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Thermodynamic and economic analysis of a deployable and scalable process to recover Monomer-Grade styrene from waste polystyrene

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ABSTRACT

Less than 5% of polystyrene is recycled, motivating a search for energy efficient and economical methods for polystyrene recycling that can be deployed at scale. One option is chemical recycling, consisting of thermal depolymerization and purification to produce monomer-grade styrene (>99%) and other co-products. Thermal depolymerization and distillation are readily scalable, well-established technologies; however, to be considered practical, they must be thermodynamically efficient, economically feasible, and environmentally responsible. Accordingly, mass and energy balances of a pyrolysis reactor for thermal depolymerization and two distillation columns to separate styrene from α-methyl styrene, styrene dimer, toluene, and ethyl benzene co-products, were simulated using ASPEN to evaluate thermodynamic and economic feasibility. These simulations indicate that monomer-grade styrene can be recovered with energy inputs <10MJ/kg, comparable to the energy content of pyrolysis co-products. Thermodynamic sensitivity analysis indicates the scope to reduce these values and enhance the robustness of the predictions. A probabilistic economic analysis of multiple scenarios combined with detailed sensitivity analysis indicates that the cost for recycled styrene is approximately twice the historical market value of fossil-derived styrene when styrene costs are fixed at 15% of the total product cost or less than the historical value when feedstock costs are assumed to be zero. A Monte Carlo and Net Present Value-based economic performance analysis indicates that chemical recycling is economically viable for scenarios assuming realistic feedstock costs. Furthermore, the CO_2 abatement cost is roughly \$1.5 per ton of averted CO_2, relative to a pyrolysis process system to produce fuels. As much as 60% of all polystyrene used today could be replaced by chemically recycled styrene, thus quantifying the potential benefits of this readily scalable approach.

1. Introduction

Since their commercialization in the late 1950 s, plastics have grown into a billion-dollar industry. Today, plastics are found in a wide variety of products due to their desirable properties and low cost.[1] Unfortunately, disposal of plastics contributes to landfilled municipal solid waste (MSW) and environmental litter. Plastic wastes, and especially microplastics formed from plastic deterioration, represent a major source of environmental pollution.[1] Potential adverse human health effects include disruption of immune function and neurotoxicity.[2] Finally, it should be pointed out that since the most commonly used plastics are not biodegradable, they can persist in the environment for many years.[3].

In particular, one of the most commonly used plastics, polystyrene is especially difficult to replace. Commonly used for packaging and to protect consumer goods and food, polystyrene is a lightweight, inexpensive, and dimensionally stable material that reduces damage during shipping and provides superior insulation to protect food from temperature changes. Currently, polystyrene is produced from polymerization of styrene obtained from catalytic dehydrogenation of ethyl benzene,[4] which is sourced from petroleum.[5] Consequently, new methods of producing polystyrene and especially for recycling existing polystyrene stocks are required for a low-carbon economy and adverse climate change effects mitigation.[6].

Polystyrene recycling can reduce the need for production of virgin polymer, and hence play a role in decarbonization of plastics. Unfortunately, polystyrene is recycled at an average rate less than 5%.[2] Furthermore, polystyrene can be mechanically recycled, but repeated

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thermal treatment causes irreversible degradation and the corresponding loss of key properties such as mechanical strength and flexibility.[7] Thakur et al.[8] recently reviewed the challenges facing mechanical recycling of polystyrene, including thermal degradation and impurity control. Because of the challenges to mechanical recycling, many materials recycling facilities, or MRFs, do not accept polystyrene waste as it requires a more specialized facility to mechanically recycle it.[9] Due to its light weight and bulkiness, polystyrene is costly to transport which makes polystyrene recycling using mechanical methods cost ineffective. Difficulties with polystyrene recycling have prompted several states to propose bans on the material.[3–7] While plastic bans may help reduce waste in some cases, they can have unintended consequences that limit their effectiveness.[10].

One promising alternative to mechanical recycling is chemical recycling, an umbrella term which includes many thermal and catalytic processes that aim to convert polymer macromolecules into smaller molecules useful as fuels, chemicals, or chemical feedstocks.[11] Ragaert et al.[12] recently reviewed the field of chemical recycling of solid plastic waste in great detail, including experimental procedures and data analysis methods. The technology readiness and scalability of chemical recycling technologies vary considerably from one another. For example, some recent studies report on the use of novel catalysts to convert plastic wastes into specialty chemicals.[13–18] Unfortunately, the scalability of these types of chemical recycling are in doubt as the markets for the specialty chemicals they produce will be completely saturated by conversion of vast amounts of available plastic wastes. For example, a new photocatalytic technology was recently reported for converting polystyrene into benzylic acid.[19] While scientifically interesting, photocatalytic processes are notoriously difficult to scale up.[20] Further detracting from technology readiness, the costs and stability of the catalysts they require introduce economic uncertainty, especially when homogeneous [18] or precious metal catalysts [14] are used.

Because of the long use of similar reactors in petroleum refineries,[21] fluidized bed pyrolysis possesses the advantages of high technology readiness, familiarity, scalability, and deployability compared to other chemical recycling methods.[22] Typically, plastic pyrolysis aims to produce a pyrolysis oil that can be upgraded into a fuel or commodity chemical feedstock,[23] associated with markets that are nearly impossible to saturate. Moreover, producing fuels or chemical feedstocks does not reduce the need to produce virgin polystyrene from petroleum. Separation prior to pyrolysis offers the prospect of greater selectivity to produce a given product. Interestingly, unlike most other common polymers, monomer yields obtained from polystyrene pyrolysis can exceed 50%.[24] Furthermore, several technologies, including flotation [25] and magnetic field separation,[26] are available for separating polystyrene from mixed plastic waste streams. Accordingly, polystyrene separation from mixed plastics followed by pyrolysis represents a potential method of chemical recycling that can replace petroleum-derived styrene with waste-derived styrene for the production of virgin-like recycled polystyrene from plastic waste.

The major challenge preventing a broad use of chemical recycling by pyrolysis of segregated polystyrene is that the styrene in the product stream is typically contaminated with side products including α-methyl styrene, toluene, ethyl benzene, and styrene dimer.[27] Catalytic pyrolysis can increase liquid oil yields, but typically with the detrimental side effect that styrene yield is reduced relative to production of side product contaminants.[24]The presence of these contaminants prevents the use of styrene as a feedstock for polystyrene manufacturing, since monomer purity >99% is required for polymerization.[28] Recovering monomer-grade styrene from the polystyrene pyrolysis mixture can be achieved using distillation without detracting from scalability or technology readiness. Unfortunately, including distillation steps adds process complexity, increases energy inputs, and potentially undermines economic viability.[29] Therefore, a critical question focuses on how much energy is required for distillation and how much cost does it add. In light of the above considerations, the present study introduces a systematic and potentially insightful process simulation framework of polystyrene pyrolysis followed by distillation to recover monomer-grade styrene for chemical recycling. Within the above context, both thermodynamic performance and process cost profiles are critically evaluated and probabilistically characterized for a wide range of technological readiness and process economics-relevant assumptions/scenarios that are carefully selected to characterize the robustness of technological projections pertaining to the viability prospects of the proposed option. Collectively assessed, the results derived encourage further development of pyrolysis as a viable technology option for chemical recycling of waste polystyrene.

The paper is organized as follows: Section 2 encompasses the basic structure of the proposed methodological and process modeling/simulation framework, followed by Section 3 containing the study's main results and a pertinent discussion. Finally, a few concluding remarks are offered in Section 4.

2. Preliminaries and Methodology

2.1. Process modeling framework

Thermodynamic and economic performance of the polystyrene pyrolysis process system were evaluated using Aspen Plus V12. The process model consists of a pyrolysis reactor, a heat exchanger, and two distillation columns as shown in Fig. 1. Pure polystyrene is fed to the pyrolizer at 25 °C and 1 atm, which operates at a set temperature to achieve pyrolysis. The stream exiting the pyrolysis reactor is cooled by a heat exchanger to 25 °C, before the products are sent to two distillation columns for separation and purification. The pyrolysis reactor was modeled as the RYield model, which permits direct input of literature values for the yields of styrene product and all byproducts. The heat exchanger was modeled as a HEATER block to cool pyrolysis products to 25 °C at 1 bar. Distillation columns were analyzed using the Winn-Underwood-Gilliland model, i.e., DSTWU model in Aspen. The Winn-Underwood-Gilliland model requires as inputs the number of stages, and recovery of the light and heavy keys in the distillate; it outputs estimates of the required reflux ratio, number of stages, as well as energy requirements [30,31].

Due to its volatility relative to byproducts, two distillation columns were needed to recover styrene with purity >99%. As shown in Fig. 1, the first column separates styrene from the light fraction consisting primarily of benzene, toluene, ethylbenzene and the second separates styrene from α-methyl styrene and the remaining heavy fraction. Dimers and higher oligomers were not included in the analysis due to a lack of data. However, since dimers and higher oligomers are much less volatile than α-methyl styrene and since they are much less abundant than other products, their exclusion has a negligible impact on thermodynamic results. Furthermore, since the heavy fraction is not valorized, excluding dimers from the analysis does not impact estimates of process economics.

2.2. Thermodynamic property model selection and validation

The accuracy of any process simulation framework depends on the selection of appropriate property models. Accordingly, the NRTL (Non-Random Two-Liquid) thermodynamic model was selected for modeling vapor–liquid equilibrium, due to its proven effectiveness in describing non-ideal interactions in mixtures consisting of aromatic hydrocarbons such as toluene and styrene [32]. The gas phase itself was modeled as ideal, which is appropriate given that all processes operated at a pressure of 1 bar.

A comparative study was conducted to assess the effectiveness of the NRTL model for estimating vapor pressures. The evaluation utilized empirical data obtained from published sources, including the data set reported by Krase et al [33], White et al. [34] and the National Institute

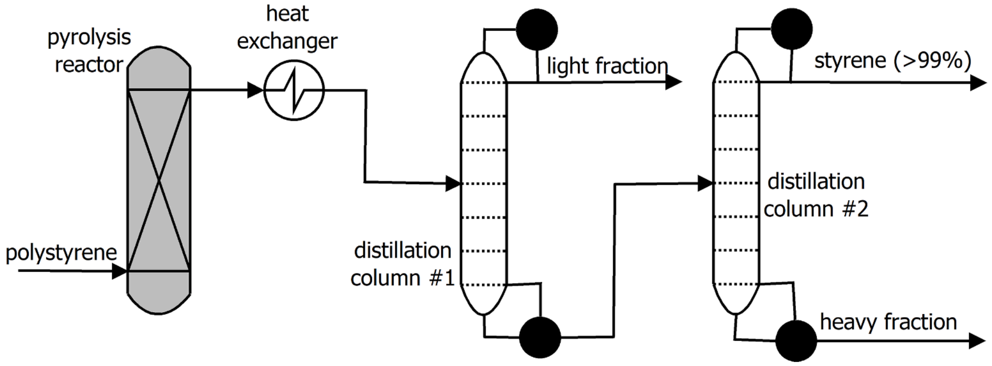

Fig. 1. Aspen Plus model simulation flowsheet. The input is waste polystyrene. The process consists of a pyrolysis reactor, condenser, and two heat exchangers. The outputs are monomer grade styrene (>99%), a light fraction consisting primarily of toluene and ethyl benzene, and a heavy fraction consisting of a-methyl styrene and styrene dimer.

of Standards and Technology (NIST) available in Aspen Plus. Vapor pressure of single components predicted using the NRTL model matched the available data with r^2 coefficients of 0.998 and 0.995 for toluene and styrene, respectively and 0.999 for ethyl benzene/styrene mixtures. In all cases, model accuracy is deemed sufficient for process design purposes.

2.3. *Sensitivity and uncertainty analysis*

Propagation of various key model input variable and process parameter uncertainties through the underlying techno-economic process model and the assessment of their combined effect on the derived overall thermodynamic and economic performance distribution profiles of the proposed technology option were comprehensively studied. In particular, the sensitivity of the process was assessed by analyzing the energy requirements (used for the condenser and the reboiler), number of stages in each column, as well as the recovery and purity levels of styrene at various feed compositions for benzene, toluene, ethylbenzene, α-methyl styrene and styrene. Variability in pyrolysis yield and product composition were both expected to be particularly important variables governing thermodynamic and economic performance. Accordingly, a thorough review of all relevant literature on polystyrene pyrolysis was performed to determine a "base case scenario", as shown in Table 1.[24] Extensive simulations were performed around this base case scenario, which included varying both styrene yield and pyrolysis temperature independently. When the sensitivity of thermodynamic performance to styrene yield was evaluated, the relative concentrations of all other byproducts to one another were maintained constant at the specific ratios shown in Table 1.

2.4. *Technoeconomic assessment*

Comprehensive baseline capital investment models for Total Capital Investment (TCI), Total Product Cost (TPC), and the Levelized Production Cost were systematically developed to evaluate the technoeconomic features of the proposed chemical recycling process. Please notice that TCI and TPC represent the two primary components of any comprehensive cost analysis also known capital expenditure (CAPEX) and operating expenses (OPEX), respectively. In particular, TCI was estimated as the sum of working capital (WC) and fixed capital investment (FCI) encompassing both direct and indirect costs, as shown in Equation (1):

$$TCI = WC + FCI \tag{1}$$

Furthermore, TPC is calculated by forming the sum of production cost (PC) (such as operating and maintenance costs) and general expenses (GE), as shown in Equation (2):

$$TPC = PC + GE \tag{2}$$

Tables 2 and 3 provide additional salient details on the inputs to TPC and TCI. All pertinent economic performance indicators were computed following standard practice in engineering system economic analysis [35–38]. Table 2 shows all cost items considered along with estimated values and ranges; TCI values were estimated using the average of all ranges, while the maximum and minimum values were used to assess risks and opportunities (please see below). The cost figures of purchased equipment related to the heat exchanger, reactor and distillation columns were obtained using the Aspen Plus Economic Analyzer. Table 3 shows all cost components considered to compute the TPC during the operation of the process system under consideration, as well as the Levelized Production Costs as used previously by Reichelstein et.al. and Morrow et.al. [39,40]. As some items that contribute to TPC depend on the value of TPC itself (e.g., plant overhead costs, labor, patents, administrative costs, etc.), a numerical solver was used [29–32]. Similar to the TCI case, average values were calculated, and the maximum and minimum values were used to assess potential risks and opportunities. Monomer grade styrene is the only product that is valorized in this process; the light and heavy fractions might be valorized or used to provide heat, with additional potential benefits either to economic or thermodynamic performance.

Multiple scenarios were evaluated to assess the effect of process scale on economic performance. In particular, classical sensitivity analysis was first performed over the ranges of key uncertain input variables shown in Tables 2 and 3 by considering each one of them as varying over its specified range while all others remaining constant at their respective "average" baseline values. In order to overcome both a limitation associated with the traditional multi-variate sensitivity analysis where only the effect of one uncertain input variable on economic performance assessment is considered each time, as well as the "flaw of averages" known in probability theory cautioning that economic performance evaluated at average baseline conditions does not represent average economic performance, detailed Monte Carlo simulation techniques were employed and implemented using the @Risk software package in the present study as well [33]. In particular, uncertainty associated will all key model input variables was quantified through uniform

Table 1
Baseline composition of stream exiting pyrolysis reactor.

Component	Yield of reaction (mass %)
styrene	60
benzene	8.4
toluene	11.9
ethylbenzene	8.4
α-methyl styrene	11.3

Table 2
Estimation of the Total Capital Investment (TCI) for a pyrolysis depolymerization process.

Direct Costs
A. Total Installed Equipment Cost [$, US]
B. Buildings, process and auxiliary (10–70% of equipment cost)
C. Service, facilities and yard improvements (40–100% of equipment cost)
D. Land (4–8% of equipment cost)
Indirect Costs
A. Engineering and supervision (5–30% of direct costs)
B. Legal expenses (1–3% of FCI)
C. Construction expense and contractor's fee (10–20% of FCI)
D. Contingency (5–15% of FCI)
Fixed Capital Investment (FCI) (Direct + indirect)
Working Capital (10–20% of Total Capital Investment)
Total Capital Investment (TCI) (FCI + Working Capital)

Table 3
Estimation of Total Product Cost and the Levelized Production Costs.

Manufacturing Costs (direct production costs + fixed charges + plant overhead costs)
Direct production costs
1. Raw materials (10–20% of TPC)
2. Operating labor (10–15% of product cost)
3. Direct supervisory and clerical labor (10–20% of operating labor)
4. Utility costs [$ US/Year]
5. Maintenance and repair (2–10% FCI)
6. Operating supplies (0.5–1% FCI)
7. Laboratory charges (10–20% of operating labor)
8. Patents and royalties (0–6% of TPC)
Fixed charges
1. Depreciation (10% of FCI)
2. Local taxes (1–4% of FCI)
3. Insurance (0.4–1% of FCI)
4. Financing interest (6–10% of FCI)
Plant overheads (5–15% of TPC)
General Expenses
1. Administrative costs (2–5% of TPC)
2. Distribution and selling costs (2–20% of TPC)
3. R&D costs (5% of TPC)
Total Product Cost (TPC) (Direct production costs + General expenses)
Levelized Production Cost (TPC/production rate) [$ US/kg]

probability distributions (with minimum and maximum values listed in Tables 2 and 3) and propagated through the underlying TCI and TPC models using a Monte Carlo simulator and performing 10,000 simulation runs by randomly sampling from the aforementioned probability distributions.

The derived probability distribution profiles of TCI and TPC offer a range of economic performance outcomes rather than single-point estimates associated with conventional approaches that conveniently ignore the combined effect of irreducible uncertainties encountered in the process system's operating environment. Furthermore, the above TCI and TPC profiles are amenable to an insightful probabilistic characterization that allows multiple performance metrics to be considered and calculated in a mathematically sound manner such as expected values (avoiding the "flaw of averages'), standard deviations (a measure of "riskiness"), P5 and P95 values associated with downside risks as well as upside opportunities, etc.[41]. By establishing such a transparent link between key economic performance metrics with the project's risk profile under uncertainty, a Monte Carlo-based probabilistic economic viability assessment framework such as the proposed one offers more nuanced and realistic insights into the technology's overall prospects.

A Net Present Value (NPV) calculation was performed to evaluate economic viability. NPV was defined as the difference between the gross present value (GPV) and the TCI:

$$NPV = GPV - TCI \tag{3}$$

$$GPV = \sum_{t=1}^{30} \frac{CF_t}{(1+r)^t} \tag{4}$$

where CF_t represents the net cash flow in year t that includes the annual revenue. The Monte Carlo simulation framework used for TPC was used again for NPV. Probability distributions for key uncertain input variables were assumed to be triangular following the ranges shown in Tables 2 and 3, with the exception of feedstock cost which was assigned fixed values on a per mass basis. Otherwise, the NPV analysis assumed a 30-year payoff period; a 10% real discount rate or internal rate of return (i.e. a nominal discount rate $n = 13\%$ and inflation rate $i = 3\%$); 3-year plant build; 50% annual sales in year 1; 100% annual sales in year 2. Revenues and expenses are calculated as for TPC.

CO_2 emissions were calculated based on energy flows estimated by ASPEN, while the CO_2 abatement cost was calculated using Equation (4):

$$Abatementcost = \frac{(CAPEX_{30yrlifetime})_{newcase} - (CAPEX_{30yrlifetime})_{baselinecase}}{(CO2emissions)_{baselinecase} - (CO2emissions)_{newcase}} \tag{5}$$

where CAPEX is defined as the standard capital expenditure required by each scenario. CAPEX was put onto a time basis by evenly distributing it over the 30-year project lifetime. The basis for converting energy flows into CO_2 equivalents assumes full, stoichiometric combustion for all components, and that all heating utilities follow the US-EPA-Rule E9-5711. When refinery emissions were included for refining pyrolysis oil into fuel, a constant value was assumed, consistent with recent reports.[42]

3. Results

This study evaluates a chemical recycling process for converting polystyrene into monomer-grade styrene. The process assumes that a feed of segregated polystyrene is available with negligible contamination. Polystyrene segregation might reasonably be achieved using density-based methods [25] or newer magnetohydrodynamic methods.[26] The energy required for either of these processes is much less than those expected for the thermal process analyzed in this study. Accordingly, the present study consists of three parts: 1) thermodynamic analysis of polystyrene pyrolysis and product purification, 2) economic analysis, 3) emissions analysis.

The objective of the thermodynamic analysis was to identify one or more designs that achieve acceptable energy requirements and also opportunities for further improvements. Tradeoffs often exist between energy efficiency and cost minimization, and so specific emphasis was placed on identifying a process requiring less than 25% of the higher heating value of styrene (45.8 MJ/kg) rather than strictly minimizing energy requirements. Processes which required more energy than this were deemed infeasible, whereas processes which required less energy than this value were not emphasized since these processes could prove to be unnecessarily costly. Following the thermodynamic analysis, the costs of the design option judged most capable to balance energy efficiency and cost was analyzed in detail at different relevant scales and in the presence of irreducible uncertainty.

3.1. Thermodynamic analysis

Fig. 1 is a schematic of the process analyzed for converting waste polystyrene into styrene and other hydrocarbons. Polystyrene is fed to a pyrolysis reactor which depolymerizes polystyrene to produce the monomer along with other hydrocarbon byproducts, including toluene, ethyl benzene, and α-methyl styrene – as reported in the literature.[43–47] The stream exiting the pyrolysis reactor is condensed in the heat exchanger and styrene is then recovered by distillation in two columns. The first of these removes a light fraction consisting of toluene and ethyl benzene. The second strips styrene as the distillate from a bottoms stream consisting of a-methyl styrene and other heavy components. Heavy components are incompletely reported in the literature, but several studies indicate that styrene dimer and possibly trimer (and even higher oligomers) might be present in the bottoms fraction. Styrene dimers and higher oligomers are not included in this study as data on their concentrations are not generally available. That stated, styrene dimers and higher oligomers are much less volatile than either styrene or α-methyl styrene, meaning that separating them into the bottom stream exiting the second column will be trivial and does not impact any of the present results.

The thermodynamic analysis consisted of evaluating the total energy requirements of the pyrolysis reactor, heat exchanger, and both distillation columns. All designs were required to achieve a minimum styrene purity of 99%, which should satisfy requirements for its use as a monomer instead of as a fuel or solvent. [28] Heat integration was not considered at this stage; however, the scope for heat integration in this process is minimal (<10%). The Gilliland graphical method [48] was used as an iterative process to determine the minimum number of stages in each of the two distillation columns. The Gilliland method accounts for the tradeoff between the minimum number of stages required for a given separation considering the volatilities of the key components and the minimum reflux ratio required to achieve the targeted purity of the product. For the styrene process, the Erbar-Maddox method indicated that achieving >99% styrene purity requires that column 1 has >30 stages and a minimum reflux ratio of 4.95, whereas the second column must have at least 38 stages and a minimum reflux ratio of 1.87.

Using the ASPEN model combined with the Gilliland method for stage number optimization, the total energy required was calculated for different process designs with the number of stages in column 1 set to 40, 50, or 65, and the number of stages in column 2 set to 40, 50, 60, 70, or 80. In all cases, the fractional styrene yield was set to 0.60, consistent with the consensus of previously reported values,[43–47] and the composition of the byproducts was specified as shown in Table 1. The pyrolysis reactor temperature was fixed at 450 °C, consistent with previously reported values.[44,45].

Fig. 2 shows the results of the distillation energy analysis. Any design consisting of fewer than 50 stages in column 2 was energetically unfeasible as it required >15 MJ/kg. Similarly, any design consisting of fewer than 50 stages in column 1 required >10 MJ/kg. A design in which both columns consist of 50 stages satisfied the stated energy efficiency requirement (<10 MJ/kg) and was similar to the minimum design indicated by the Gilliland method. Fig. 2 shows that, if desired, further improvements in energy efficiency could be achieved by increasing the number of stages in either column. Specifically, increasing the number of stages in column 1 to 65 or in column 2 to 60 decreases the energy requirement to <7 MJ/kg. Increasing the number of stages beyond these values (i.e., 65 in column 1 or 60 in column 2) faces diminishing returns and is not recommended to maintain cost effectiveness.

A process consisting of a pyrolysis reactor and two distillation columns each with >50 stages meets the stated efficiency goal. That stated, the analysis summarized in Fig. 2 assumes a fixed styrene yield (0.60) that has been reported at the labscale [43–47] but may not be achieved at industrial scale. Accordingly, a sensitivity analysis was performed to determine the risks associated with underperforming relative to the 0.60 yield as well as the opportunities to be gained from achieving yields greater than 0.60. To make this analysis tractable, the relative ratios of all byproducts were fixed at the values used for the case when styrene yield was set to 0.60, as shown in Table 1.

Fig. 3 provides the results for seven different column designs and with total energy requirements estimated as a function of styrene yield varying from 0.10 to 0.90. The most likely scenario, at which styrene yield equals 0.60, is shown as a vertical line. As expected, total energy requirements decrease monotonically with increasing styrene yield. The steepness of the relationship between styrene yield and energy requirement and especially the minimum energy that can be achieved depends strongly on the number of stages in each column. Any design consisting of 40 stages in column 2 cannot achieve energy requirements less than 10 MJ/kg, even for the extreme case of a styrene yield of 0.90.

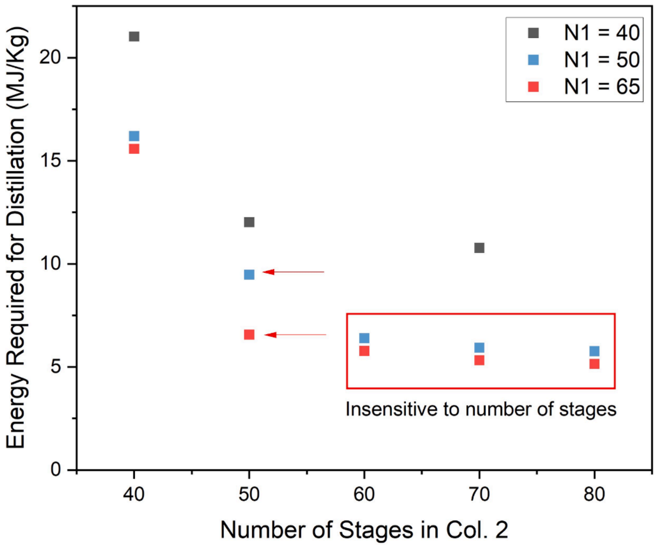

Fig. 2. Total energy required for recovery of monomer-grade styrene (>99% purity) from the pyrolysis-separation process shown in Fig. 1. The effects of the number of stages in columns 1 and 2 were considered in this analysis, which was performed using ASPEN.

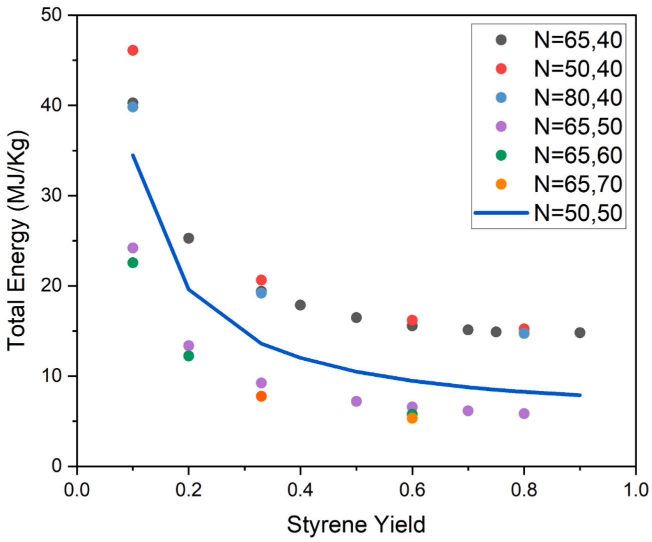

Fig. 3. Total energy required for recovery of monomer-grade styrene (>99% purity) as a function of the styrene yield obtained by polystyrene pyrolysis. The effects of stages in columns 1 and 2 were considered in this analysis, which was performed using ASPEN.

On the other hand, any design consisting of 65 stages in column 1 required <10 MJ/kg provided that styrene yield is greater than 0.3. The base design, consisting of 50 stages in both columns 1 and 2, is intermediate to these extremes, achieving a total energy requirement <10 MJ/kg at a styrene yield of approximately 0.50. Accordingly, the base design provides the desired energy efficiency for the scenario deemed most likely (styrene yield = 0.60) and safeguards against the risk of achieving less than 0.60 styrene yield without resorting to unnecessary overdesign. In comparison, designs consisting of 65 stages in column 1 and ≥50 stages in column 2 can achieve greater maximum energy efficiency than the base design while safeguarding aggressively against the risk of not achieving 0.60 styrene yield. These design options may be favored over the base design if a very risk averse strategy is preferred over the more aggressive one represented by the case consisting of 50 stages in each of the distillation columns.

The analysis shown in Fig. 3 assumes that styrene yield is independent of pyrolysis reactor temperature, which is not consistent with theoretical considerations.[27] The temperature of the pyrolysis reactor impacts energy requirements and so an additional sensitivity analysis to pyrolysis temperature was performed for the base case (i.e., in which both columns 1 and 2 consist of 50 stages). The results of the pyrolysis temperature analysis are shown in Fig. 4, in which pyrolysis reactor temperature varies from 300 to 450 °C independently of styrene yield, which was varied from 0.10 to 0.90. Experimentally, styrene yield depends on pyrolysis temperature, and the results of Fig. 4 should be considered solely as a thermodynamic sensitivity analysis. Fortunately, the pyrolysis temperature energy analysis indicates that energy requirements are nearly insensitive to pyrolysis reactor temperature, provided that styrene yield is greater than 0.33 which should be easily achievable. For the base case with a styrene yield of 0.60, the entire range of estimated energy requirements varies by less than 1.5 MJ/kg for the extremely conservative range of temperatures considered here, from 300 to 450 °C. Accordingly, Fig. 4 indicates that the base design is very robust in the presence of minor deviations in pyrolysis temperature that may be required to achieve a styrene yield of 0.60 in industrial practice.

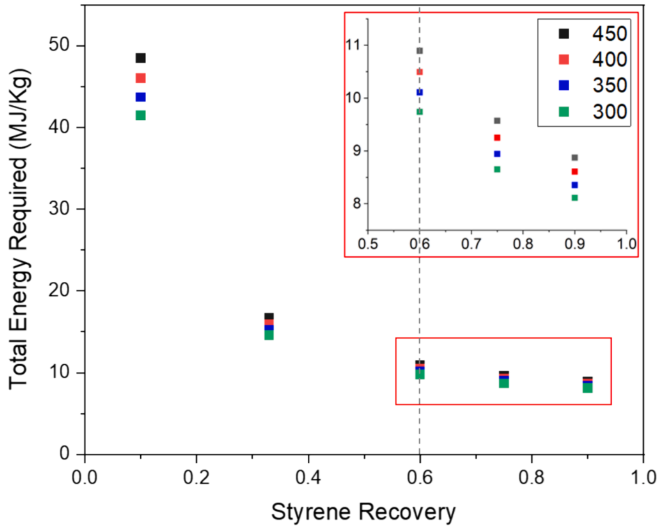

Fig. 4. Total energy required for recovery of monomer-grade styrene (>99% purity) as a function of the styrene yield obtained by polystyrene pyrolysis for a base case consisting of equal numbers of stages (50) in both column 1 and 2. The effects of different pyrolysis reactor temperatures on energy requirements are considered as a sensitivity analysis. The vertical line depicts the most likely styrene yield based on values reported at the labscale [43–47].

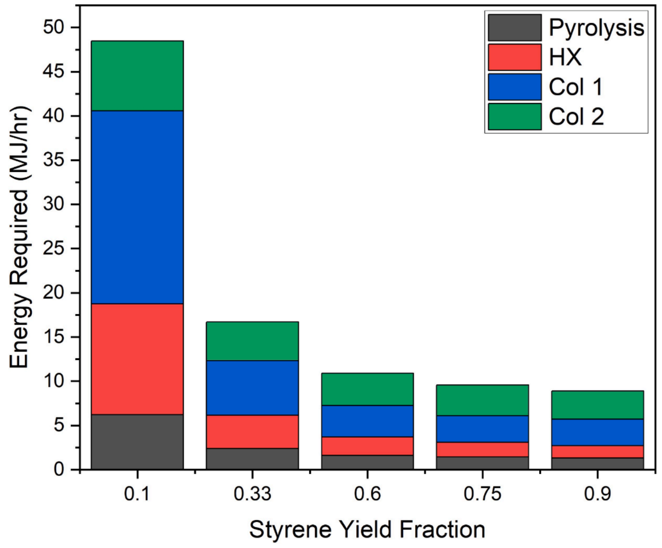

Fig. 5. Total energy required by the styrene process consisting of two columns each with 50 stages and a pyrolysis reactor operating at 450 °C. Contributions from the four main steps, pyrolysis, heat exchange, and the two columns, are shown for each case at different fixed value of styrene yield.

Next, the contributions of different process steps to the total energy were analyzed to rationalize the lack of sensitivity of total energy requirements on pyrolysis reactor temperature and to identify approaches for future improvements in energy efficiency. Fig. 5 summarizes the results, showing individual contributions to total energy requirements at styrene yields varying from 0.10 to 0.90 at a fixed pyrolysis reactor temperature of 450 °C and for a design consisting of two columns each with 50 stages. In all cases, the energy requirements of the two columns represent >50% of the total energy required by the process. For what is deemed the most likely scenario, corresponding to a styrene yield of 0.60, distillation accounts for approximately 65% of the total energy required by the process. For any styrene yield equal to or greater than 0.60, the energy requirements of the two columns are nearly equal to one another, indicating that improving the energy efficiency of either of these two columns can be effective for reducing overall energy requirements. Improving the energy efficiency of the pyrolysis reactor heat duty or heat exchanger condenser are secondarily important compared with improving the efficiency of the distillation columns. The results of Fig. 5 are therefore entirely consistent with process design experience gathered primarily from petrochemicals feeds, [49] despite the fact that this process is for chemical recycling of a waste plastic rather than production of monomers from petroleum feedstock.

One final thermodynamic analysis was performed to evaluate the relationship between process design and performance, specifically the effects of design on styrene recovery and purity. Both recovery and purity are key performance parameters, since achieving a styrene purity >99% is required for its use as a monomer; and, at the same time, maximizing styrene recovery is required both for atom and energy efficiency. Fig. 6 summarizes results obtained from a series of simulations performed at a fixed pyrolysis reactor temperature of 450 °C. Results obtained from various column designs, all of which consisted of ≥40 stages in both column 1 and column 2, are shown in Fig. 6. Interestingly, the effect of the number of stages and styrene recovery or purity was negligible (less than 0.1%), resulting in purity and recovery values that are indiscernible from one another in Fig. 6. Consistent with the Gilliland method, which was performed at a styrene yield of 0.6 to achieve >99% purity, all of the column configurations considered here can produce monomer-grade styrene provided that the styrene yield exceeds 0.60. In fact, styrene purity >99% can be achieved provided that styrene yield is greater than equal to 0.20, a value which should easily be achieved at industrial scale given that 0.60 is routinely observed at the labscale. Styrene recovery nearly matches styrene yield, consistent with recovery of >98% of all styrene produced by polystyrene pyrolysis at all values of styrene yield. Fig. 6 therefore establishes that the styrene monomer process can easily and robustly achieve purities greater than 99% with >98% recovery of all styrene produced from pyrolysis.

The thermodynamic analysis presented here is appropriate for pyrolysis in the absence of catalysts. Various types of catalysts have been reported for polystyrene depolymerization, as recently summarized in a

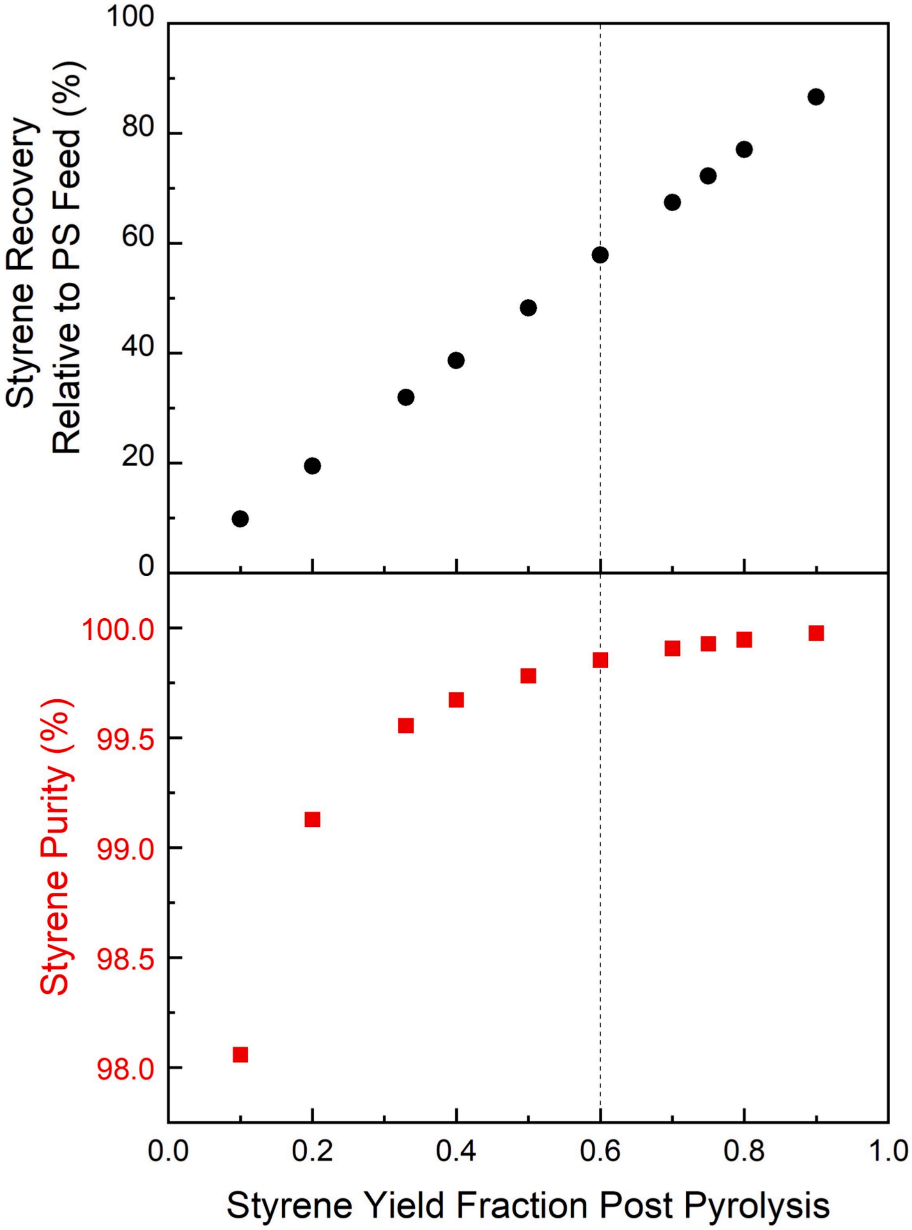

Fig. 6. Styrene recovery (top panel) and styrene purity (bottom) panel achieved for different column designs at different fixed values of styrene yield. All designs considered here required that both columns have ≥ 40 trays and the pyrolysis reactor temperature was fixed at 450 °C. No dependence on the number of columns was observed, resulting in all of the different designs corresponding to numerically identical (within 0.1%) values of both styrene recovery and styrene yield. The vertical line depicts the most likely styrene yield based on values reported at the lab scale [43–47].

review paper by Maafa.[24] In many cases, addition of catalyst boosts yields of liquid pyrolysis oil. However, the effect on styrene yields is not uniform and typically leads to decreases relative to the uncatalyzed case; [50] in some cases, even the liquid oil yield is decreased by catalyst addition.[51] Moreover, catalyst lifetime for this process has not yet been established, greatly detracting from the near-term deployability of catalytic polystyrene pyrolysis. For these reasons, catalyzed depolymerization was not included in the current study, though future catalyst approaches that boost styrene yields would certainly be of value. In that case, the present study serves as a baseline for comparison and a target for styrene yields that must be achieved in order to have the desired improvement in energy efficiency – for example, by using Figs. 3 and 4 to predict energy requirements corresponding to the styrene yields that can be achieved catalytically.

3.2. *Technoeconomic analysis*

Thermodynamic analysis establishes that monomer grade styrene can be obtained from waste polystyrene using a scalable process consisting of a pyrolysis reactor and two distillation columns. A base case, consisting of two columns each with 50 stages, a pyrolysis reactor operating at 450 °C, and at a fixed styrene yield of 0.60, was identified for producing >99% purity styrene with a total energy requirement <10 MJ/kg. Table 4 is a stream chart showing mass flows and associated heating values for all of the streams in the base case at a scale of 30 TPD. Interestingly, the heavy fraction produced in the base case scenario, which consists primarily of a-methyl styrene and styrene dimers, contains sufficiency exergy to offset 82% of the total energy requirement – assuming that the process requires 10 MJ/kg of styrene produced (i.e., total energy requirement is 133 kg/hr × 10 MJ/kg = 6550 MJ/h, compared with 5,300 MJ/h from Table 4). The light fraction, consisting primarily of ethyl benzene and toluene, provides opportunities for coproduct design – either as solvent,[52] as an octane booster to gasoline,[53] or as individual chemicals if they are separated from one another using an additional distillation column. If all of these high-value applications are deemed intractable, the light fraction can be used to offset internal energy requirements, which would render the styrene process energy neutral when considering the combined exergy of the heavy and light fractions. Any of these options can be explored in future work to improve economics by adding side products or improve energy efficiency.

The next step was to evaluate the economic performance of the base case in which neither the light nor heavy fraction is valorized. The ASPEN Economic Process Analyzer was used for cost analysis for a range of process scales. As an example, equipment costs are shown in Table 5 for a process scale of 30 TPD of polystyrene. Interestingly, the distillation columns account for 95% of the total equipment costs, supporting the decision to focus on configurations with the fewest number of stages as feasible to achieve the desired energy efficiency. The estimated pyrolysis reactor cost is <5% of the total equipment cost, a value which may appear unrealistically optimistic. However, comparing the cost estimated here with one reported recently by the National Renewable Energy Laboratory [54] and accounting for a scale factor of 0.7 indicates that the ASPEN-based estimate here agrees with previous reactor cost estimates within 20%, which is more than adequate for cost projection of the type presented here.

Table 4
Stream Table with Mass Flow Rates and Stream Heating Content for 30 TPD Polystyrene Chemical Recycling Process.

	Stream Feed	Light Fraction	Styrene Product	Heavy Fraction
Total Flowrate (kg/h)	1134	350	655	128
Mass Fraction				
Styrene	0	0.073	0.999	0.001
Benzene	0	0.272	0	0
Toluene	0	0.385	trace	trace
Ethylbenzene	0	0.27	0.001	trace
α-methyl styrene	0	0	trace	0.999
Polystyrene	1	0	0	0
HHV (MJ/kg)	41.7	42.8	48.7	41.6
Stream Heat Content (MJ/h)	47,300	15,000	31,900	5,300

Table 5
Total equipment cost based on ASPEN Economic Process Analyzer for a plant processing 30 TPD of polystyrene.

Equipment	Cost [$ US]
Heat Exchanger	11,200
Column 2	633,700
Pyrolysis Reactor	53,500
Column 1	632,600
Total Equipment Cost [$ US]	1,331,000

Process economics depend strongly on scale,[38] and achieving profitable scales is a common challenge for waste processes. Unlike petroleum sources, which are either spatially localized or easy to transport by pipeline or tanker, waste feedstock is spatially distributed and not easily transported due to its low energy density. Accordingly, the scale of processes that utilize waste feeds is a crucial consideration for costs and unrealistically optimistic costs can be projected if data about source availability is not considered. A reasonable basis for scaling the styrene process is the size of municipal recycling facilities (MRFs), for example in the U.S., and the relative quantity of polystyrene available in their waste streams. Based on available data on municipal recycling facility scale [55] and the composition of plastic waste in the U.S.,[56] process scales from 15 to 120 TPD are realistic for a polystyrene process. The higher end of this scale is larger than any single municipal recycling facility in the U.S., meaning that the inputs of several facilities could be combined in a single pyrolysis location, a type of hub-and-spoke approach. Heavily populated regions of the U.S., EU, or Asia are reasonable candidates for the hub-and-spoke configuration. Analyzing the costs associated with aggregating the waste from multiple recycling facilities has been considered for similar problems elsewhere. [57].

A further consideration relevant to process economics is feedstock cost. In many cases, real negative costs can be realized for waste feedstocks, especially in locations with legislation that incentivizes landfill diversion.[58] As a first estimation, we analyzed process costs using the conservative rule-of-thumb that feedstock costs are 15 ± 5% of total product costs, calculated as the sum of direct production costs and general expenses (see Table 3). Other feedstock costs scenarios are considered later.

With the range of process scales determined and with the assumption of fixed positive feedstock costs settled, total capital investment and total production costs (as defined in Table 3) were estimated for styrene processes ranging from 15 to 120 TPD, on a polystyrene feed basis. Monte Carlo simulations were performed at each scale to estimate the effects of irreducible uncertainty on costs [59]. Fig. 7 summarizes the results. Interestingly, total product cost far outweighs total capital investment, indicating that the initial investment should not be prohibitive in most cases. The low initial investment is a definitive advantage for distributed processes, with the additional benefit that new capacity can be brought online simply by adding new factories, and is a direct consequence of selecting familiar, technology ready process units. Low capital cost argues for a modular design that can benefit from technological learning to further reduce costs [60]. Similarly, projected uncertainties for total capital costs are always less than 10%; total product cost uncertainties, on the other hand, are on the order of 25%, indicating greater uncertainty associated with operating expenses than are predicted for capital investment. Actual experience at pilot scale will reduce this uncertainty.

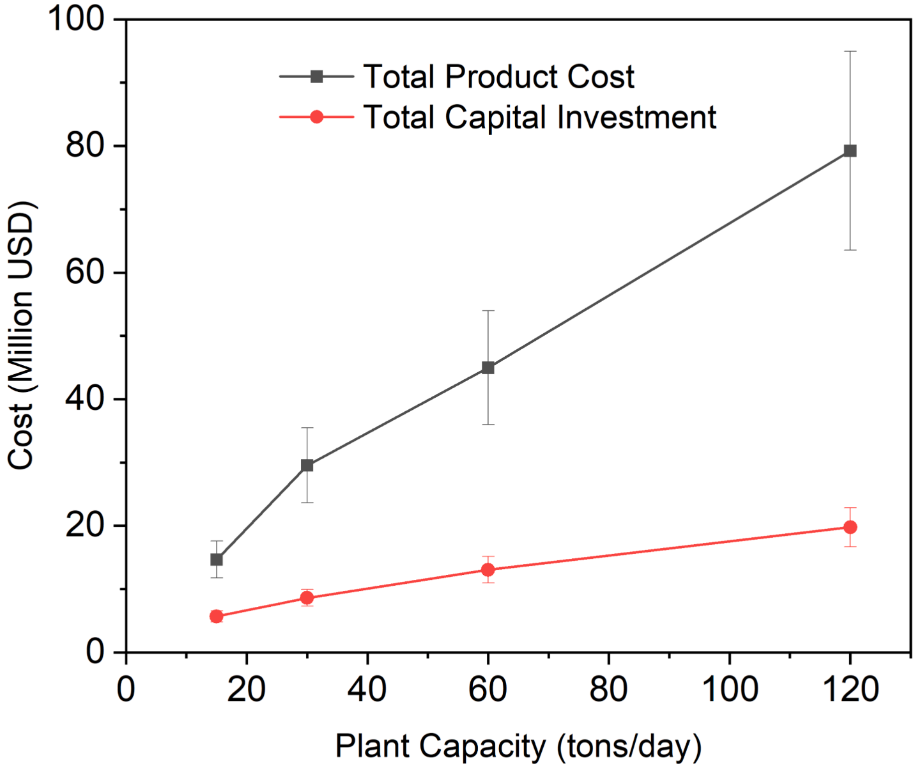

Fig. 7. Total product cost (per year) and total capital investment for the base case styrene process scenario (i.e., 60% styrene yield, 450 °C pyrolysis reactor temperature, 50 stages in each distillation column) as a function of plant capacity. Uncertainty bars represent standard deviations corresponding to 10,000 simulations performed using uniform distributions for key input parameter values, an analysis performed using Monte Carlo simulation methods.

The next analysis was to calculate the Levelized Production Cost of styrene production, as defined in Table 3 and as used in previous studies. [36,39,40] The analysis was performed at different scales, corresponding to the entirety of the range shown in Fig. 8, and for the conservative estimate that feedstock costs are equal to 15 ±5% of total product cost as well as a new scenario in which feedstock costs are set to zero. The four scenarios corresponding to positive feedstock cost indicate decreasing levelized styrene production costs with increasing scale, as expected. Interestingly, at a scale of 120 TPD, the levelized styrene production cost is $2.09 ± $0.21 per kg, where the uncertainty is determined as the standard deviation of 10,000 Monte Carlo simulations. These costs are roughly twice the 2023 selling price of styrene on the commodities market [61]. While doubling the cost of styrene – and hence polystyrene – is not a favorable economic outcome, some context is required. The primary application for polystyrene is in packaging, especially for markets such as electronics, automotive parts, and food. In these cases, packaging accounts for a small fraction of the total product cost, meaning that doubling the cost of packaging might easily be absorbed. Of course, further cost reductions might be realized by further increases in process scale by aggregating feeds from multiple recycling facilities, up to the limits that are feasible in the presence of transportation costs. On the other hand, Levelized Production Costs presented here do not include depreciation of capital expenses; including these would tend to increase costs. That correction is modest given the relative values of Total Capital Cost and Total Product Cost, shown in Fig. 7.

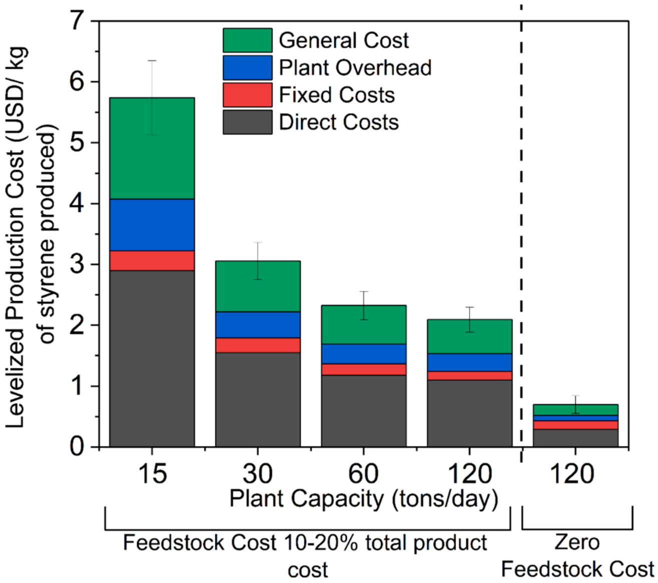

Fig. 8. Levelized styrene cost for the base case styrene process scenario (i.e., 60% styrene yield, 450 °C pyrolysis reactor temperature, 50 stages in each distillation column) as a function of plant capacity and for feedstock costs equivalent to 10–20% of total product cost. An additional scenario is shown at a capacity of 120 TPD and at zero feedstock costs. Total costs are apportioned into general costs, plant overhead, fixed costs, and direct costs as shown. Uncertainty bars represent standard deviations corresponding to 10,000 simulations performed using different values for key input parameters, an analysis performed using Monte Carlo simulation methods.

A single analysis of the zero feedstock cost scenario is provided in Fig. 8, at a fixed scale of 120 TPD. Real negative feedstock costs can often be realized for waste feeds, even when accounting for transportation costs.[58] Accordingly, a zero feedstock cost is a reasonable scenario to consider on its own merits. Furthermore, results from the zero feedstock cost scenario serves to estimate sensitivity. Assuming zero feedstock cost, reduces the projected Levelized Production Cost to less than $1/kg of styrene, substantially less than its average historical selling price. Uncertainty for the zero feedstock cost scenario estimated assuming a feedstock cost uncertainty of ±$60/ton was $0.70/kg ±

$0.14/kg. The reasonable cost and manageable cost uncertainty for the zero feedstock cost scenario both indicate a potential avenue for commercialization.

Assuming 60% styrene yield from polystyrene pyrolysis and complete conversion of the recovered monomer back into polystyrene corresponds to a maximum polystyrene recycle rate of 60% that can be achieved by chemical recycling. This estimate is the upper ceiling for 60% styrene yield from pyrolysis since it assumes 100% recovery of in use polystyrene. Given that no existing technology can recycle polystyrene, the estimated 60% possible yield via pyrolysis and distillation is a useful value framing the discussion. Increasing the potential maximum recycling rate requires increasing the styrene yield from pyrolysis, which is an interesting observation given that the thermodynamic performance of the process is relatively insensitive to styrene yield. The potential to achieve 60% polystyrene recycling using familiar, scalable technologies, to a direct replacement, at near cost parity, and with manageable energy inputs can therefore be considered a surprising and promising result.

Fig. 8 breaks out different cost categories that contribute to the overall Levelized Production Cost of styrene production. In all cases, direct costs – which include feedstock costs among other contributions as summarized in Tables 1 and 2 – represent the single greatest cost category. In the four cases in which feedstock is assigned a positive value, direct costs represent approximately 65% of total production costs. For the zero-cost feedstock scenario, direct costs are roughly 50% of the total production cost, which is a natural consequence of the inclusion of feedstock costs in direct costs. Accordingly, the cost category data included in Fig. 8 further emphasizes the importance of minimizing feedstock as a means of managing production costs.

The effects of uncertainty on the total production cost for the proposed process system were analyzed through Tornado diagrams and the results of the analysis are presented in Fig. 9. A Tornado diagram graphically summarizes the relative impact of variations of key uncertain cost model inputs over their respective ranges (from the lowest to the highest value) under the assumption that all other model inputs remain fixed at their baseline values. In a Tornado diagram each model input is represented by a bar as it varies over its prescribed range, thus depicting its impact on total production cost. In this manner, a Tornado diagram ranks and prioritizes the most consequential model inputs (sources of uncertainty) in terms of bar length and facilitates the

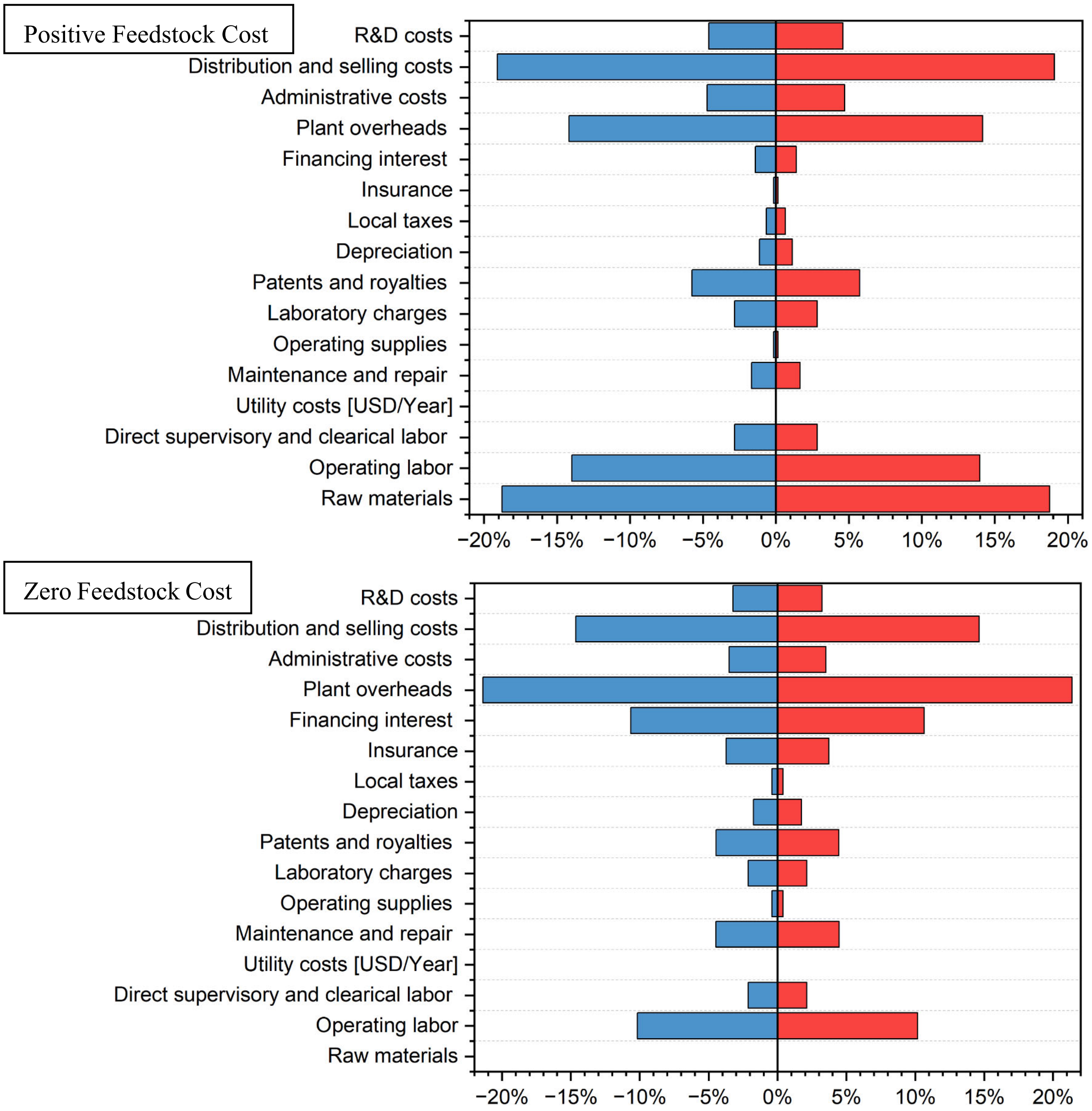

Fig. 9. Results from economic sensitivity analysis to key input parameters. Sensitivity is independent of scale. Two scenarios are considered, one with positive feedstock cost corresponding to 15% of total product costs (with ± 5% uncertainty) and one with zero feedstock cost.

visualization of their respective impact on process system economic performance.

Fig. 9 summarizes the results of the above sensitivity analysis. Preliminary calculations, not included here, revealed that sensitivity is independent of scale. Accordingly, sensitivity analysis is shown to feedstock cost, choosing two specific scenarios: the positive cost and zero cost cases considered in Fig. 8. In both of these scenarios, total costs are most sensitive to uncertainty in raw material costs and product selling costs, followed by uncertainty in plant overhead and operating labor. Sensitivities to all other input parameters are much less than to these four. Fig. 9 therefore clearly indicates that stability in the styrene selling price and the polystyrene purchase cost are key factors that control risk.

Historical variation of styrene prices is ± 14% during the time period including 2017–2022.[62] Given the turbulent economic conditions during this time period, 14% variation likely represents acceptable uncertainty. Sensitivity to feedstock cost and competitiveness with styrene market prices shown in Figs. 8 and 9 motivate further analysis. In particular, the assumption that feedstock cost is a fixed percentage of total product cost, long used as a valid assumption when petroleum is the feedstock,[38]may not apply in cases with waste feeds. Fig. 10 is a Monte Carlo sensitivity analysis of the net present value (NPV) of a 120 ton/day polystyrene process that produces styrene monomer and heavy and light byproducts. The value of feedstock is fixed at three values in Fig. 10: −60, 0, and 60 $/ton. Other inputs are allowed to vary randomly and independently of one another as in previous analyses and as shown in Tables 2 and 3, resulting in probability distribution curves. Consistent with Figs. 8 and 9, the expected NPV of the zero feedstock cost scenario is positive. Interestingly, Monte Carlo analysis predicts a 100% chance that the zero feedstock cost scenario results in positive NPV, indicating a low level of risk. Similarly, the negative feedstock cost scenario results in 100% probability of positive NPV, as should be expected from the results obtained from the zero feedstock cost analysis. Surprisingly, the expected NPV for the scenario with feedstock cost fixed at +$60/ton is positive, indicating that even realistically positive feedstock costs [63] can reasonably be expected to result in promising economic projections. In fact, the probability that the scenario with a feedstock cost of +$60/ton is predicted to result in positive NPV 96% of the time. Accordingly, realistically positive feedstock costs are predicted to result in viable economics with low risk of loss. Table 6 summarizes expected NPVs and other key values corresponding to the Monte Carlo NPV analysis shown in Fig. 10.

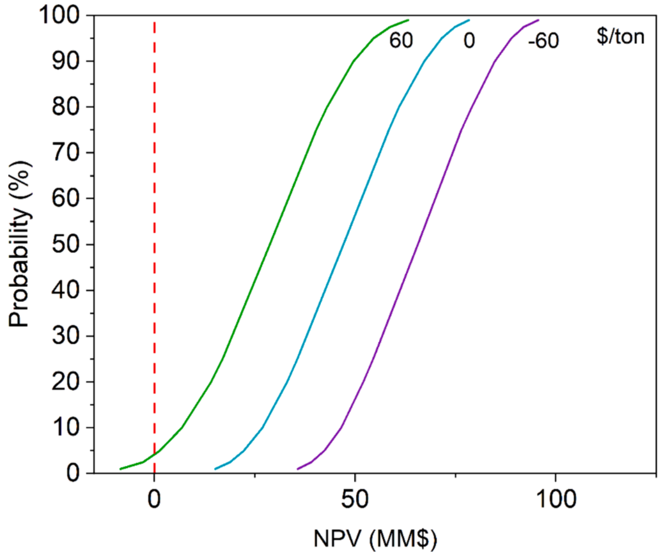

Fig. 10. NPV probability distribution curves predicted for a 120 ton/day at fixed values of polystyrene feedstock cost, as shown.

Table 6
Key Values and Economic Performance Metrics Derived from the NPV profile's (shown in Fig. 10) probabilistic analysis and characterization.

Feedstock Cost →	−60	0	+60
Expected Value $MM	66	47	28
Standard Deviation $MM	14	15	16
5% Probability Value ("Value at Risk"), $MM	42	22	1
95% Probability Value ("Value at Opportunity"), $MM	89	72	55
% Probability of Negative NPV	0	100	96

3.3. *Emissions analysis.*

Promising economic projections encourage consideration of greenhouse gas emissions. Two scenarios were included in the analysis: 1) pyrolysis to produce a crude oil that is refined to produce a fuel, 2) pyrolysis to produce styrene monomer (60%) and a crude oil that is refined to produce a fuel. The analysis was performed with the refining emissions set to zero and to a value of 2.5 Mton/yr, following the recommendation by van Straelen et al.[42] Refinery emissions depend on many factors, including the refinery itself, the characteristics of the petroleum feed being processed, and the product slate that the refinery is targeting.[64,65] The value used here is considered a composite average that accounts for these factors. The first step, shown in Table 7, was to calculate the CO_2 emissions for the two scenarios, both with and without inclusion of refinery emissions. Styrene production reduces CO_2 emissions by roughly 50%, since the styrene that constitutes 60% of the product is not combusted to form CO_2 unlike the pyrolysis oil. Including refinery emissions in the analysis increases CO_2 emissions by approximately 5%, indicating a minor correction. On the other hand, recovery of secondary products – such as ethyl benzene, toluene, and benzene – has the potential to reduce the CO_2 emissions by amounts corresponding roughly to their respective compositions in the pyrolysis oil product stream (Table 1), minus the emissions associated with the energy input to purify them by distillation. The analysis shown in Table 7 indicates that the distillation emissions will be much less than those associated with combustion.

The next step was to calculate an associated cost. Since the NPV of the 120 ton/day scenario was always positive, the CAPEX of this scenario was used for calculating abatement costs. Values are provided in Table 7, averaged over the assumed 30-year project lifetime and

Table 7
CO_2 Abatement Analysis.

Scenario	Process Components	CAPEX over 30 yr lifetime ($/h)	Additional emissions	CO_2 Emissions (ton/h)
Polystyrene conversion to fuel with combustion	Feeding system, heat exchanger, pyrolysis reactor	0.52	Refinery Emissions Excluded	15.5
			Refinery Emissions Included	16.3
Polystyrene conversion to monomer (60%) and fuels with combustion (40%)	Feeding system, heat exchanger, pyrolysis reactor, distillation columns	12.87	Refinery Emissions Excluded	7.3
			Refinery Emissions Included	7.7
CO_2 Abatement Costs				
Excluding refinery emissions $/ton	1.50	Comparison of monomers (60%) and fuels (40%) to fuels only		
Including refinery emissions $/ton	1.43			

calculated on an hourly basis. Inclusion of the distillation columns required for styrene recovery increases the CAPEX relative to the pyrolysis to fuel scenario by a factor of roughly 20, as shown in Table 7.

Combining the CAPEX values and CO_2 emissions from Table 7 results in CO_2 abatement cost values, as explained in the Methodology Section 2, which is calculated for cases both including and excluding refinery emissions. In both cases, CO_2 abatement costs are approximately $1.5/ton, a very reasonable value compared with other technologies.[66] In fact, the CO_2 abatement costs are comparable to low-hanging fruit associated with voluntary conservation practices.[66] The CO_2 abatement analysis, when combined with the NPV analysis, establishes the feasibility and desirability of the polystyrene chemical recycling process. Because distillation emissions are much less than those associated with combustion, addition of more distillation columns to recover more chemicals – especially from the light fraction – has the potential to reduce the CO_2 abatement costs relative to those shown in Table 7, provided that the CAPEX of the additional distillation columns justifies the emissions reductions. Evaluating further valorization of the chemical content of the light fraction is justified especially by the large markets and high values. As a representative example, the price of benzene in 2022 was $800/ton [67] with a total market size of $94B (US) that is forecast to grow to $122B by 2030.[68] Alternatively, the light fraction mixture might be valorized without separation as a crude solvent product, albeit with less market value than the purified constituents. The major constituent in the bottoms fraction is α-methyl styrene, which has applications in the synthesis of acrylonitrile–butadiene–styrene type polymers,[69] making α-methyl styrene a potential chemical of interest that can be recovered from polystyrene pyrolysis products.

A major implicit assumptions embedded in the CO_2 abatement analysis is that landfilling plastics is not an option, since landfilling plastics might sequester carbon entirely at least until the year 2100.[70] Landfill saturation is being approached in many locations, [71,72] and diverting plastics from landfills is an obvious solution to reduce the burden on existing landfills. In this case, conversion of waste plastics to chemicals can play a clear role. While the predicted economics of converting polystyrene to monomer are competitive, they are sensitive to key technological factors such as feedstock cost and scale. Policies that incentivize recycling so that customers are willing to pay a premium for recycled polystyrene can benefit economics, provided that the incentives are stable. Similarly, policies that incentivize diversion from landfill can have a major impact on process economics. On the other hand, uncertainties in these policies will necessarily increase the risks made to any investment. Regardless of policies that favor recycling or their political uncertainties, a chief barrier to translation is risk. Lastly, the study advocates for distributed chemical recycling capacity, with the size of each individual factory a fraction that of a full-scale petroleum refinery. For this distributed manufacturing approach, concerns about the impact on the local environment cannot be neglected since it could potentially be felt by many communities. Local environmental considerations introduce risk. However, with appropriate mitigation efforts, the polystyrene approach presented here minimizes risk by using well-known, scalable unit operations configured in a novel way, as opposed to entirely novel unit operations with unknown scalability.

4. Conclusions

Polystyrene is an ideal candidate for chemical recycling: no viable alternative is available at scale and its depolymerization provides much higher selectivity to the monomer than depolymerization of any of the other commonly used plastics. This study used ASPEN and @Risk software to probabilistically evaluate the thermodynamic and economic performance profile of a proposed polystyrene chemical recycling process consisting of a pyrolysis reactor, condensation heat exchanger, and two distillation columns in the presence of multiple sources of uncertainty. Thermodynamic analysis indicated that when pyrolysis can achieve a >0.60 monomer yield at 450 °C the total energy requirement is <10 MJ/kg. Sensitivity analysis of the distillation column design indicated scope to decrease this value to roughly 7 MJ/kg, albeit for distillation column designs that are typically considered sub-optimal balances of energy use and capital cost. Sensitivity analysis to the styrene yield and pyrolysis temperature indicated that reasonable variance from the assumed conditions (0.60 styrene yield and 450 °C pyrolysis conditions) resulted in acceptable differences in total energy requirement and a negligible loss of styrene purity. Economic analysis evaluated the effects of process scale and feedstock costs on levelized styrene production costs. At the largest scale considered reasonable, 120 TPD, and with positive feedstock cost, the levelized styrene production cost was approximately twice the historical average. At the same scale and with zero feedstock cost, the Levelized Production Cost was less than $1 kg of styrene. It was also found that the Net Present Value of the zero feedstock scenario over a range of operating conditions remains positive and the corresponding CO_2 abatement costs are roughly $1.5 per ton of CO_2 averted, relative to a scenario in which polystyrene is pyrolyzed for fuel production. Finally, it was demonstrated that chemical recycling and landfill diversion programs can play a key role in promoting reduced production of virgin polystyrene and ultimately less waste in landfills and the environment.

CRediT authorship contribution statement

Madison R. Reed: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Elizabeth R. Belden:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Nikolaos K. Kazantzis:** Writing – review & editing, Writing – original draft, Supervision, Methodology. **Michael T. Timko:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **Bernardo Castro-Dominguez:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Elizabeth R. Belden reports financial support was provided by National Science Foundation. Madison R. Reed reports financial support was provided by National Science Foundation. Michael T. Timko reports financial support was provided by National Science Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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