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Aromatics from Lignocellulosic Biomass: Economic Analysis of the Production of p-Xylene from 5-Hydroxymethylfurfural

Zhaojia Lin and Marianthi Ierapetritou
Dept. of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey,
98 Brett Rd, Piscataway, NJ 08854

Vladimiros Nikolakis
Catalysis Center for Energy Innovation and Dept. of Chemical & Biomolecular Engineering,
University of Delaware, Newark, DE 19716

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A novel production of biobased p-xylene from hydroxymethylfurfual has been investigated and presented. This is an important part of a process for the production of aromatics from lignocellulosic biomass. The detailed flow sheets are designed based on laboratory experiments by Leshkov et al. and William et al. and economic analysis has been performed. The minimum biobased p-xylene cost is estimated as $3,962/metric ton, of which the main contribution comes from the HMF cost. Sensitivity analysis has been used to assess the impact of uncertainties of economic parameters and also to determine the most significant reaction factor in the technological development, i.e., selectivity and conversion. It has been shown that high selectivity is favored at the same yield.
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Introduction

Most fuel and chemicals are commonly made from petroleum resources. As a result during the last few decades, petrochemical processes have reached maturity leading to inexpensive production of most commonly used chemicals. However, depleting oil reserves, increasing petroleum price and rising environmental concerns motivated the development of renewable alternatives. Biomass has the potential to become such an alternative to the production of both high-volume, low-value fuels and high-value chemicals at the same time.[3] Among these high-valued chemicals, biomass-based p-xylene has caught considerable attention because it is widely used as a raw material to produce polymers. Particularly, p-xylene can be oxidized to terephthalic acid (TA) with high selectivity that results to a minimum 95% yield of TA.[4] Consequently, TA can react with ethylene glycol to produce polyester poly(ethylene terephthalate) (PET)—a polymer resin broadly used in the synthesis of fibers, films, and beverage containers.[5] Several big companies, such as Coca Cola, Pepsi, and Procter and Gamble, have announced that they plan to replace their PET products with biobased PET.[6–8]

To the best of our knowledge, there are few scale-up production units of biobased p-xylene as well as of other biobased chemicals. Gevo, Inc. and Virent Energy system, Inc. have both reported new technologies to produce biobased p-xylene in pilot scale.[9,10] In Gevo's invention, isobutanol derived from biomass fermentation is converted to p-xylene following dehydration, dimerization and dehydrocyclization (described in detail in Appendix A).[10] Virent developed the conversion process to produce a series of chemicals via hydrocarbon oxidation, which includes p-xylene.[11] No details are provided to enable the evaluation of Virent process.

P-xylene production from 5-hydroxymethylfurfural (HMF) can become another biobased alternative. HMF is noted as one of the 10 most promising biomass-derived intermediate chemicals to produce fuels, chemicals and polymers,[12] and can be produced from the isomerization of glucose to fructose and the subsequent dehydration of fructose to HMF.[1,2,13–16] One big advantage of this route is that only p-xylene, but not benzene, toluene or other xylene isomers are formed, which are byproducts in existing petroleum process that produces p-xylene via catalytic reforming of naphtha and the other alternative commercial biobased processes patented by Gevo.[10,17] As a result, simpler purification processes are needed.

The production of p-xylene from HMF mainly involves three reactions: the hydrodeoxygenation of HMF to 2,5-dimethylfuran (DMF)[1,15,16] and the Diels–Alder cycloaddition of ethylene to DMF followed by dehydration of the intermediate to p-xylene.[2,13,14] In terms of the hydrodeoxygenation of HMF, Leshkov et al. demonstrated the DMF synthesis from HMF in either the liquid-phase or vapor-phase using a 3:2 Cu:Ru/C catalyst. The vapor-phase hydrogenolysis had better performance in terms of selectivity and conversion. The overall yield of DMF is 76 to 79%.[1] Later,

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Correspondence concerning this article should be addressed to M. Ierapetritou at marianth@soemail.rutgers.edu.

Chidambaram et al. reported that the production of DMF using heteropolyacids in ionic liquids showed low DMF yields from HMF despite nearly 100% yield of HMF from fructose.[16] Improved DMF yields can be obtained by using formic acid as a hydrogen source in THF solvent via Pd/C catalyst. The reaction achieved 88% yield of DMF.[15] In addition, Brandvold introduced the idea to produce the p-xylene from DMF from a cycloaddition reaction using high-surface-area activated carbon mixed with H_3PO_4. The minimum achieved selectivity and conversion were 60 and 50%, respectively.[13] Another alternative path for p-xylene synthesis, studied by Shiramizu et al. is the reaction of DMF with acrolein, formed by glycerol dehydration. The reaction was carried out at 213 K with 34% overall yield of p-xylene.[14] Most recently, William et al. were able to achieve 95% conversion and 75% selectivity of p-xylene starting with DMF and ethylene and using n-heptane as solvent/diluent and H—Y zeolite as dehydration catalyst.[2] Each of the different aforementioned conversion paths has different advantages in terms of biomass feedstock, high yield and low-utility costs.

The commercial production of biobased products is restricted due to the different nature of raw materials, especially related to oxygen content, that require different reaction and separation processes.[18] A number of technological developments of conversion process as mentioned[1,2,13–16] provide some alternatives to overcome some barriers. Economic analysis is a useful tool to evaluate these alternatives and to determine the most important parameters of the process that have to be improved to promote process commercialization.

A biobased p-xylene production process can be envisioned to use cellulose as starting raw material that on depolymerization forms glucose, which can be considered as raw material for HMF production. Kazi et al. and Torres et al.[19,20] performed an economic analysis of HMF production from fructose and roughly reached similar conclusions. The effect of using a glucose as starting raw material together with efficient isomerization processes on HMF economics has also been considered.[20] Given the facts that PET production from p-xylene is exactly the same as its oil-based alternative, this work will focus on the economic analysis of the production of p-xylene from HMF using the economic estimations of Kazi et al. and Torres et al.[19,20] The different reaction alternatives[1,2,13–16] have been evaluated based on the rough estimation of costs from raw materials, utilities and equipment. It has been found that the path combining the reactions proposed by Leshkov et al. and William et al.[1,2] is the most economical route. Thus, we have proposed the corresponding flow sheets and assess the costs of this process in detail.

The aim of this work is to study the feasibility of the production of biobased p-xylene from HMF and estimate the minimum cost of biobased p-xylene. Sensitivity analysis is performed to address the impacts of uncertainties of economic parameters such as the plant capacity, the costs of raw materials and catalysts cost, and the most significant reaction factor of the technological development, i.e., conversion and selectivity of the involved reactions. The rest of the manuscript is structured as follows. In the section of method, we compare the production paths and give a detailed description on the block diagram of the production of p-xylene from HMF. Next, the methods and the assumptions of the simulation and economic analysis are also defined in this section. Finally, the results of different scenarios are studied and discussed, which involves both simulation and economic analysis results. In Appendix A, we describe and discuss the existing Gevo process.

Method

Production and purification of p-xylene

The theoretical minimum product price for the aforementioned process alternatives[1,2,13–16] is calculated mainly based on the estimation of raw materials, utilities and equipment cost. High yield is always preferred in terms of low-theoretical product price. The major equipment cost is assessed by order-of-magnitude estimation based on cost data of the similar size.[21] The raw material and utilities costs are also important factors to select a promising process. For example, the DMF yield of the reaction of HMF and formic acid is 88%,[15] whereas the formic acid price is around $1,250/metric ton.[22] Thus, the effective hydrogen cost is around 52 times that of pure hydrogen; whereas the reaction of DMF and acrolein[14] is less attractive since high-utility costs are roughly estimated in order to meet the refrigeration needs, and due to the fact that acrolein is an extremely hazardous chemical that requires special handling.[23] Thus, the synthesis path shown in Figure 1 appears to be the most promising and realizable.

The synthesis path involves two reactions. In the first reaction a 10 wt % HMF in 1-hexanol solution reacts with hydrogen to produce DMF via two intermediates (2,5-dihydroxymethylfuran and 2-methyl,5-hydroxymethylfuran). The reaction proceeds in the vapor phase using copper-ruthenium catalyst. Both intermediates and other unidentified byproducts are reported to coexist with the product.[1] For the simulation purposes, we assumed that 2,5-dihydroxymethyltetrahydrofuran is the only existing byproduct; however, other byproducts may also co-exist. In the next reaction, DMF reacts with ethylene using a zeolite catalyst in the presence of n-heptane solvent and produces p-xylene through a Diels–Alder cycloaddition and subsequent dehydration reaction. The competitive side reactions include the hydrolysis of DMF to 2,5-hexanedione, which is expected to oligomerize/polymerize and

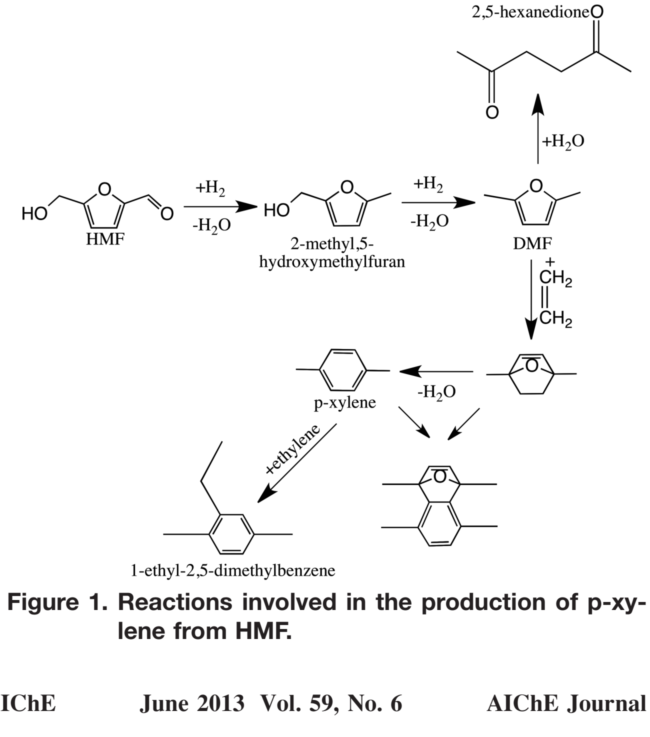

Figure 1. Reactions involved in the production of p-xylene from HMF.

Table 1. Normal Boiling Point of the Substances

Substance	Normal boiling point (K)
HMF	564
1,4-dihydro-1,4,5,8-tetramethyl-1,4-epoxynaphthalene	537
2,5-dihydroxymethyltetrahydrofuran	535
2,5-hexanedione	465
1-ethyl-2,5-dimethylbenzene	460
2-methyl,5-hydroxymethylfuran (MHMF)	452
n-hexanol	431
Water	373
n-heptane	372
DMF	366
Ethylene	170

Table 2. Main components of Each Stream

Stream	Main components
1,3,7	Hydrogen
2,4,5	n-hexanol, HMF, MHMF
6	n-hexanol, DMF, water, MHMF, hydrogen, byproduct 1[a]
8	n-hexanol, DMF, water, MHMF, byproduct 1
9, 13	DMF, water
10	n-hexanol, MHMF, byproduct 1
11	n-hexanol, MHMF
12	byproduct 1
14	Water
15	DMF
16,17	n-heptane, DMF
18	n-heptane, DMF, ethylene, water
19,20,22	Ethylene
21,23	n-heptane, p-xylene, byproduct 2[b], ethylene, water, DMF
24	Water
25	n-heptane, ethylene, p-xylene, byproduct 2, ethylene, DMF, water,
26,27	n-heptane, DMF, ethylene, water
28	p-xylene, byproduct 2
29	byproduct 2

[a] byproduct 1 contains 2,5-dihydroxymethyltetrahydrofuran.
[b] byproduct 2 contains 1-ethyl-2,5-dimethylbenzene, 1,4-dihydro-1,4,5,8-tetramethyl-1,4-epoxynaphthalene and 2,5-hexanedione.

alkylation of p-xylene to form other products like 1-ethyl-2,5-dimethylbenzene.[2]

Aspen Plus is used to simulate the flow sheets since it has the largest reliable thermodynamic library.[24] The process design of p-xylene production is based on the laboratory-scale reaction information such as operating conditions and byproducts because no pilot-scale data are available due to the early stage of technological development. According to the phase diagrams of the substances participating in the reactions at the operating conditions, the process is limited to vapor and liquid phases. The purification processes use either liquid-gas separation or liquid-liquid separation. Liquid-gas separation (a flash or a distillation column) is mainly used and the normal boiling points of main substances are listed in Table 1. However, the boiling points of DMF and water are close, thus, a decanter is used to separate DMF and water.

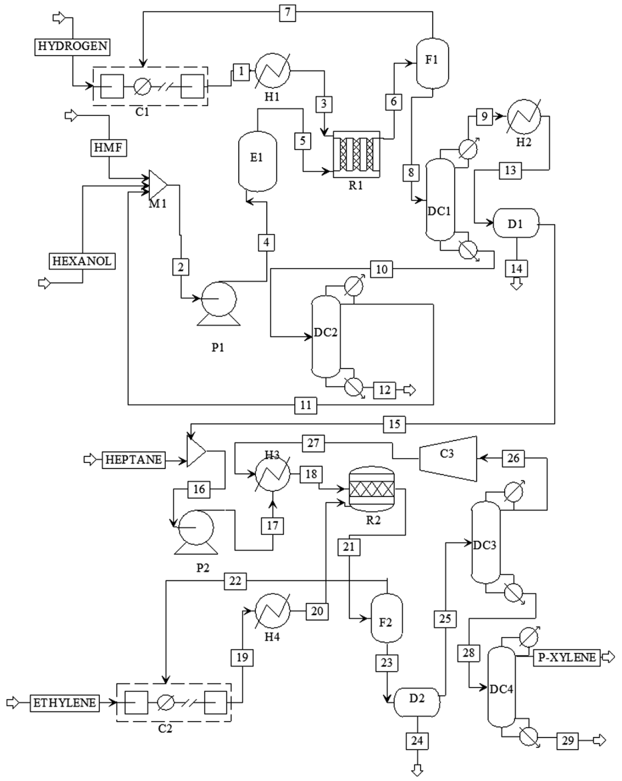

Figure 2. The flow sheet of the production of p-xylene from HMF.

Compressor (C), decanter (D), distillation column (DC), evaporator (E), flash (F), heat exchanger (H), pump (P), and reactor (R).

The detailed flow sheet diagram is shown in Figure 2, and the main components present on each stream are listed in Table 2. 10 wt % HMF in 1-hexanol solvent are vaporized at 493 K and 0.69 MPa that are the reaction operating conditions, and then enter a fluidized-bed reactor (R1). At the same time, hydrogen is compressed and fed to the reactor via a two-stage compressor. In reactor R1, HMF reacts with hydrogen and mainly produces DMF.[19] The excess hydrogen (stream 7:1175 metric ton/year) is removed from the top of a flash (F1) and recycled to the reactor R1. Stream 8 from the bottom enters a subsequent distillation column (DC1). DMF, as well as water, (stream 9) are collected from the vapor phase and then DMF is further purified through a decanter (D1) to remove water given that DMF is slightly soluble with water. The liquid stream 10 from the bottom of DC1 enters another distillation column (DC2) where the intermediate and the solvent (stream 11) are separated from the byproduct 2,5-dihydroxymethyltetrahydrofuran and recycled to reactor R1. DMF (stream 15) obtained above is mixed with some n-heptane solvent and pumped to a CSTR (R2) together; ethylene is compressed to the reactor R2 from external source using a two-stage compressor. In the reactor R2, p-xylene is produced at 573 K and 5.7 MPa.[2] The main byproducts consist of 1-ethyl-2,5-dimethylbenzene, 2,5-hexanedione and oligomers products, all of which have higher boiling points than p-xylene. A flash (F2) is then used to separate the low-boiling point component, which is mainly ethylene (stream 22), followed by a decanter (D2) where most of water is removed. The organic stream 25 from D2 is fed to another distillation column (DC3) to remove and recycle the unreacted raw materials and solvents. Heavy compounds (stream 28) are purified using a distillation column (DC4) and essentially over 99.5 wt % pure p-xylene is produced. Notably, none of the byproducts is recycled and neither one is considered to have a value as commodity (or fine) chemical.

Process simulation and economic analysis

Most technologies of the conversion processes of biomass-based chemicals are still at the early stage of development.[1,2] thus, there is limited information about reaction and unit operation conditions. In addition, the biomass-based processes are very different from conventional petroleum-based processes, especially the substances such as raw materials and byproducts. Therefore, to enable the investigation of different scenarios and evaluate the economic feasibility of various alternatives, different assumptions have to be made. These involve the following:

- The capacity of the plant is assumed as an estimation of the HMF production from fructose given by Kazi et al.[19] which is based on the capacity optimization of the upstream lingo-cellulosic biorefinery. [25] It is defined by the feed rate of 174.2 metric ton/day of HMF, namely 57,960 metric ton/year.
- Because reaction kinetics are not known, the reactor models consider only the information about stoichiometry, conversion and selectivity. The reaction of DMF from HMF is conducted at 493 K and 0.69 MPa with 100% conversion of HMF and 78% selectivity of DMF,[1] whereas the production of p-xylene is obtained at 573 K and 5.7 MPa. At these conditions, the DMF conversion is 95% and selectivity of p-xylene is 75.7%.[2]
- Some of the chemicals, such as HMF, DMF and byproducts (seen in Table 2), formed in the process have not been extensively studied. As a result their physical properties are less known and are not included in Aspen database. Therefore, these substances are defined by their molecular structures. All the missing parameters are estimated by the structures using the thermodata engine (TDE) that is a thermodynamic data correlation, evaluation, and prediction tool provided by the collaboration of Aspen plus and the National Institute of Standard and Technology.[24] Other conventional components are directly selected from the Aspen database.

ASPEN Plus V7.3[24] is used to simulate the proposed processes. To predict the liquid-liquid and liquid-vapor behavior, NRTL-RK is used to determine the thermodynamic properties, that uses NRTL activity coefficient model for the liquid phase, the Redlich-Kwong equation of state for the vapor phase, and the Rackett model for liquid molar volume.[26] Peng-Robinson equation of state is selected for the decanter because it is found to produce more reliable results compatible with the solubility properties of DMF which is known to be slight soluble in water.

We studied several alternatives considering different unit operations such as using of flash or decanter to separate water and DMF and different order and combination of purification units. For instance, to separate DMF, the decanter can be placed before the distillation column; to purify the p-xylene, the alternative is that high-boiling-point byproducts are separated by the first distillation column, then in a decanter is water removed, and finally p-xylene is purified in another distillation column. Different operating conditions that involve pressure, temperature, reflux ratio, tray numbers and feed tray are determined by preliminary process optimization results.[27] The pressure ranges of main equipment's are listed in Table 3. Preliminary process optimization is used to ensure that the results are in the neighborhood of the optimal solutions[27]; however, no rigorous optimization has been performed due to uncertainties in many of the involved parameters.

Table 3. Pressure Ranges of the Main Equipment

Equipment name	Pressure[a] range (MPa)
F1	0.55∼0.65
F2	4.5∼5.65
DC1	0.45∼0.55
DC2	0.3∼0.5
DC3	2.5∼3.5
DC4	1∼2
D1	0.3∼0.5
D2	3.5∼4.5

[a]Pressure refers to condenser pressure of a distillation column.

In addition to process simulation, to evaluate the production cost of p-xylene, economic assessment has been performed in ASPEN Economic Analyzer V7.3.2. The minimum p-xylene cost is defined as the selling price of the product when net present value (NPV) is zero. According to the net present value rule that an investment is worth making if NPV is greater than zero.[28] All the costs are based on the price of the first quarter in 2011.[29] All substances costs are also escalated to the 2011 basis using the same rate of escalation (3.5%) in the economic analysis. Some additional assumptions are necessary to perform the economic estimation:

- The plant is assumed to operate in a continuous and steady state mode for 8,000 h per year. The economic life of the project is 20 years. The salvage value after 20 years is 10% of original capital costs. The straight-line method, as the simplest and most popular of accounting methods of depreciation, is selected and 30% tax is applied to the earnings. The internal rate of return (ROR) on investment and the rate of escalation are assumed as 15 and 3.5%, respectively.
- The cost of HMF is assumed as $1,070/metric ton, which is based on the economic analysis by Kazi et al. considered $300/metric ton fructose cost and all the raw materials are 2007 basis.[19] Therefore, it is converted to the 2011 basis with 3.5% escalation rate so that the cost of HMF is $1,228/metric ton. Under comparative fructose cost, i.e., $331/metric ton, similar price has been also reported by Torres et al. of $0.15/mol, namely $1,189.44/metric ton.[20] The main difference between the two studies is the different cost of fructose due to the dominant impacts of fructose cost on the HMF cost. Given the varying price of HMF, sensitivity analysis is also used to evaluate the impact of HMF cost.
- The costs of other raw materials are listed as $1,202 per metric ton of ethylene[30] and $631 per metric ton of hydrogen (2007 basis: $550/metric ton).[19]
- The market price of 1-hexanol is $1943/metric ton.[30] The market price of n-heptane is estimated as $1,500/metric ton for 50 metric ton/month consumption based on the prices reported at www.alibaba.com,[22] which is a worldwide e-commerce market site originally from P. R. China.
- Cu-Ru/C catalyst cost is escalated to $41.76 million as initial investment plus an additional cost of $157,104/year.[19] The consumption of zeolite is estimated at 210 metric ton/year based on the accumulated zeolite loading needed for the batch reaction with equal capacity.[2] Since we assume complete deactivation of zeolite catalysts, this is the worst case scenario and depicts the highest possible zeolite costs to be expected. Zeolite catalyst cost is fixed at $5,000/metric ton, which is selected as the median of zeolite catalysts cost listed in www.alibaba.com.[22] However, due to the

Table 4. The Flow Rates of the Feed and Production Streams

Stream	Flow rate (metric ton/year)	Mass fraction (wt%)
HMF	57960	100
Hydrogen	2781	100
Ethylene	11689	100
p-xylene	29723	99.54
12 (byproduct 1)	11429	99.56
14 (water)	13267	99.999
24 (water)	5356	99.999
29 (byproduct 2)	11637	98.998 (total)

uncertainty caused by the wide range of various types of zeolite catalysts, we assess the effect of this cost variation using sensitivity analysis.

- The byproducts are not further purified and considered to have zero value since there is not enough information about their use; whereas the wastewater treatment cost for byproducts is also not included given the low concentration and the limited toxicity information of other chemicals in the wastewater. However, additional treatments may be needed to dispose wastewater since the maximum concentration depends on the toxicity of pollutants.

All these assumptions are necessary to perform the simulation and evaluate the economic viability of different options. However, they also introduce a number of uncertainties, and, thus, sensitivity analysis is used to assess their impact to the value of the final product.

Results and Discussion

Process simulation

The flow rates of the feed and product streams are listed in Table 4. For a plant capacity of 57,960 metric ton/year of HMF, 2,781 metric ton/year of hydrogen and 11,689 metric ton/year of ethylene are required. Correspondingly, 29,723 metric ton/year of p-xylene is produced. The worldwide p-xylene production capacity is around 22 million metric ton per annum,[31] so biobased p-xylene has the potential to penetrate a huge market. The limitation of biobased p-xylene capacity would mainly result from feedstock availability. The purity of p-xylene exceeds 99.5 wt %, which, therefore, can be directly used in the next oxidation step to produce terephthalic acid.

The unidentified byproducts from the production of DMF from HMF are 12,523 metric ton/year, and the 1-ethyl-2,5-dimethylbenzene, 2,5-hexanedione and oligomers from the conversion of DMF to p-xylene are accumulated to 12,751 metric ton/year. The byproducts add up to 23,066 metric ton/year. Since the amounts of the byproducts equal to about 75% of the p-xylene capacity assigning a value is expected to improve the economics of the overall project. As an initial approach we assigned a price based on their higher heating value (HHV), which was estimated using the formula proposed by Sheng et al.[32]: $HHV\left(\frac{MJ}{kg}\right)=-1.3675+0.3137C+0.7009H+0.0318O$, where the C, H and O denote the composition of elements in wt %.

The calculated HHVs of the byproduct 1 and the byproduct 2 are 30.14 and 29.76 MJ/kg, which are close to that of ethanol (29.7 MJ/kg). Therefore, we assume that they have a similar price to that of ethanol fuel, namely $2.2/gal ($736/metric ton) based on the current market price.[33] Thus, it would approximately reduce the minimum product cost by $552/metric ton. To explore the value of byproducts, more research is needed to study their usage. Otherwise, increasing selectivity of p-xylene and decreasing the production of the byproducts is another option to reduce the minimum p-xylene cost. In addition, despite the high purity of water stream, we may expect additional cost for the wastewater treatment to satisfy the maximum concentration requirement of pollutants.

The total cost primarily involves the capital and operating costs. The detailed costs are listed in Table 5. The fractions of the capital and operating costs are shown in Figure 3. The total capital cost of the process is estimated as $100.63 million. The most expensive part is the initial costs of CuRu/C catalyst which is around 41.5% of the total capital cost. Moreover, besides the fact that CuRu/C is easily deactivated due to the accumulation of carbon,[1] new cheap catalysts with long life cycle will be useful to lower the initial costs and improve further the annual operating costs. The equipment purchasing and installation costs are $33.56 million. Among the costs, more than 75% comes from the production of DMF to p-xylene especially the purification of p-xylene and the rest is from the conversion of HMF to DMF. The other costs such as administration, contract, design, etc. are $25.31 million in total.

The total operating cost is estimated as $119.19 million. The main contributors are the raw materials cost (including solvents), which constitutes the 82.5% of the total operating cost. The predominant fraction is from the biomass feedstock

Table 5. Project Cost Summary

Item	Cost (million $)	Item	Cost (million $/yr)
Initial catalysts cost	41.76	Raw materials (including solvents)	98.38
Purchased equipment	18.14	Catalysts costs	1.21
Equipment setting	0.46	Operating labor and maintenance cost	0.73
Piping	9.58	Utilities	9.76
Civil	0.88	Plant overhead	0.37
Steel	0.29	General and administrative cost	8.75
Instrumentation	2.14	**Total operating cost**	**119.19**
Electrical	0.80		
Insulation	1.15		
Paint	0.11		
Other[a]	13.43		
General and administrative overheads	1.28		
Contract fee	1.62		
Contingencies	8.98		
Total project capital cost	**100.63**		

[a] Other cost includes: design, engineering, and procurement costs; material charges; and construction field indirect costs.

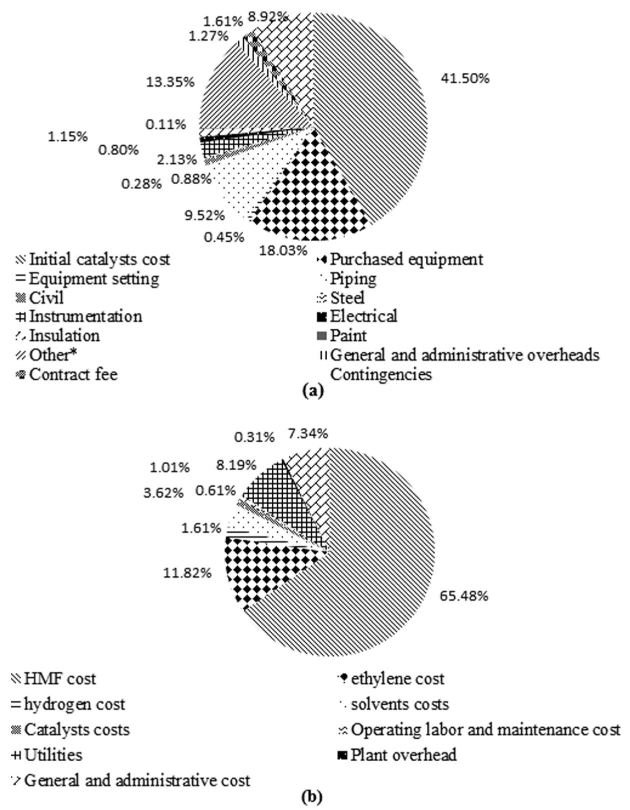

Figure 3. (a) The main factors of capital cost, and (b) the main factor of operating cost.

and accounts for 65.5% of the operating cost. Thus reducing the price of HMF would have great effect in the cost of p-xylene. Hereby, $1228/metric ton of HMF is estimated based on $344/metric ton of fructose. 20% decrease of fructose price would be able to reduce the HMF price to $1,098/metric ton.[19] Similar final price could be reached by improving the yield of HMF to 100%.[19] Other raw materials such as ethylene and hydrogen contribute 14.3% and 1.9%, respectively; whereas solvents costs add up to 4.4% of the raw materials (including solvents) cost. The utilities cost correspond to 8.2% of the operating cost. Thus, the annual catalysts costs are around $1.21 million.

According to the simulated results in Tables 4 and 5, the minimum p-xylene cost is around $3,962/metric ton, which corresponds to the selling price at zero NPV. This minimum p-xylene cost is based on the oil-based quotes of the other raw materials price, such as ethylene and hydrogen, and the solvents. A drawback of this assumption is that using biobased raw materials and solvents would further increase the minimum p-xylene cost. In addition, all biobased raw materials and solvents are still limited to the accessibility due to the early stage of this technology. In comparison, the market price of p-xylene from petroleum source is around $1,630/metric ton.[30] Hence, the biobased p-xylene is estimated to be two and half times more expensive than the oil-based p-xylene. However, as the oil price increases and the technologies of biomass conversion develop, the biobased p-xylene becomes more competitive and attractive.

Sensitivity analysis

Process optimization is often used to achieve the minimum total cost balancing capital and utility cost. However, in this case, because the kinetic mechanisms of the reactions involved are not known, sensitivity analysis has been performed to determine the impact of different parameters in the total cost.

The impact of several economic parameters is considered based on a 30% change of their base scenario value (shown in Figure 4a). The economic parameters comprise of plant capacity, the internal rate of return, the tax rate, HMF price, ethylene price and zeolite catalyst cost. The plant capacity affects both capital cost and operating costs. It is found that 30% decrease of plant capacity raises the minimum cost to $4,291/metric ton, whereas 30% increase results in only 1% cost reduction. Thus, we expect the plant capacity of the base scenario to be close to the optimum value. The feasibility of the project is sensitive to the parameters such as ROR and tax rate, which are often specific based on the location and time of the project. 30% of ROR and tax rate variations change the minimum cost by about 6 and 2%, respectively.

The HMF price is the most significant factor affecting the minimum cost. A 30% decrease of HMF, and ethylene prices being lower at 17.4% and 3.1% of the minimum p-xylene, respectively. The combining reduction of both HMF and ethylene prices at the same time results in 20.5% decrease of the minimum cost. In other words, if HMF price is $860/metric ton and ethylene price is $841/metric ton, the corresponding p-xylene cost is $3149/metric ton. Therefore, inexpensive raw material is necessary to reduce the biobased p-xylene price and promote the commercialization of the project. In addition, given the wide range of the price of zeolite catalysts that are used in the conversion of p-xylene from DMF, notably, the change of the final product costs caused by the zeolite catalyst costs is under 0.5%. Hence, the uncertainty resulted from the zeolite catalyst cost is negligible at the current stage.

The impact of conversion and selectivity on the production costs is also investigated and shown in Figure 4b. The variability considered for reactions from HMF to DMF and from DMF to p-xylene is 15%. Increasing the DMF yield from HMF and the p-xylene yield in the reaction from DMF reduce the formation of byproducts and improve productivity thus leading to reduction in p-xylene minimum cost which is found to be $3308/metric ton and $3,075/metric ton,

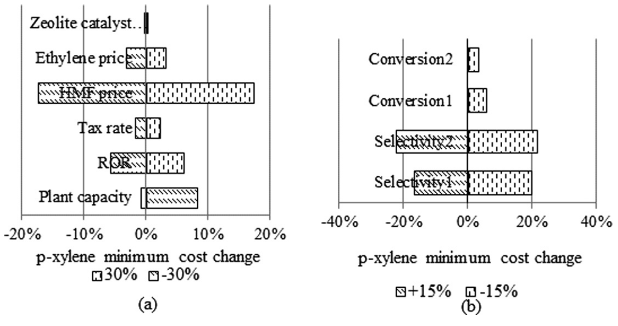

Figure 4. Impacts of parameters on p-xylene minimum cost (a) impacts of economic parameters, and (b) impacts of reaction parameters (Conversion1: conversion of HMF in the reaction from HMF to DMF; Conversion2: conversion of DMF in the reaction from DMF to p-xylene; Selectivity1: selectivity of DMF in the reaction from HMF to DMF; Selectivity2: selectivity of p-xylene in the reaction from DMF to p-xylene).

respectively. Reduction of 15% of the selectivity of the product in the reactions results in increase in the minimum cost by 19.8% and 21.7%, respectively. The production capacity of the p-xylene has a dominant effect of the cost. Decreasing selectivity results in additional cost in product and consequently raises the costs.

Given the high conversion of the current processes, only a 15% decrease of conversion is applied to study the impact on the final cost. It is noted that in this scenario (low DMF conversion), another distillation column is added after DC2, and used to separate the byproduct and HMF and recycle the HMF stream. Remarkably, 15% decreases of conversion in processes, respectively change around 5.6% and 3.3% of the minimum p-xylene cost, which is less impacting. This small change mainly results from the recycling stream of the raw materials and intermediates. The higher selectivity is more useful to reduce the production costs than higher conversion. Thus achieving high-selectivity process will be able to make the project more profitable.

Comparison

In comparison to the existing pilot-scale Gevo process described in Appendix A, this process is considered promising. The main advantage of Gevo process[10] is that it is entirely based on biomass treatment since the raw material (isobutanol) comes from the fermentation of biomass feedstocks. The yield of isobutanol from glucose at the experimental level is reported as 90.4% of theoretical yield, namely 0.3706 g isobutanol can be obtained from 1 g of glucose,[10] so the theoretical minimum cost of isobutanol is estimated as $929/metric ton regardless of the cost of production and purification processes. However, the production and purification processes are known to be more difficult requiring more steps compared to conventional chemical processes because during fermentation more factors are needed to be controlled such as pH, temperature, dissolved oxygen, and nutrient concentration, and it produces low concentration of product broth.[34] The other costs such as microorganisms and chemicals, labor, utilities and overhead are estimated to be the same as the production of biobased n-butanol, which is $489/metric ton.[35] Thus, isobutanol cost is estimated around $1,418/metric ton. Moreover, if we assume that the same contribution of raw material of Gevo process has the same weight as in the process of the production of p-xylene from HMF, i.e., raw material is 79% of the total cost, the final p-xylene cost is then roughly $3,400. As discussed in Appendix A, utilities and capital costs are expected to be higher due to the difficulties in product purification, thus, the cost of p-xylene from Gevo process is probably underestimated.

Conclusions

With the increasing attention on biomass-based p-xylene, the economic analysis of various production alternatives becomes very important. This work has focused on the economic analysis of p-xylene production from HMF. It is found that the minimum cost of biobased p-xylene is $3,962/metric ton, which predominantly comes from the raw materials costs, especially biomass feedstocks. To produce a pure biomass-based product, all biobased raw materials and solvents are needed including hydrogen, ethylene, n-heptane and 1-hexanol. Thus, it is imperative to also study and investigate the biomass feedstock conversion processes to these substances.

In order to decrease the price of p-xylene, three main targets have been identified: reduce raw materials cost, increase the yield of reactions, and raise byproducts value. The accessibility of the cheap raw materials is significant to lower the minimum cost of p-xylene dramatically. Thus, research on the upstream conversion is essential to achieve lower HMF cost by reducing production cost or by increasing its production rate. Second, consideration of the byproducts values is also helpful to reduce the p-xylene cost given the large amounts of byproduct. This is the main idea behind biorefinery integration in order to utilize the byproducts to produce high-value chemicals. Alternatively, higher product yields can increase the production rate and reduce the byproduct stream. Particularly, higher selectivity is favored even at the expense of sacrificing the conversion to some extent provided that recycling of intermediates and unreacted raw materials can be achieved. The impact of other factors such as catalyst cost, solvent cost, and plant capacity have been found to be much smaller.

Although the price of biobased p-xylene is not very competitive to the oil-based p-xylene, biobased conversion processes are still promising to study. With the improvement of technology and the increasing price and depleting petroleum sources, the price of biobased p-xylene is expected to be comparable to that of the oil-based p-xylene. In comparison to other biobased p-xylene conversion process, the conversion process from HMF is promising.

To perform more detailed and accurate analysis, additional research is needed to enhance the information regarding the reactions and the molecules involved in the process.[20,25] The main problem results from the unknown physical and thermodynamic properties of the involved molecules. Thus, in the simulation studies it is difficult to select reliable thermodynamic models. Although we use chemicals with similar molecular structures or boiling points to choose a reasonable thermodynamic model, the prediction accuracy is still uncertain. Another problem is that we do not have detailed information about the kinetics of the involved reactions, which is very important for the design and scale up of the processes. Moreover, if the reaction kinetics are available, then they can be used to evaluate and optimize the operating conditions of the processes.

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Appendix: A

Description of Gevo Process

The flow sheet of the production of p-xylene from isobutyl alcohol by Gevo, Inc., is shown in Figure A1.[10] The normal boiling points of substances and stream compositions are listed in Table A1 and A2, respectively. Isobutanol is fed in a fixed-bed catalyst reactor and dehydrated to isobutene using a γ-alumina catalyst. The reaction is conducted at 563 K and 5.15 MPa. The production stream 2 enters a decanter D1 to remove most water and pumped to the oligomerization reactor R2, as well as recycling stream 13. Isooctene is produced in reactor R2 using HZSM-5 catalyst at 343 K and 5.27 MPa. The byproduct involves trimers of isobutene. Stream 6 from reactor R2 combined with recycling stream 18 enters another dehydrocyclization reactor R3 to produce p-xylene with 90% selectivity. Reaction R3 is performed at 823 K and 0.14 MPa. Side reactions produce o-/m-xylene, isooctane, isobutane, benzene, toluene, C_{9+} aromatics, isoolefins and methane. A flash F1 is used to remove the light components. The vapor stream 9 is forwarded to another flash F2 to remove hydrogen and methane and to recycle isobutane, isooctane and isobutene. The existence of diluents isobutane and isooctane can enhance the conversion of both olimerization and dehydrocyclization reactions. Stream 10 is pumped to a distillation column DC1. The light byproducts such as benzene and toluene are collected from the top, whereas the heavy byproducts from the bottom involve C_{9+} aromatics, isoolefins, and trimers. A side

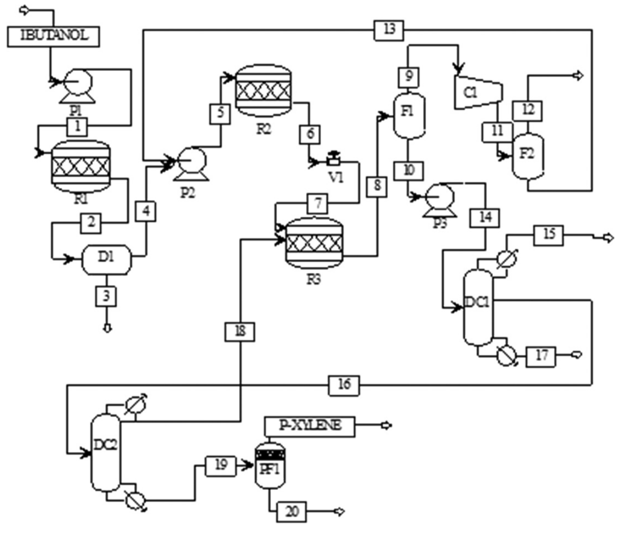

Figure A1. Flow sheet for the production of p-xylene from isobutanol.[10]

Compressor (C), decanter (D), distillation column (DC), flash (F), heat exchanger (H), pump (P), purification process (PF), and reactor (R).

Table A1. Normal Boiling Point of the Substances

Substance	Normal boiling point (K)
o-xylene	418
p-xylene	411
Toluene	383
iso-butanol	381
iso-octene	375
Water	373
iso-octane	372
benzene	353
n-butene	267
iso-butene	266
iso-butane	251
hydrogen	20

Table A2. Stream Compositions

Stream	Main compositions
1	iso-butanol
2	iso-butene, water, n-butene, iso-butanol
3	Water
4	iso-butene, n-butene, water, iso-butanol
5	iso-butene, n-butene, iso-butane, iso-octane
6,7	iso-butane, iso-octene, iso-octane, iso-butene, n-butene, trimers
8	iso-octane, iso-butane, p-xylene, isooctene, iso-butene, n-butene, hydrogen, o-/m-xylene, benzene, toluene, C_{9+} aromatics, iso-olefins, trimers, methane
9,11	iso-butane, iso-octane, iso-butene, n-butene, hydrogen, and methane
10,14	iso-octane, p-xylene, iso-octene, o-/m-xylene, benzene, toluene, C_{9+} aromatics, iso-olefins, trimers
12	hydrogen, methane
13	iso-butane, iso-octane, iso-butene, n-butene
15	benzene, toluene
16	iso-octane, iso-octene, p-xylene, o-/m-xylene
17	C_{9+} aromatics, iso-olefins, trimers
18	iso-octane, iso-octene
19	p-xylene, o-/m-xylene
20	o-/m-xylene

stream 16 enters another distillation column DC2. Stream 18 containing iso-octene and isooctane collected from the top is recycled to reactor R3. The bottom stream 19 is fed to a purification process to achieve a 99.99 wt % pure p-xylene product.[10]

According to the normal boiling points shown in Table A1, it is found that a number of problems can arise in the aforementioned purification steps since many of the components have very close boiling points. In our simulations, a liquid-gas separator and a distillation column (F1 and DC1) cannot achieve the target product specifications as described in[10]. Moreover, water and isobutanol form azeotropes with products and intermediates such as xylene and iso-octane, respectively; thus, it is very difficult to purify and separate further using the flow sheet A1 as proposed in[10]. Therefore, some additional separation steps may be expected to enhance the purification of the intermediate and final products enabling better recycle. However, this will also have an effect on the final cost of the production. In addition, separation of low-boiling point compositions using liquid-gas separator requires really low temperature and, consequently, increases the utility cost. More specifically the separation of hydrogen from isobutene and isobutane can only take place at 223 K in order to be able to recycle the entire isobutene and isobutane.

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