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Research Article

Economic and Environmental Benefits of Modular Microwave-Assisted Polyethylene Terephthalate Depolymerization

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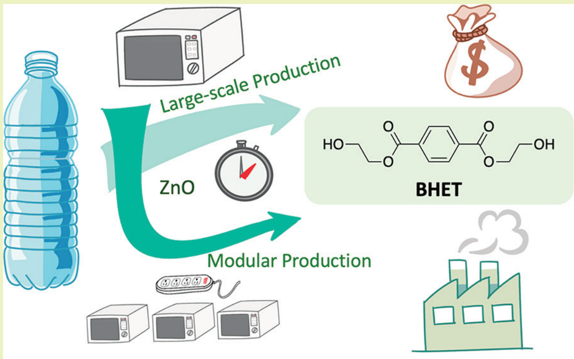

ABSTRACT: The growing amount of plastic waste endangers the environment. Polyethylene terephthalate (PET) is among the most widespread plastics due to its extensive use in fibers and packaging. Recently, chemical recycling and upcycling approaches have been proposed to produce valuable products from bale PET feedstocks. This work performs techno-economic analysis and life cycle assessment to evaluate the environmental and economic performances of various technologies, including electrification via microwaves over a heterogeneous catalyst. We demonstrate that using a microwave-assisted heterogeneous glycolysis process to produce bis(2-hydroxyethyl) terephthalate (BHET) could have lower production costs and emissions than the traditional dimethyl terephthalate (DMT) route due to the high reactivity and excellent reusability of the catalyst. The fast reaction rate and high selectivity render this process ideal for handling spatially distributed PET waste effectively.

KEYWORDS: *plastic, life cycle assessment, techno-economic analysis, modular production, glycolysis*

INTRODUCTION

Polyethylene terephthalate (PET) is one of the most produced plastics globally due to its packaging and textile industry use.[1] Around 6000 kt of PET plastic waste was managed in the United States (US) in 2019, 89% of which was used in containers and packaging.[2] Plastic waste is drawing significant attention because of the staggering amount of greenhouse gas (GHG) emissions associated with plastic production, the lack of proper end-of-life management,[3] and the threat from microplastics in the air and ocean[4] and plastic incineration pollutants.[5] PET is currently the most recycled polymer.[6] Yet less than 20% of the waste was actually recycled, and most of it was combusted or landfilled in 2018. Furthermore, mechanical recycling degrades product quality.[7] Consequently, its chemical recycling and upcycling, via processes such as glycolysis and methanolysis, have gained popularity.[8,9]

PET glycolysis utilizes ethylene glycol (EG) to break the macromolecules into bis(2-hydroxyethyl) terephthalate (BHET).[10] Glycolysis is a very promising PET chemical recycling strategy due to the strong nucleophilicity of EG and easy separability of the monomer, BHET.[11] BHET, the esterification product of terephthalic acid (TPA) with EG, can be recycled directly, eliminating the esterification step.[12] Most PET glycolysis studies have employed homogeneous catalysts, such as metal salts (acetates, chlorides, and carbonates) of transition metals, e.g., Zn, Pb, Mn, Co, Fe, and organometallics.[11,13−16] These catalysts are often hard to separate and may affect end-product quality. Hence, there is interest in developing heterogeneous catalysts and ionic liquids to overcome the aforementioned challenges.[17−22] Another significant challenge for chemical recycling is the heating of plastics, which is energy intensive due to their low thermal conductivities. Microwave heating has massive potential to selectively and rapidly heat materials, but plastics are generally not good microwave-absorbing materials. On the other hand, the high tan δ of EG makes it an excellent solvent for microwave heating[19,23] (Table S1).

In many industrial PET production routes, BHET is an intermediate before the final polycondensation step.[24] Hence, a comparison of BHET production technologies was made between the waste PET glycolysis process and the traditional DMT-based route (Figure S1). BHET could also be used in the production of other polyester materials than PET with widespread applications in biocompatible and biodegradable regenerative materials.[25−27] After obtaining BHET, the rest of the polymerization process is identical for both virgin or recycled BHET.[28−30]

Early stage evaluation of a technology's economic and environmental impacts could avoid unnecessary investment

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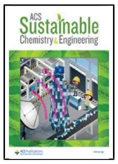

and guide the technology development during scale-up and commercialization.[31] Therefore, techno-economic analysis (TEA) and life cycle assessment (LCA) are vital for the emerging waste plastic recycling and upcycling.[32] For instance, Singh et al. illustrated that the enzymatic recycling process of PET waste could produce recycled TPA with 69%−83% less greenhouse gas emissions but at a higher cost.[33] Rorrer et al. studied the application of reclaimed PET in value-added fiber-reinforced (FRP) plastic production, which reduced up to 40% the greenhouse gas emissions compared to the standard petroleum-based FRP.[34] Excitingly, fibers from recycling showed a lower environmental footprint than virgin PET fiber manufacturing.[35]

Conventional chemical plants are typically designed as large and centralized facilities due to the economy of scales. This strategy works well for oil refineries and petrochemical plants with abundant and steady supplies of raw materials.[36] However, this is not always the case with waste plastics. Although big populations provide significant amounts of municipal solid waste containing bale PET, extensive sorting and separation are needed to obtain relatively pure feedstock from mixed waste input at the material recovery facility. Seasonal variations in the waste PET supply also affect the bale PET prices significantly and could threaten the centralized plant's normal operations.[37] The distributed modular production has more flexibilities in construction and expansion decisions to handle the risks of disruption and time-varying supply chain conditions.[38,39] Moreover, there are many geographically distributed sources of packaging PET waste (e.g., small towns, ocean islands, and coastal areas) requiring appropriate and efficient treatment.[40] Incineration and landfill should be avoided as they cause damage to the scenery, and transportation and land resources are also limited. It is more appropriate to consider a distributed-scale modular production instead of a large centralized plant to manage the waste. Other benefits of the modular system include a shorter start-up time and lower initial capital cost, dramatically reducing investment and investment risks.[41,42] All these features are beneficial for treating waste PET.

In this work, we designed the process of waste PET glycolysis using microwave heating and a heterogeneous ZnO catalyst and use our experimental reactivity performance data for the simulations. This process is benchmarked against traditional BHET production based on environmental impacts and production costs. Our TEA indicates that centralized (large scale) and modular (small scale) microwave-assisted glycolysis plants can produce BHET at a reduced price than the traditional DMT route. LCA underscores that microwave-assisted PET glycolysis could substantially reduce the global warming potential (GWP) of the BHET production.

In the following process simulation, a large-scale microwave-assisted PET glycolysis plant is designed to treat 50,000 t waste PET every year,[33] comparable with current glycolysis-based chemical recycling facilities that consume 75,000 to 125,000 t of PET annually.[43] At the same time, an average PET plant in the US produces 88,000 t of PET resin each year, corresponding to 116,000 t of BHET intermediate for the traditional DMT-based technology.[33] A modular plant of five 20 kW microwave reactors is considered to explore the effects of distributed and modular production.

■ METHODS

Microwave-Assisted Depolymerization of PET and Performance Quantification. Experiments were performed using a Monowave 450 microwave reactor (Anton Paar GmbH) with temperature, time, and power control (Figure S1). An in-built I.R. sensor and an external Ruby thermometer allow precise temperature control. Typically, 500 mg of PET (pellets/flakes), 5 mL of EG, and 5 mg of the catalyst were placed in a microwave reaction vial. Commercial ZnO nanopowder (<5 μm particle size) purchased from Sigma-Aldrich was used as the catalyst for the reactivity tests. Prior to the experiment, the contents of the reaction vial were mixed thoroughly using a vortex mixer to ensure good dispersion of the ZnO catalyst in the ethylene glycol. The reactor was programmed to maintain a constant temperature. Upon completion of a reaction, the reaction vial was cooled down rapidly to room temperature. Here, 100 mL of distilled water was added and heated to 80 °C to separate BHET and other small oligomers. The unreacted polymer and larger oligomers were removed by filtering using a Whatman filter paper. The filtrate, consisting of the products dissolved in water, was analyzed using high-performance liquid chromatography (HPLC). The residual water from the product solution was then evaporated under vacuum (72 mbar) at 40 °C using a rotary evaporator. The resulting BHET was crystallized by cooling the residual solution overnight to 4 °C after the addition of distilled water to the residue. The resultant crystals were filtered using a glass filter and dried in air at 80 °C. The conversion of PET is calculated as follows:

$$\text{PET Conversion (\%)} = \frac{W_{\text{PET},i} - W_{\text{PET},f}}{W_{\text{PET},i}} \times 100 \tag{1}$$

$W_{\text{PET},i}$ corresponds to the initial weight of PET and $W_{\text{PET},f}$ to the unreacted PET obtained via filtration. The yield of the BHET is defined as

$$\text{BHET Yield (\%)} = \frac{\text{mol}_{\text{BHET}}}{\text{mol}_{\text{PET}}} \times 100 \tag{2}$$

$$\text{mol}_{\text{PET}} = \frac{W_{\text{PET},i}}{\text{MW}_{\text{PET-RU}}} \times 100 \tag{3}$$

where mol_{BHET} are the moles of BHET produced, mol_{PET} the initial moles of PET, and $\text{MW}_{\text{PET-RU}}$ the molecular weight of the PET repeating unit ($\text{MW}_{\text{PET-RU}}$ = 192 u).

Characterization and Analysis of Reaction Products. HPLC analysis was conducted using an Agilent 1260 Infinity HPLC with a UV detector and a Zorbax Eclipse Plus C8 column (Agilent). The mobile phase was a methanol aqueous solution (50v:50v) at a flow rate of 0.6 mL min^{-1} with an injection volume of 10 μL and a runtime of 15 min (Figure 1S). Unknown peaks were identified with an Agilent gas chromatography−mass spectrometer (GC-MS) with a DB5 column (Figure 2S). ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker AVIII400 and AVIII600 spectrometers in a d_6-DMSO solution (Figures S3 and S4). The NMR spectra were analyzed using MestReNova software.

Characterization and Reusability of Catalyst. The fresh and spent catalyst samples were characterized using a Bruker D8 X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å) at 40 kV and 40 mA and a scanning rate of 0.05 per second in the 2θ range of 20°−80°. The catalyst reusability tests were performed by separating the catalyst from the product at 100% conversion of PET via filtration and drying overnight in air at 80 °C. The catalyst performance was then tested for three subsequent cycles of reuse.

Aspen Plus Process Simulation. The process simulation is performed in Aspen Plus v11 (Aspen Technology). The nonrandom two-liquid (NRTL) thermodynamic model captures the liquid−liquid phase and liquid−vapor phase equilibriums. Most of the compounds in the reactions were selected from the Aspen Plus physical property database. Compounds not included in the database (such as the BHET dimer) were defined by their structures and boiling points,[44] and missing physical properties were retrieved from the NIST

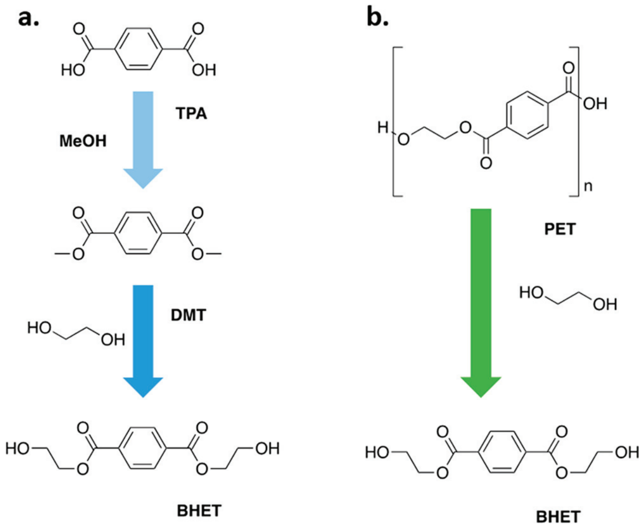

Figure 1. Reaction routes of BHET synthesis: (a) DMT transesterification and (b) PET glycolysis.

Thermo Data Engine (TDE) or estimated using the Aspen Plus Property Constant Estimation System (PCES). Lab-scale yields were taken for calculations. The electricity for the microwave reactor was calculated with a net electricity efficiency of 85.5%.[45]

Byproducts from EG are suppressed in our heterogeneous glycolysis due to the mild reaction conditions and the short reaction time—no EG byproduct was observed in our NMR analysis, as shown in Figure S4. This finding is consistent with the yields of diethylene glycol (DEG) and triethylene glycol (TEG) being low (<0.3% in 25 min under subcritical conditions).[46]

Techno-Economic Analysis (TEA). The Aspen Process Economic Analyzer V11 was used to determine the capital and operating cost for conventional chemical plants. The fixed capital cost for modular plants was estimated using the method of Sievers et al.[41] Discounted cash flow analysis was conducted, and the minimum selling price (MSP), defined as the selling price of the product when the net present value is zero, was calculated. Heat integration was implemented for the traditional BHET production using the Aspen Energy Analyzer (Aspen Technology 2019). Scenario analysis was performed on critical process parameters to account for uncertainties. Additional TEA assumptions are in the Supporting Information (SI). The microwave reactor includes two parts: a reactor vessel and microwave generator. The cost of the microwave generator is estimated from $400−2500/kW.[45,47] To avoid being overly optimistic, $2500/kW is taken as the base case; other values are used in the scenario analysis.[34,35] The ZnO catalyst powder (<5 μm particle size) was assumed to be separated by filtration, following the experimental catalyst recovery procedure. Several commercial filter

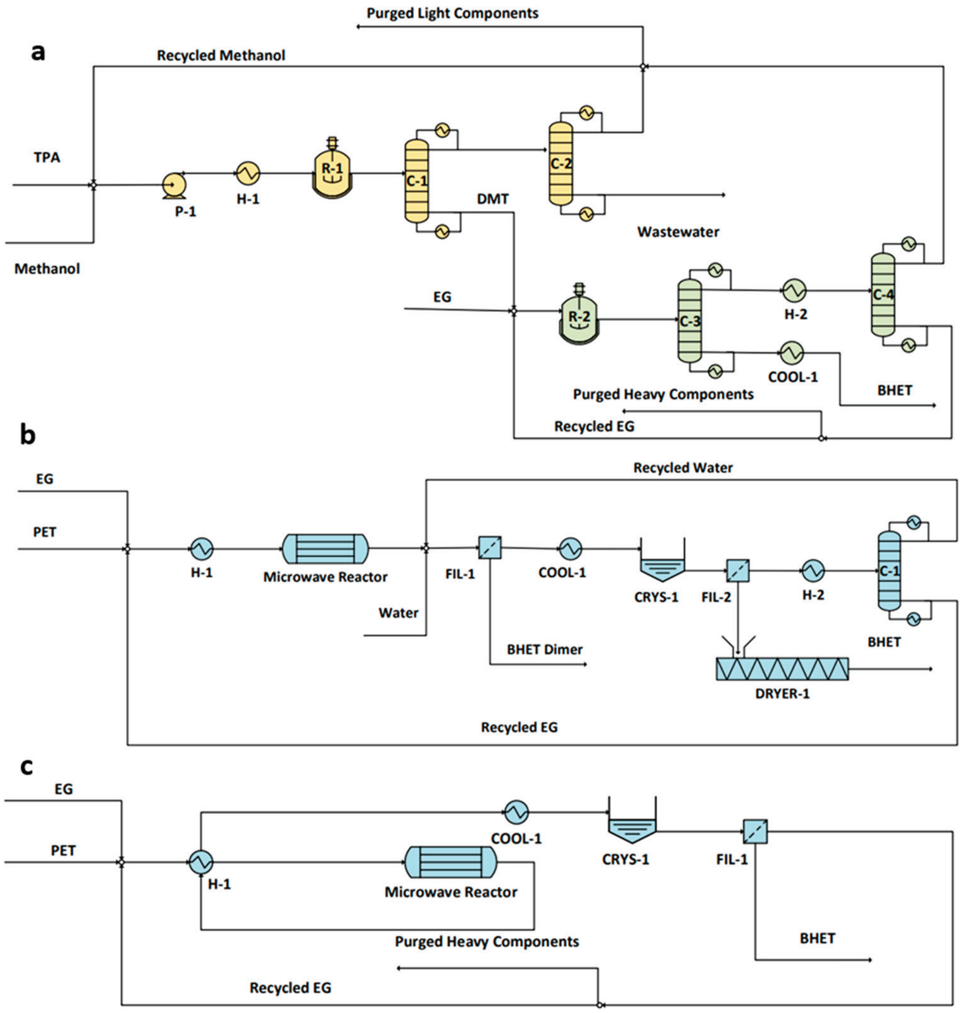

Figure 2. Process flowsheets: (a) DMT transesterification route for BHET production, (b) microwave-assisted glycolysis with BHET precipitation by adding water (MW-ZnO-Water), and (c) microwave-assisted glycolysis with BHET crystallization by cooling (MW-ZnO).

systems are economically viable for this task, including the PTFE membrane unit,[48] pressure leaf filter equipment,[49] recirculating hydropulse filter,[50] and the hollow tubular filter with the nonwoven web of fibers.[51] The cost of such a filtration system (from a few hundreds to few thousand dollars)[52,53] is much lower than the microwave reactor ($2500/kW), and it does not significantly affect the capital and final production cost.

Capital Cost Estimation of Modular Production. The well-established "power-law" scaling and Lang's factor method apply to centralized plants of large capacities. They are unsuited for evaluating the capital costs of modular plants of small sizes. On the other hand, the cost estimation for modular production is still in the early stage of development. Sievers et al. proposed a systematic fixed capital cost evaluation methodology for modular plants with a backbone facility and several production line modules.[41] Unlike traditional plants, the backbone facility provides utilities and other services for production. This configuration enables easy capacity expansion since the backbone facility could cater to a greater future demand than the initially installed capacity. Each production line is identical and contains the same reaction and separation units, which qualifies for potential cost reduction by the "economy-of-numbers".[39] When the demand increases, more modules are added to an existing plant as long as they are within the backbone facility limit.[41,54]

Life Cycle Assessment. The SimaPro software with the Ecoinvent 3.3 database is used for the LCA.[55] A "cradle-to-gate" system boundary was defined for all BHET production processes, including waste plastic transportation and pretreatment, raw material extraction, upstream utility generation, and production stage. This study utilized the Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI) 2.1 method for impact assessment.[56] We evaluated the most commonly used environmental metrics, including the global warming potential (GWP).[57] The "cutoff" method was applied on the waste PET, which assigned no credit or emission burden when using waste as the feedstock.[35] Other LCA assumptions are listed in the SI. The bale PET bottle pretreatment steps include sorting, washing, milling, and drying, based on similar processes used for producing clean PET flakes of high purity for recycling.[58,59]

■ RESULTS AND DISCUSSION

Traditional BHET Production: Transesterification of DMT. As an essential intermediate in the first step of PET production, BHET is traditionally synthesized through two routes: direct esterification of TPA and transesterification of DMT.[60] The direct esterification route is more challenging because TPA has a high melting point and minimal solubility in industrial solvents. As illustrated in Figure 2a, the DMT feedstock in the transesterification route is obtained by reacting TPA with MeOH.[1,61] The feed molar ratio of TPA and MeOH was 1:15 based on the typical values reported in the literature and patents.[62−65] This stream was then pumped to 7.6 bar in P-1 and heated to 300 °C in H-1 before sending to reactor R-1.[66−68] The reaction yielded around 98% DMT in 90 min without any catalyst.[69] After the reaction, flash column F-1 was used to evaporate products, recirculate unreacted TPA, and purge heavy impurities. Next, the distillation column C-1 collected DMT from the bottom, while C-2 recycled the excess methanol from the top.

The DMT product was then dissolved in excess EG with a molar ratio of 1:3.[1] Reactor R-2 performed the transesterification reaction at 180 °C and ambient pressure. Zinc acetate is the most effective catalyst commonly used in industry.[24] This reaction could also be carried out with three consecutive continuous stirred tank reactors (CSTRs). Ravindranath et al. illustrated with reactor simulation that a total residence time of 3 h and a catalyst loading of 5.6×10^{-4} mol/L led to 86.8% conversion.[70] Other byproducts were substantially suppressed. Methanol was produced and evaporated during the reaction along with some EG in distillation column C-3 at reduced pressure. Finally, the distillation column C-4 separated EG from methanol, which was recycled to R-1 and R-2, respectively.

Based on the simulation, 9860 kg/h of TPA and 7210 kg/h of EG are required to produce 116,000 t of BHET/year (14,600 kg/h) by the traditional DMT-based BHET route.

BHET Processes from PET Glycolysis. The initial design of the PET glycolysis process using waste PET feedstock and a ZnO catalyst is demonstrated in Figure 2b based on the experimental setup and results (referred to as "MW-ZnO-water"). PET was first mixed with EG and heated to 210 °C for glycolysis in the microwave reactor. The microwave reactor power (4565 kW) includes the energy required to increase the reactant temperature to 210 °C and the reaction heat. Currently, a single industrial microwave reactor could utilize as much as 400 to 480 kW for the heating.[71,72] The centralized microwave PET glycolysis system is thus assumed to have eleven microwave reactors (415 kW each) to cover a total of 4565 kW power requirement. As a linear cost relationship with respect to the reactor power is used to estimate the capital investment, having 11 parallel reactors does not affect the overall process economics.[45,47] Because of the high catalyst productivity, 100% PET conversion and 95% BHET yield were achieved in just 10 min (Table S2 and Figure S6). BHET was typically purified by adding an antisolvent (water) and cooling to 60 °C in benchtop experiments to remove oligomers and unreacted solid waste, as shown in many benchtop experiments and patents.[46,73,74] The temperature of the remaining solution was further reduced to 5 °C to facilitate BHET crystallization in CRYS-1.[74] The solubility of BHET in EG and water was taken from the detailed analysis by Yao et al.[75] After filtration, the BHET crystals were dried, and the water/EG solution was heated and distilled in C-1 to reuse both components. Due to the high EG and water usage, this distillation unit was the leading consumer among utilities.[74]

BHET monomer's solubility is sensitive to temperature.[75] As separating EG from water is energy intensive, an alternative PET glycolysis process ("MW-ZnO") is proposed, precipitating BHET through cooling. To fully use the heat of the product stream, the PET and EG feed mixture was first preheated by the outlet of R1 before being sent to the microwave reactor (Figure 2c). The preheat stream can raise the reactant mixture's temperature to 196 °C before the EG component evaporates, which drastically reduces the microwave energy requirement. Based on this heat integration, the microwave reactor used 968 kW of electricity, leading to a total microwave reactor cost of $2,850,000. If there is no preheating and all hot utility required to increase the reactant temperature is provided by microwaves, the electricity requirement is 10,900 kW, adding to both reactor and utility costs. The product stream was then cooled to 30 °C to precipitate BHET, while the EG stream, along with the remaining BHET and dimer, was sent back to R1. The BHET crystals were eventually collected by filtration.

High PET conversion and monomer selectivity of the heterogeneous ZnO-catalyzed glycolysis enable easy separation of BHET from the product mixture through crystallization. Moreover, the absence of distillation units and the short reaction time (10 min) under ambient pressure make this process very suitable for distributed modular production.

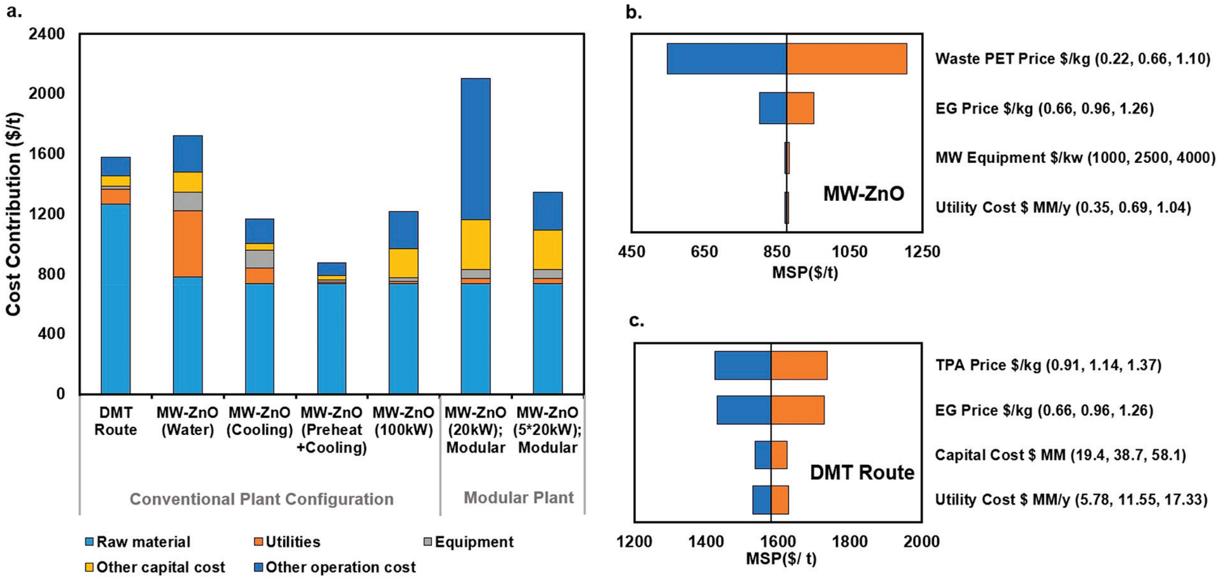

Figure 3. Economic performance of BHET production alternatives: (a) minimum selling price comparison between different BHET production processes, (b) sensitivity of BHET minimum selling prices of the MW-ZnO process on different economic factors, and (c) sensitivity of BHET minimum selling prices of DMT route on different economic factors. The three values in parentheses indicate the lower, nominal (base case), and higher numbers in the scenario analysis.

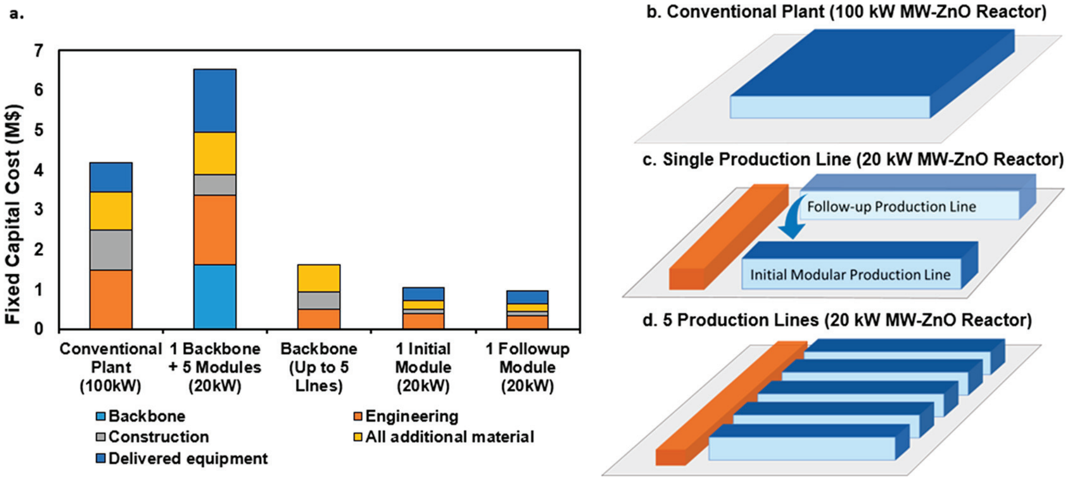

Figure 4. Fixed capital cost of conventional plants and modular MW-ZnO: (a) cost breakdown for modular production, (b) configuration of conventional plant, (c) configuration of one backbone facility and one production line for modular plant, and (d) configuration of one backbone facility and five production lines for a modular plant.

TEA of DMT Route and Waste-PET-Based BHET Production. The MSPs of different BHET production routes are compared in Figure 3a. The capital investment and operating cost breakdowns are listed in Tables S6−S10. The main contributor to the petrochemical-based BHET cost is the raw material, especially TPA. Other operating and capital costs are less significant due to the large plant scale (14,600 kg BHET/h). In contrast, microwave-assisted PET glycolysis processes benefit from the low cost of plastic scrap, which accounts for 495 $/t in the MSP. The microwave-assisted glycolysis also operates under ambient pressure without the need for expensive pumps and compressors required in some conventional-heating glycolysis systems.[76−78]

Isolation of BHET monomers by adding water creates a large amount of water/EG mixture for separation by energy-intensive distillation, resulting in a much higher utility cost than the traditional DMT route. However, the utility consumption is low when BHET precipitates via cooling and heat integration (preheating reactor inlet with the outlet stream). The reduced hot utility usage for the microwave reactor also yields a lower reactor cost and a final MSP of merely $877/t. Even after scaling down to 100 kW electricity and 628 kg/h PET waste, this glycolysis configuration ("MW-ZnO (100 kW)" in Figure 3a) still has a lower MSP than the incumbent large-scale DMT route ($1216/t vs $1580/t). In all cases, the total catalyst cost is almost negligible due to its low loading, short residence time, and efficient separation of the heterogeneous ZnO catalyst.

Scenario Analysis. Scenario analysis is performed to understand the effects of uncertainties on performance. As indicated by Figure 3a, the raw materials account for most of the production cost in almost all cases. Furthermore, the waste

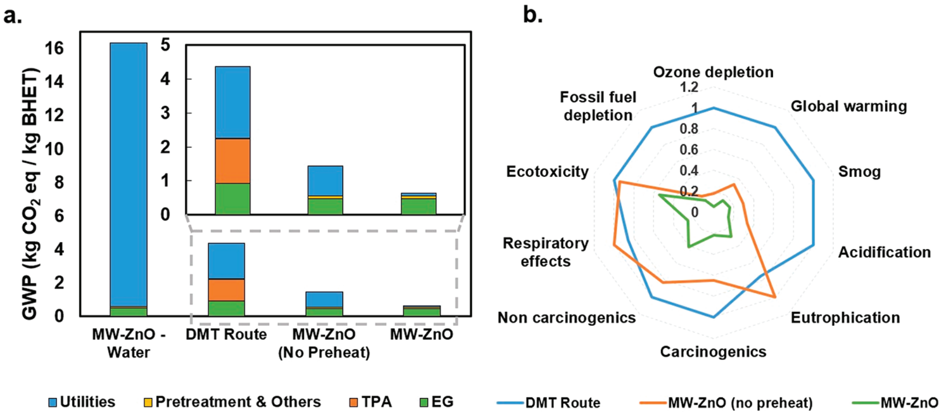

Figure 5. Life cycle assessment results: (a) global warming potential of DMT-based and waste PET-based BHET production and (b) comparison of environmental impacts among the systems normalized by the highest scores.

PET price fluctuates significantly over the years due to the variation in supply and demand.[33,34] Other essential factors affecting the process economics include the EG price, utilities, and microwave reactor cost. The influence of waste PET and EG prices,[33,34] microwave equipment,[34,35,45,47] and ±50% utility costs on the BHET produced by the MW-ZnO process is illustrated in Figure 3b. As a comparison, the sensitivity of traditional DMT-based BHET production's MSP under different raw material prices[33,34] and ±50% capital or utility costs is also depicted in Figure 3c

Figure 3(b and c) underscores that both MW-ZnO and DMT routes for BHET production are controlled mainly by raw material costs. For instance, the high variability of waste PET price could cause up to a 37% fluctuation of the MSP. Even under extreme cases, the MW-ZnO process still has lower MSPs than its DMT-based counterpart.

TEA with Modular Production. The highly distributed PET waste supply poses a severe challenge to traditional plants. The proposed MW-ZnO process has a simple structure and small equipment sizes owing to efficient microwave heating and heterogeneous catalytic reactions. Consequently, it is suitable for modular production to handle the distributed availability of the waste feedstock.[38] Benefits of modular production have been discussed extensively, including faster scale-up, lower risk, and more robustness to supply chain disruption.[79,80] The "economy-of-numbers" is also proposed to capture the learning effects of the modular manufacturing, meaning the modular plants could be built at a very small scale and gradually expand by duplicating production lines at lower prices.[81] Based on the "distributed" scale defined in a microwave reactor case study by Serra et al.,[45] the modular MW-ZnO production line will have a 20 kW microwave reactor. The 20 kW microwave reactor can process 132 kg PET/h with a size of 0.4 m^3, making it readily portable.[82] Next, the capacity expansion for this MW-ZnO modular process is considered based on the configuration by Sievers et al., which has up to five modules sharing a backbone facility (Figure 4).[41]

The fixed capital cost breakdown is shown in Figure 4a. As expected, the modular plants with five identical production lines and one backbone facility (Figure 4d) will have a higher total capital investment than the conventional MW-ZnO with the same capacity (Figure 4b). This is because of the "economy-of-scales" effect on the equipment and the cost of the backbone facility. However, the initial investment to build the first module and backbone facility is much lower (Figure 4c), giving this modular production process more flexibility to expand and avoid risks.

The TEA is conducted on the modular MW-ZnO processes, and the results are shown in Figure 3a and Tables S11−S13. Although a single MW-ZnO 20 kW modular production results in a higher MSP than conventional DMT-based BHET production, it is mainly due to the striking difference in the process scales (167 vs 14,600 kg/h BHET). The modular MW-ZnO plant with five identical production lines and one backbone facility after capacity expansion significantly reduces the MSP to \$1350/t due to operating cost reduction. In contrast, the conventional MW-ZnO plant with a 100 kW microwave reactor only performs slightly better than the modular plants at the same scale because of its lower capital cost.

Owing to its simple plant configuration and efficient glycolysis chemistry by the heterogeneous ZnO catalyst, the microwave-assisted PET glycolysis is more cost effective. Overall, conventional size and modular MW-ZnO processes with 837 kg BHET/h capacity have lower BHET MSPs than the DMT-based process at a much larger scale (14,600 kg BHET/h). With a slightly higher (\$130/t) production cost, the modular plant could have 36% lower initial investment and faster start-up, which could be favored by investors.[42,80]

Life Cycle Assessment. Next, LCA is performed to evaluate the environmental impacts of different BHET production routes. The raw material and utility usage of each case are listed in Table S15. As illustrated in Figure 5a, the global warming potential (GWP) of the MW-ZnO-Water process is significantly higher than the rest due to the high utility usage of water/EG distillation. The MW-ZnO process with BHET precipitation by cooling has a much lower GWP regardless of whether heat integration is performed or not. As the "cutoff" approach is taken for bale PET feedstocks, no emission burden is associated with the PET waste,[35] which gives the glycolysis routes advantages on the raw material aspect. The MW-ZnO process with preheating and crystallization through cooling has a GWP of 0.636 kg CO_2-eq/kg BHET, a 6.9 times reduction from the traditional DMT route (4.37 kg CO_2-eq/kg BHET).

Although the utilities typically account for less than 10% of the MSP for most of the processes mentioned above, their contributions to the GWP can be pronounced. Consequently, energy-efficient heating and separation, as well as heat integration, can effectively reduce greenhouse gas emissions.

Moreover, with the decarbonization of the electricity grid, the microwave-assisted process is expected to have a significant impact.

Figure 5b compares other crucial environmental impact categories. As each environmental impact has its own unit, the results are orders of magnitude different. Thus, each index is normalized by the LCA results of the highest scores in all aspects. The MW-ZnO process without preheating outperforms the traditional DMT routes in almost all impact categories except for the respiratory effects and eutrophication, where the results are still close. The preheated MW-ZnO process benefits from lower utility usage and has the lowest environmental impact in all categories.

More recent research on the chemical conversion of waste PET does not typically focus on selling BHET as the final product. Therefore, different choices of functional units make it challenging to compare their environmental impact directly with the current work. For instance, Rorrer et al. analyzed the fiberglass-reinforced plastic (FRP) production from glycolyzed rPET, which has the potential to reduce GHG emissions by 40%. However, PET components only account for less than 24% of the final plastic product.[34] Singh et al. analyzed the supply chain GHG emission to convert 1 kg of waste PET into TPA and EG through the enzymatic process has 17% less GWP but higher MSP than the current petroleum-based TPA market price.[33]

Our current microwave-assisted PET glycolysis route shows a clear advantage over the traditional DMT-based BHET production both economically and environmentally. Given that the recycled BHET monomer could easily replace its petroleum-based counterpart in PET or other resins, significant market demand would be secured.[83]

CONCLUSIONS AND OUTLOOK

This work compares the economic and environmental performance of BHET production from the traditional DMT route and a PET glycolysis technology. Process design and simulation are performed based on experimental reaction conditions and literature data. Owing to the efficient microwave-assisted heterogeneous catalytic process, this new PET depolymerization route demonstrates a lower production cost and emission at a much smaller scale. Water for separating BHET, a common practice in benchtop experiments, is not an economically viable choice due to the high utility requirement to recover EG and water. The high-purity product stream (95% BHET selectivity) of the glycolysis makes it possible to perform BHET crystallization through cooling. Additionally, heat integration is achieved using the hot product stream to preheat the inlet reactant mixture. With these improvements, a centralized BHET production plant using microwave-assisted glycolysis technology could achieve a minimum selling price reduction of 44%. Modular production was also explored to handle the distributed nature of PET waste. Using a modular configuration of five production lines and one backbone facility, the distributed MW-ZnO plant outperforms the conventional large-scale DMT-based technology. Life cycle assessment indicates a considerable decrease in all environmental impact categories by adopting the proposed MW-ZnO glycolysis technology.

Moreover, it is worth noting that the results of this study were modeled based on experiments performed using a 2.45 GHz microwave source. However, typical industrial-scale microwave reactors in the United States employ a 915 MHz frequency source, which can lead to changes in the dielectric properties and penetration depths of the materials used. For instance, Fal et al. demonstrated that the dielectric properties of EG change with changing the microwave source frequency, and their results suggest that EG's tan δ does not significantly change when going from 2.45 GHz to 915 MHz. However, it decreases more drastically when operated at much lower frequencies (<400 MHz).[84] Hence, some differences can be expected when operating at 915 MHz, but these are less likely to be drastic. Nevertheless, the implications of the results from the 2.45 GHz experiments should be semiquantitatively transferable. Another property that influences scale-up is the microwave penetration depth. It is understood that the penetration depth is significantly enhanced (>2.5 times) at 915 MHz than at 2.45 GHz, and the capital and operation costs of microwave equipment with lower frequencies tend to be lower, suggesting that 915 MHz is better for scale-up.[85] The effects of varied microwave reactor costs are shown in the sensitivity analysis. Furthermore, introducing foams/monoliths of suitable dielectric materials,[86] which have superior penetration and heat transfer capabilities, and smaller-scale modular operation[87] can further assist with scale-up.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c07203.

> Solvent dielectric properties, experimental set, HPLC and GC-MS chromatogram, NMR spectra, glycolysis conditions and results, X-ray diffraction pattern of ZnO catalysts, performance comparison with literature, simulation and TEA/LCA assumptions, detailed processs flowsheets, capital and operating costs for each process, process input and output for LCA, and detailed LCA results on BHET production (PDF)

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Notes

The authors declare no competing financial interest.

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