., and Turek, M. (2016). Model of environmental life cycle assessment for coal mining operations. Sci. Total Environ. 562, 61–72. https://doi.org/10.1016/j.scitotenv.2016.03.202.

107. U.S. Energy Information Administration (EIA) (2023). Annual Energy Outlook. https://www.eia.gov/outlooks/aeo/.

108. Essien, J.P., Ikpe, D.I., Inam, E.D., Okon, A.O., Ebong, G.A., and Benson, N.U. (2022). Occurrence and spatial distribution of heavy metals in landfill leachates and impacted freshwater ecosystem: An environmental and human health threat. PLoS One 17, e0263279. https://doi.org/10.1371/journal.pone.0263279.

109. Nicholson, S.R., Rorrer, N.A., Uekert, T., Avery, G., Carpenter, A.C., and Beckham, G.T. (2023). Manufacturing Energy and Greenhouse Gas Emissions Associated with United States Consumption of Organic Petrochemicals. ACS Sustainable Chem. Eng. 11, 2198–2208. https://doi.org/10.1021/acssuschemeng.2c05417.

110. Bie, f.d., Sart, G.G.d., Ravard, M., Scola, P.L., and Veras, R. (2022). Stay in the cycle, rethinking recycling with PLA bioplastics. TotalEnergies Corbion. https://www.totalenergies-corbion.com/media/xy4a3pcj/stay-in-the-cycle-whitepaper-about-pla-recycling-totalenergies-corbion.pdf.

111. Berg, L. (1990). Recovery of ethylene glycol from butanediol isomers by azeotropic distillation. US patent 4966658.

112. Wang, J., Shen, R., Cao, Y., Li, W., and Zhou, J. (2023). Separation of ethylene glycol, 1,2-butanediol and 1,2-propanediol with azeotropic distillation. Can. J. Chem. Eng. 101, 4217–4229. https://doi.org/10.1002/cjce.24771.

113. Kubic, W.L., Jr., and Tan, E.C.D. (2023). Reactive Extraction Process for Separating 2,3-Butanediol from Fermentation Broth. Ind. Eng. Chem. Res. 62, 5241–5251. https://doi.org/10.1021/acs.iecr.2c04307.

114. Copelin, H.B. (1981). Preparation of High Purity 1, 4-butanediol. US patent 4294998.

115. Wang, T., Li, X., and Dong, J. (2020). Ethylene Glycol Purification by Melt Crystallization: Removal of Short-Chain Glycol Impurities. Ind. Eng. Chem. Res. 59, 8805–8812. https://doi.org/10.1021/acs.iecr.0c00347.

116. Misra, A., and Garg, S.N. (1986). Block copolymers of poly(ethylene terephthalate–polybutylene terephthalate). I. Preparation and crystallization behavior. J. Polym. Sci. B Polym. Phys. 24, 983–997. https://doi.org/10.1002/polb.1986.090240504.

117. Olewnik, E., Czerwiński, W., Nowaczyk, J., Sepulchre, M.-O., Tessier, M., Salhi, S., and Fradet, A. (2007). Synthesis and structural study of copolymers of l-lactic acid and bis(2-hydroxyethyl terephthalate). Eur. Polym. J. 43, 1009–1019. https://doi.org/10.1016/j.eurpolymj.2006.11.025.

118. Sohrabi, A., and Rafizadeh, M. (2021). Effects of introducing Bis(2-hydroxyethyl) terephthalate (BHET) units on crystalline structure, polymorphism and hydrolysis degradation of poly(butylene adipate-ethylene terephthalate) random copolyesters. J. Polym. Res. 28, 339. https://doi.org/10.1007/s10965-021-02679-8.

119. Paciorek-Sadowska, J., Borowicz, M., and Isbrandt, M. (2019). New Poly(lactide-urethane-isocyanurate) Foams Based on Bio-Polylactide Waste. Polymers 11, 481.

120. Nim, B., Opaprakasit, M., Petchsuk, A., and Opaprakasit, P. (2020). Microwave-assisted chemical recycling of polylactide (PLA) by alcoholysis with various diols. Polym. Degrad. Stabil. 181, 109363. https://doi.org/10.1016/j.polymdegradstab.2020.109363.

121. Pereira, P., Savage, P.E., and Pester, C.W. (2024). Acid catalyst screening for hydrolysis of post-consumer PET waste and exploration of acidolysis. Green Chem. 26, 1964–1974. https://doi.org/10.1039/D3GC03906D.

122. Walzberg, J., Sethuraman, S., Ghosh, T., Uekert, T., and Carpenter, A. (2023). Think before you throw! An analysis of behavioral interventions targeting PET bottle recycling in the United States. Energy Res. Social Sci. 100, 103116. https://doi.org/10.1016/j.erss.2023.103116.

123. Bergsma, G., Vendrik, J., and Veen, R.v.d. (2021). PLA sorting for recycling. In Experiments performed at the National Test Centre Circular Plastics (NTCP) (CE Delft) https://cedelft.eu/publications/pla-sorting-for-recycling-experiments-performed-at-the-national-test-centre-circular-plastics-ntcp/.

124. Ahamed, A., Huang, P., Young, J., Gallego-Schmid, A., Price, R., and Shaver, M.P. (2024). Technical and environmental assessment of end-of-life scenarios for plastic packaging with electronic tags. Resour. Conserv. Recycl. 201, 107341. https://doi.org/10.1016/j.resconrec.2023.107341.

125. Huang, P., Ahamed, A., Sun, R., De Hoe, G.X., Pitcher, J., Mushing, A., Lourenço, F., and Shaver, M.P. (2023). Circularizing PET-G Multimaterials: Life Cycle Assessment and Techno-Economic Analysis. ACS Sustain. Chem. Eng. 11, 15328–15337. https://doi.org/10.1021/acssuschemeng.3c04047.

126. Nordahl, S.L., Baral, N.R., Helms, B.A., and Scown, C.D. (2023). Complementary roles for mechanical and solvent-based recycling in low-carbon, circular polypropylene. Proc. Natl. Acad. Sci. USA 120, e2306902120. https://doi.org/10.1073/pnas.2306902120.

127. Davis, R., Aden, A., and Pienkos, P.T. (2011). Techno-economic analysis of autotrophic microalgae for fuel production. Appl. Energy 88, 3524–3531. https://doi.org/10.1016/j.apenergy.2011.04.018.

128. Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., Schoen, P., Lukas, J., Olthof, B., Worley, M., et al. (2011). Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol: Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover (National Renewable Energy Lab. (NREL)). NREL/TP-5100-47764.

129. Peters, M.S., and Timmerhaus, K.D. (2003). Plant Design and Economics for Chemical Engineers, 5th Edition (McGraw-Hill).

130. National Renewable Energy Laboratory Biorefinery Analysis Process Models. https://www.nrel.gov/extranet/biorefinery/aspen-models/ .

131. Service, I.R. (2009). How to Depreciate Property (Washington, DC: Department of the Treasury Internal Revenue Service). http://www.irs.gov/pub/irs-pdf/p946.pdf.

132. Internal Revenue Service (2022). Publication 542 (01/2022), Corporations. https://www.irs.gov/publications/p542#en_US_202201_publink1000257885.

133. Green, D.W., and Maloney, J.O. (1997). Perry's Chemical Engineers' Handbook, 7th Edition (McGraw-Hill).

134. Gary J.H., Handwerk G.E. Petroleum Refining: Technology and Economics. 3rd Edition Marcel Dekker, Inc.

135. Garrett, D.E. (1989). Chemical Engineering Economics (Springer Dordrecht).

136. Gani, R., Widagdo, S., Ng, K.M., Seider, W.D., Seader, J.D., and Lewin, D.R. (2016). Product and Process Design Principles: Synthesis, Analysis and Evaluation, 4th Edition (John Wiley & Sons).

137. Ho, J., Becker, J., Brown, M., Brown, P., Chernyakhovskiy, I., Cohen, S., Cole, W., Corcoran, S., Eurek, K., Frazier, W., et al. (2021). Regional Energy Deployment System (ReEDS) Model Documentation (Version 2020). 2021-06-01. https://www.osti.gov/servlets/purl/1788425.

138. Yarkova, A.V., Novikov, V.T., Glotova, V.N., Shkarin, A.A., and Borovikova, Y.S. (2015). Vacuum Effect on the Lactide Yield. Procedia Chem. 15, 301–307. https://doi.org/10.1016/j.proche.2015.10.048.