ENVIRONMENTAL AND ECONOMIC ANALYSIS OF THE POLYETHYLENE TEREPHTHALATE PRODUCTION FROM BIOMASS-BASED P-XYLENE

Yuan E. Liu, Yuqing Luo, Aikaterini Anastasopoulou, and Marianthi Ierapetritou[*]
Department of Chemical and Biomolecular Engineering, University of Delaware
Newark, DE 19716

Abstract

With the increasing demand and interest in environmentally friendly products, polyethylene terephthalate (PET) from renewable resources is gaining popularity as it is one of the most widely used fossil fuel-based polyesters. The production of PET's precursors, *p*-xylene, from biomass using molten salt hydrates (MSHs) has been investigated in previous work by Athaley et al. (2019) and it was found to be promising both economically and environmentally. This work designed and simulated the heat-integrated PET production facility utilizing the biomass-based *p*-xylene as its feedstock. A techno-economic analysis is performed to identify the main cost contributors as raw material and equipment costs. The life-cycle assessment is also conducted to demonstrate that the bio-based PET process performs better than industrial virgin PET (vPET) and recycled PET (rPET) products in the global warming category, but less environmentally friendly in most others.

Keywords

Polyethylene terephthalate, Techno-economic analysis, Life-cycle assessment, Process simulation, Heat integration

Introduction

Polyethylene terephthalate (PET) is a widely used polymer in the manufacturing of textiles and food packaging EPA (1990). With an annual production rate exceeding 26 million tons, it is the largest globally produced polyester (Rorrer et al., 2019). While traditionally a petroleum-based product in every step of its production, research efforts are being made to move away from fossil fuel-based processes and towards recycled PET (rPET) and bio-based PET production. Although rPET can be produced both mechanically and chemically, it runs into challenges with contamination from the recycling process and the collection of recycled products (Damayanti & Wu, 2021). The production of PET from biomass is a desirable pathway as an alternative to petrochemical route and the removal of CO_2 from the atmosphere during the plant growth for the

biomass feedstock. Bio-based polymers currently make up a small share compared to the total volume of fossil fuel-based polymers (about 1%), but the compound annual growth rate (CAGR) is significantly higher at 8% (Skoczinski et al., 2021). Furthermore, annual growth rates of 10 to 20% are expected if bio-based polymers become more widely promoted as an environmentally friendly solution for brands to follow and more initiatives such as (*BioPreferred*) (USA) are set in place (Skoczinski et al., 2021).

Prior work by Athaley et al. (2019) presents a novel pathway from biomass to *p*-xylene using LiBr molten salt hydrate (MSH) in the hydrolysis step developed by the Catalysis Center for Energy Innovation (CCEI) at the University of Delaware. The MSH process shows promise

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[*] To whom all correspondence should be addressed. Email: mgi@udel.edu

compared to industrially *p*-xylene production pathways and thus, this work aims to evaluate the economic feasibility and sustainability of PET manufacturing using *p*-xylene from this pathway through techno-economic analysis (TEA) and life-cycle assessment (LCA).

Detailed process design, modelling, and Aspen Plus simulation are developed on the basis of traditional processes that produce PET and its intermediates from fossil-based *p*-xylene. Although the *p*-xylene feedstock is now produced from biomass rather than fossil fuels, the underlying industrial process is expected to remain unaffected as the biorefinery designed by Athaley et al. (2019) could produce *p*-xylene with 98% purity. High-viscosity, bottle-grade PET is used as a benchmark in this work and the minimum selling price (MSP) of biomass-based PET is calculated to compare to traditional petroleum-based routes along with rPET pellets to assess economic viability. Furthermore, the LCA scores of each product are also assessed to demonstrate the sustainability of the biomass-based PET production process.

1. Methodology

1.1 Simulation

The process flowsheet was performed in Aspen Plus V12, using the NRTL thermodynamic model for the bulk of the process and the polyNRTL model for the polymerization section. The SOLIDS method was employed during the crystallization of terephthalic acid (TPA). Component structure and properties were specified from the Aspen database and missing parameters were estimated using the UNIFAC model and taken from NREL reports on biofuel component properties (Wooley & Putsche, 1996). The process model for the oxidation of *p*-xylene to TPA was based on the AMOCO MC process, as it was reported to cover roughly 70% of terephthalate feedstock worldwide (J. Sheehan, 2011). Kinetic data for the oxidation reactor were taken from work done by Wang et al. (2005) and the hydropurification reactor from Li et al. (2016). The polymerization of TPA to PET was referenced to processes reported by the EPA (EPA, 1990), with the kinetic model generated by specifying segments and their interactions in Polymers Plus (Seavey & Liu, 2008).

The catalyst behavior is inherent to the kinetic model so catalyst flows and loading were calculated separately for the TPA process. Moreover, catalysts used in the TPA synthesis process were assumed to have the same recovery as those presented by Li (2013) and the recovery process involving incineration and pyrolysis was not explicitly modeled. Filters and centrifuges were assumed to separate solids with a 99% separation efficiency. TPA crystals produced were assumed to dissolve 100% in water, utilizing Aspen's RSTOIC block.

Additional details and assumptions regarding the simulation, economic analysis, and life cycle assessment of the upstream *p*-xylene production from biomass feedstock are detailed in prior work by Athaley et al. (2019).

1.2 Techno-Economic Analysis

The Aspen Process Economic Analyzer V12 (APEA) was used to evaluate equipment and operating costs of the simulated process. The discounted cash flow analysis was performed to calculate the MSP for the comparison with incumbent technologies. Important assumptions used in this techno-economic analysis are as follows:

1) Equipment and operating costs were based on the price of the first quarter in 2019. Mixing tanks to dissolve TPA crystals were modeled as enclosed agitated tanks.
2) An economic life of 20 years with a recovery period of 10 years was assumed with a continuous plant operation of 8,000 hr every year, internal rate of return of 15% and a 35% corporate tax on profits. The straight-line model for depreciation was applied as, after 20 years, the salvage value was 10% of the original capital cost.
3) Wastewater was assumed to be treated in a third-party facility at a fixed price per unit volume and the utilities associated with the wastewater treatment plants were not modeled explicitly (Athaley et al., 2019).
4) Costs of the steam boiler and turbogenerator for the power generation unit were taken from NREL's report (Davis et al., 2013).

1.3 Life Cycle Assessment

A "cradle-to-gate" LCA was then conducted on the modeled process of bio-based *p*-xylene to PET production and the results were compared to the oil-based and recycled PET processes. EcoInvent V3.8 was the LCA database for the analysis and the Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI) was chosen as the impact assessment characterization method.

The *p*-xylene production section from prior work done by Athaley et al. (2019) was included along with the oxidation, hydrogenation, and polymerization sections presented in this work for analysis. To further reduce utility costs and improve energy efficiency in the process, heat integration was performed in Aspen Energy Analyzer on the base case model. The functional unit considered was one kg of PET produced. Additional assumptions made for the LCA include:

1) Only materials directly involved in the production of PET were considered. The materials that could be recycled or reused in other processes after the project's life cycle, such as construction, infrastructure, and catalysts, were not included for the LCA.
2) The biomass feedstock was assumed to come from a local biomass conversion facility where a 100 km transportation distance to the production facility was accounted for in the analysis. Red oak was

used as the biomass source, with a carbon percentage of 49.6% from Lamlom and Savidge (2003).

3) Excess electricity generated by burning solid waste in the steam and power generation section could be sold to other customers. Emission credit was taken based on the concept of "avoided burden" (Azapagica & Cliftb, 1999).

4) Steam and cooling water utility streams were assumed to be recycled throughout the process with a 1% loss. It was also assumed that solid lignin and humins waste was fully combusted and the CO_2 emission in the flue gas was accounted for.

5) Wastewater streams are connected to wastewater treatment units.

2. Process Flowsheet

The process flowsheet to produce PET starting from biomass-based *p*-xylene is shown in Figure 1.

2.1 Purified Terephthalic Acid (PTA)

The flowsheet to produce PTA from *p*-xylene was divided into two steps: the oxidation process and the purification process.

In the oxidation step, the feed of the R-1 reactor consisted of a homogeneous mixture of *p*-xylene, water, acetic acid solution, and a tri-catalytic system of cobalt (II) acetate, manganese (II) acetate, and hydrogen bromide. R-1 was simulated as a CSTR operating at 194°C and 20 bar, where the feed was oxidized by pressurized air. The effluent from the reactor was then fed to a series of crystallizers and intercoolers to crystallize the TPA by gradually lowering the temperature and pressure without co-precipitating too many impurities, before being sent to a centrifuge. At this point, the product is considered "crude terephthalic acid" (CTA) due to the high concentration of *p*-toluic acid and 4-

carboxybenzaldehyde (4-CBA) impurities that must be removed before polymerization (J. Sheehan, 2011; Tomás et al., 2013). The vapors from the reactor and crystallizers were sent to separation columns for the recovery of the acetic acid solvent.

The CTA crystals were sent to the purification section, where they were first dissolved with water to create a slurry. This mixture was heated and pressurized to the operating conditions of the hydrogenation reactor (R-2) of 281°C and 80 bar, which was modeled as a plug-flow reactor with a 0.5 wt.% Pd/C solid catalyst load. The reactor was fed an excess of hydrogen gas to convert the 4-CBA impurities to *p*-toluic acid. The effluent from this reactor was sent to a series of crystallizers and a centrifuge, where the slurry was then mixed with water and sent to a rotary vacuum-drum filter to separate the final PTA crystal product. The mother liquor from the centrifuge was split between recycling back to the oxidation reactor and hydrogenation reactor.

2.2 Polyethylene Terephthalate (PET)

In the polymerization of PET, the TPA from the hydrogenation section was first dissolved and formed a paste with monoethylene glycol (MEG) before being sent to a series of reactors. Antimony trioxide was used here due to its high catalytic activity and its low tendency for side reaction catalysis (Duh, 2002). The first two reactors (R-3 and R-4) acted as the esterifiers and polymerizers which combined the TPA and ethylene glycol to form the monomer bis(2-Hydroxyethyl) terephthalate (BHET) and then polymerized it to PET (EPA, 1990; Lucas et al., 2007). The following three CSTRs in series (R-5, 6, and 7) served to model and approximate the end finishers through increasing temperature and decreasing pressure. The vapor from each of the reactors was combined and sent to a distillation column, where MEG was recovered and recycled back to the first esterifier.
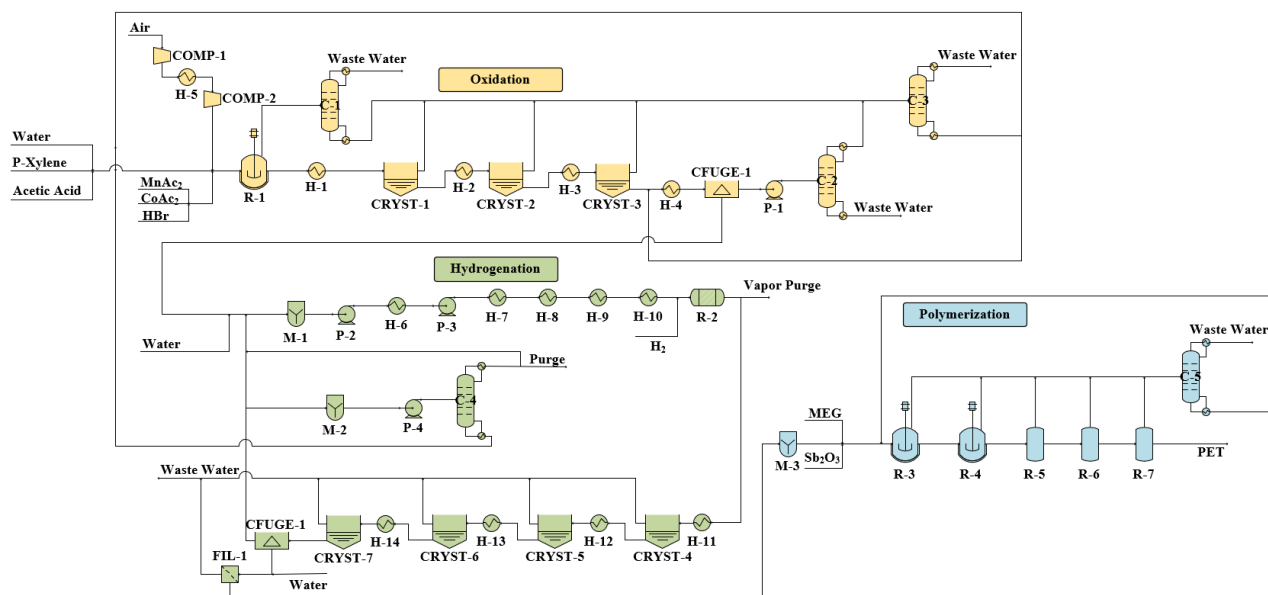

Figure 1. Process flow diagram for the production of PET from p-xylene, via oxidation, hydrogenation, and polymerization

3. Results and Discussion

3.1 Simulation

The plant capacity was designed to process 400,000 metric tons of biomass feedstock each year based on the simulation work by Athaley et al. (2019) and similar in scale to the red oak pyrolysis plant capacity presented by Hu et al. (2015). The plant produced 97,900 metric tons PET polymer annually. Each primary step of the synthesis of PET has requirements that need to be met by the modeling and simulation. Overall, the model falls within acceptable ranges for TPA impurity concentrations, and the PET polymer meets standards for use in bottle production. Consequently, bottle-grade PET was used as the benchmark for the product. But if a different intrinsic viscosity is needed for a different polymer grade, the residence times within the modeled finishing reactors could be altered to reflect different residence times within the solid-state polymerization reactor (Lucas et al., 2007).

3.2 Economics

The lignin and humins produced in the *p*-xylene synthesis were burned for electricity and steam generation. The heat from combustion was enough to cover some steam utilities. For example, this utility generation unit produced 314,300 kg/hr of the total 520,700 kg/hr HP steam needed for the process, and fully covered the 119,700 kg/hr of MP steam and 41,910 kg/hr of LP steam requirement. Additionally, 21 MW of electricity was generated, which exceeded the 9.8 MW electricity usage in the process. The amount of furfural produced is 8,170 kg/hr, which was sold to improve the profitability of the overall process as discussed in Athaley et al. (2019).

The capital and operating costs of the base case, including furfural sales and electricity generation were tabulated in Table 1. Raw materials costs were seen to have a significant impact on the total cost of the process which come primarily from the contributions of the biomass feedstock, LiBr, ethylene, and MEG as seen in Figure 2. The former three components were involved in the upstream biomass-to-*p*-xylene production, so the primary contribution from this process was the MEG costs. As MEG was consumed in the polymerization to PET, it is difficult to reduce its cost and impact although most of it was recycled in the process.

The other major cost contribution comes from equipment purchase. Of the $99.07MM in purchased equipment cost, $44.45MM comes from the power/steam generation section, 64% of which is the steam boiler. Due to the high utility usage of the process, the steam generated is maximized based on the lignin combustion. As the boiler has a large throughput of over 300 metric tons/hr of steam, its purchase cost is large as well. The 'Other' category includes non-purchased equipment, as well as equipment setting, piping costs, steel costs, etc.
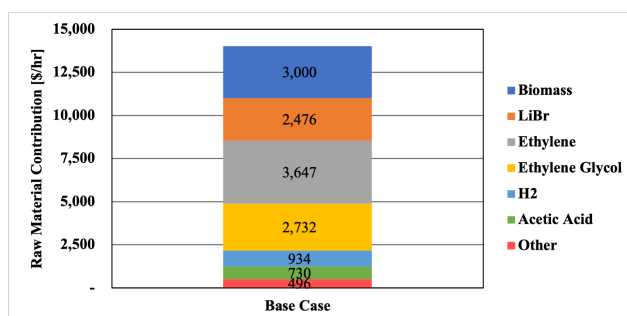

Figure 2. Impact of various compounds involved in the PET process on the total raw materials cost.

Table 1. Summary of the capital and operating costs of the PET process base case

Capital Costs	($MM)	Operating Costs	($MM/yr.)
Equipment	99.07	Catalyst	35.41
Other	66.25	Raw Materials	112.1
G&A Overheads	4.63	Utilities Cost	17.85
Contract Fee	4.96	Op. Labor Cost	2.96
Contingencies	16.53	Maintenance	2.37
Working Capital	9.57	Op. Charges	0.74
Total Capital Cost	201.0	Plant Overhead	2.67
		G&A Cost	18.90
		Total Op. Cost	193.0

Heat integration resulted in a more energy efficient process, with eight additional heat exchangers being implemented resulting in a significant reduction in cooling water and steam usage. The power generation section produced 287,100 kg/hr of the required 399,800 kg/hr of HP steam and fully covered the 23,890 kg/hr and 20,160 kg/hr of MP and LP steam, respectively, while generating 14 MW of electricity. A summary of the capital and operating costs of the heat integrated (HI) case are included in Table 2. A $9.51MM/year decrease in utilities was obtained by increasing the total equipment costs by $1.58MM. Notably, the 'Other' costs increase due to the additional heat exchangers, but 'Equipment' decreases because the boiler costs are reduced with the lowered steam requirement.

Table 2. Summary of the capital and operating costs of the PET process after heat integration

Capital Costs	($MM)	Operating Costs	($MM/yr.)
Equipment	98.91	Catalyst Cost	35.41
Other	67.98	Raw Materials	112.3
G&A Overheads	4.67	Utilities Cost	8.34
Contract Fee	5.01	Op. Labor Cost	2.96
Contingencies	16.69	Maintenance	2.37
Working Capital	9.66	Op. Charges	0.74
Total Capital Cost	202.9	Plant Overhead	2.67
		G&A Cost	18.90
		Total Op. Cost	183.6

When assuming that furfural was sold at $1,000/metric ton and excess electricity was sold to the market as Athaley et al. (2019), the minimum selling price of PET was calculated to be $1,763/metric ton, with the raw materials accounting for around half of the cost. A detailed breakdown of the MSP for both the base case and HI case can be seen in Figure 3. This selling price is roughly twice the price of PET produced by conventional petroleum-based processes at $879/metric ton, and slightly higher than the rPET pellets cited by ICIS at $1,537/metric ton (Tudball, 2021). After performing heat integration, the MSP is reduced to $1,716/metric ton, primarily from the reduction in utility costs. Importantly, since the LP steam requirement was lower, the electricity generated by the turbines and excess sold were also reduced.
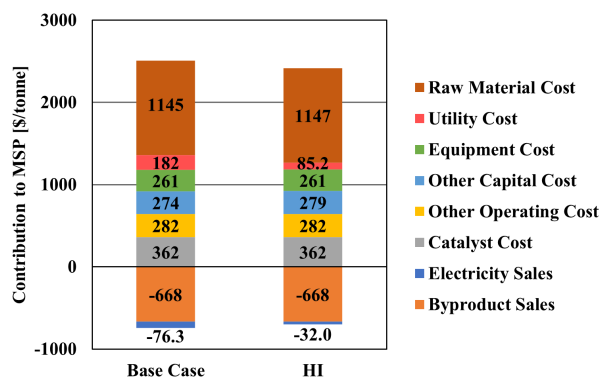

Figure 3. Breakdown of PET minimum selling price by impact of individual cost categories for both the base case and heat integrated case (HI)

Next, a sensitivity analysis was conducted to study the effects of different parameter uncertainties on MSP, shown in Figure 4. The selling price of the furfural byproduct has the most impact when varied by ±20% and the utilities have the least impact, due to being reduced by the steam generation in the process. The purchase costs of ethylene, biomass, MEG, and LiBr were also investigated, as they contributed significantly to the raw material costs.
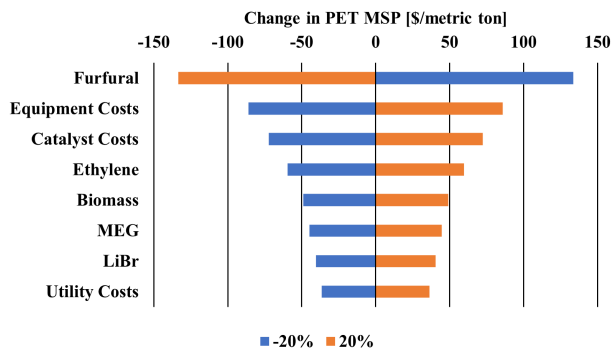

Figure 4. Sensitivity analysis on the base case PET process for 20% variations in economic parameters

3.3 Life-Cycle Assessment

The credit of producing byproducts (furfural and electricity) and the carbon sequestration during the biomass

growth stage gave the biomass-based process advantage while the flue gas during waste solid combustion emitted more greenhouse gas. Since the impact category values for furfural is not tabulated within the EcoInvent database, those values were calculated based on prior work by Raman and Gnansounou (2015) and Hong et al. (2015). A comparison of the heat integrated biomass-based PET's LCA results to the bottle-grade traditional PET and rPET are shown in Table 3 with the following impact categories used in the TRACI method: acidification (Acid.), ecotoxicity (Ecotox.), eutrophication (Eutroph.), global warming (G.W.), ozone depletion (O.D.), photochemical oxidation (Photo. Ox.), carcinogenics (Carcin.), non-carcinogenics (non-Carc.), and average respiratory effects (Respir.).

Table 3. Comparison of LCA results of the heat-integrated bio-based PET process, virgin oil-based PET (vPET), and recycled PET (rPET) production

Impact Category	Units	vPET	rPET	HI Bio-PET
Acid.	moles H+ Eq.	0.54	0.19	1.19
Ecotox.	kg 2,4-D Eq.	1.18	1.41	2.66
Eutroph.	kg N	6.0E-4	3.5E-4	-3.1E-3
G.W.	kg CO_2 Eq.	2.73	0.73	-2.09
O.D.	kg CFC-11 Eq.	10E-6	4.1E-8	1.6E-7
Photo. Ox.	kg NOx Eq.	5.7E-3	1.7E-3	1.1E-2
Carcin.	kg benzene Eq.	1.2E-2	4.4E-3	2.0E-2
non-Carc.	kg toluene Eq.	20.5	31.7	41.6
Respir.	kg PM2.5 Eq.	3.0E-3	1.3E-3	4.0E-3

The proposed biomass-based process performs better than both forms of PET in the eutrophication and global warming categories. This is primarily due to the credits of using biomass feedstock and producing furfural as a byproduct. Global warming potential and non-carcinogenic impact categories for the base case are shown in Figure 5, which shows that there are significant contributions from LiBr, cooling water, and steam. The latter two were significantly reduced through heat integration. Moreover, all impact categories show an improvement after heat integration, and the credits taken for the use of biomass now outweigh other factors, resulting in a negative global warming impact score.

Conclusions

The production of bottle-grade PET from bio-based *p*-xylene is modeled based on the traditional industrial production pathway of oxidation, hydrogenation, and polymerization. For a 400,000-metric ton/year biomass processing capacity, 97,900 kg/hr of PET is produced and can be sold at a minimum selling price of $1,755/metric ton. Heat integration not only cut the minimum selling price to $1,710/metric ton, but also reduced the environmental impacts of the biomass-based PET production. Major cost contributors were found to be the raw materials and

equipment, specifically, the units in the power generation section. While the production costs of the biomass-based PET are higher than the traditional fossil-fuel based PET, they are on a similar scale to rPET pellets. The proposed biomass-based PET production also demonstrated significant reduction in greenhouse gas emission as compared to the traditional PET production methods, which may encourage customers to choose this bio-based product.
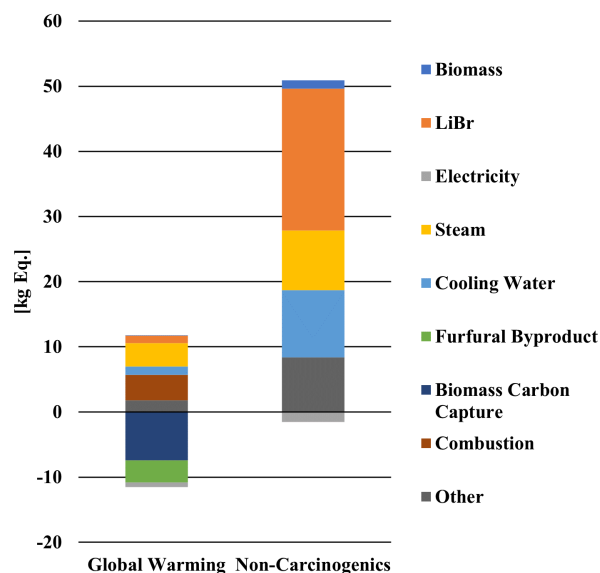

Figure 5. Impact of select factors on the TRACI impact categories for the bio-based production of PET.

Acknowledgments

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