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Comparison of 4,4′-Dimethylbiphenyl from Biomass-Derived Furfural and Oil-Based Resource: Technoeconomic Analysis and Life-Cycle Assessment

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Cite This: *Ind. Eng. Chem. Res.* 2022, 61, 8963−8972

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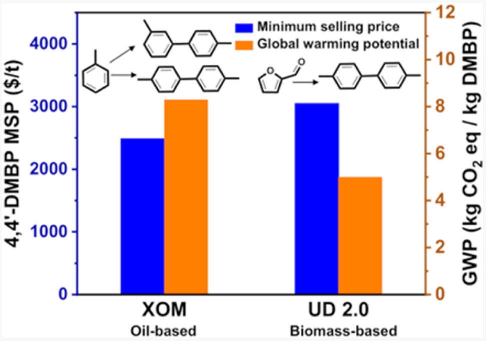
ABSTRACT: Replacing oil-based toluene with biomass-derived furfural for 4,4′-dimethylbiphenyl (DMBP) production can pave the way for sustainable polyester manufacture. This work compared the economic and environmental performances of two conceptual designs of 4,4′-DMBP production. The first toluene-based route consists of toluene alkylation to (methylcyclohexyl)toluene (MCHT), MCHT dehydrogenation to DMBP, and isomerization of lower-valued 3,3′-DMBP. The renewable furfural-based route includes hydrogenation of furfural to 2-methylfuran (MF), oxidative coupling of MF to 5,5′-dimethylfuran (DMBF), and tandem Diels−Alder dehydration of 5,5′-DMBF to 4,4′-DMBP. The reaction conditions are optimized to achieve a more economically feasible process using furfural feedstock. At a scale of 83 kmol/h feedstock, the 4,4′-DMBP minimum selling price of the furfural-based route is \$3044/t, while that of the toluene-based route is \$2488/t. The feedstock and 3,4′-DMBP isomer prices are identified as critical parameters for the economic evaluation by sensitivity analysis. A "cradle-to-gate" life-cycle assessment confirms that furfural-based DMBP production emits significantly fewer greenhouse gas (5.00 kg CO_2 equiv/kg DMBP) as compared to the toluene-based counterpart (8.28 kg CO_2 equiv/kg DMBP).



1. INTRODUCTION

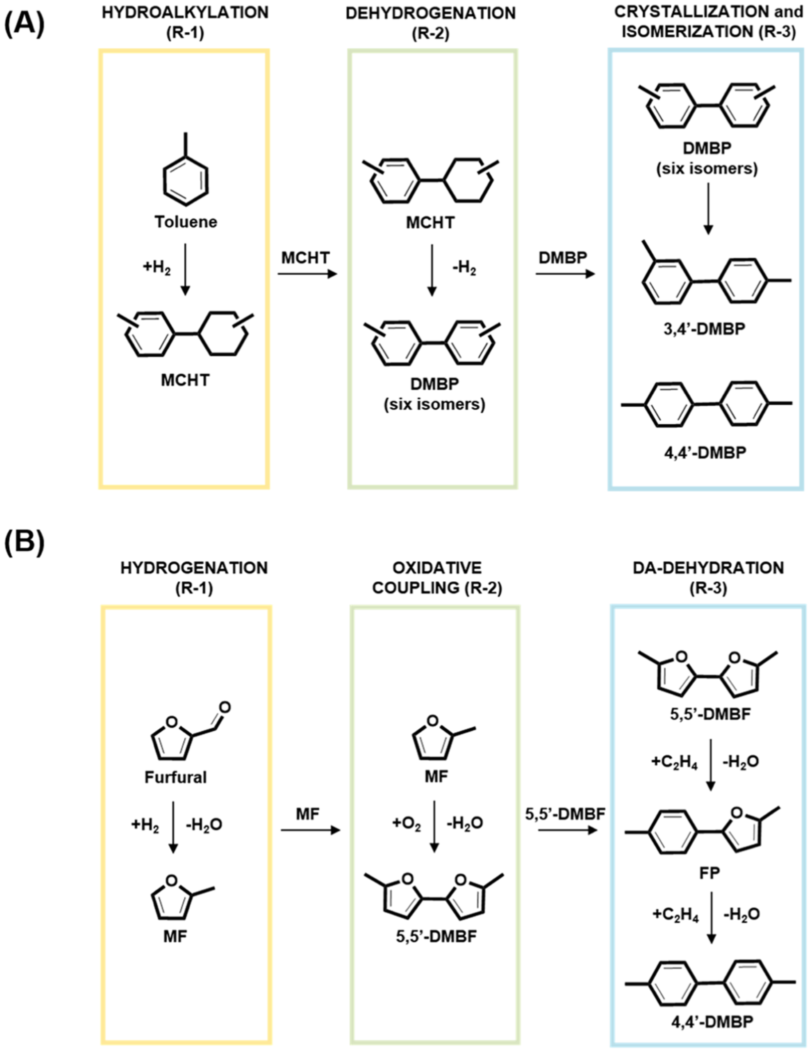
4,4′-Dimethylbiphenyl (DMBP) is an important precursor in various organic chemicals because it can be easily transformed into diacids, diols, and diamines. Particularly in the polymer industry, diaryl monomers have attracted a growing interest due to their superior chemical and physical properties. For example, 4,4′-biphenyldicarboxylic acid (BPDA), the diacid form of DMBP, has a melting point above 300 °C, which is advantageous to produce high-molecular-weight polymer products without intermediate solidification.[1] Either alone or as a modifier for poly(ethylene terephthalate) (PET), BPDA is a potential precursor in the production of polyester fibers, engineering plastics, liquid crystal polymers for electronic and mechanical devices, and films with high heat resistance and strength.[2,3] Polyesters composed of BPDA usually exhibit high tensile strength and excellent resistance to heat, chemicals, and solvents.[4] Moreover, BPDA has been used as an organic linker in the preparation of metal-organic frameworks (MOFs).[5−7] 4,4′-Biphenyldimethanol, the diol form of DMBP, could work as a substitute for the disputed bisphenol A, which is a comonomer in the production of polycarbonates.[8,9] Different DMBP isomers have also found applications as precursors of poly(vinyl chloride) (PVC) plasticizers.[10]

While 4,4′-DMBP is currently synthesized by coupling reactions of aryl chlorides or arenediazonium salts, the routes require costly substrates and generate a large amount of waste.[11,12] ExxonMobil Chemical has reported the production of 4,4′-DMBP from toluene or benzene.[13] The proposed pathway involves the hydroalkylation of toluene to produce (methylcyclohexyl)toluene (MCHT) and the dehydrogenation of the intermediates to DMBP, which leads to low selectivity towards the 4,4′-isomer (Scheme 1A). The mixture of six possible isomers makes the separation difficult and is a huge challenge for commercial production.[13−16] Alternative routes via benzene are also described in the same patent, in which benzene is initially converted to biphenyl, either by oxidative coupling or by hydroalkylation to cyclohexyl benzene (CHB), followed by dehydrogenation of the CHB and alkylation with methanol.[10] Vercammen et al. have reported the oxidative coupling of toluene to biaryls with good selectivity for the 4,4′-dimer using molecular palladium in zeolites.[14] However, this process uses petroleum-derived starting materials. Furthermore, different DMBP isomers demonstrate varying properties for the final products. For instance, diphenate esters derived from 3,3′-DMBP often exhibit improved low-temperature

Received: February 3, 2022
Revised: May 26, 2022
Accepted: May 31, 2022
Published: June 17, 2022

https://doi.org/10.1021/acs.iecr.2c00398
Ind. Eng. Chem. Res. 2022, 61, 8963−8972

Scheme 1. Process Chemistry of 4,4′-Dimethylbiphenyl Synthesis from (A) Oil-Based Resource and (B) Biomass-Derived Furfural



flexibility as plasticizers, whereas similar esters derived from 2,2′-DMBP are typically too volatile to be used as plasticizers. It was also found in a recent patent that the 4′-position methyl group DMBP isomers are more prone to oxidation than the 2′- or 3′-ones.[17] Typically, 4,4′-DMBP is the desired raw material for polyester and plasticizer production, and thus the most valuable product.[3] It is, therefore, essential to achieve high regioselectivity towards the 4,4′-isomer from biomass.

The global polyester fiber market alone was \$91.7 billion in 2020 and is predicted to grow to more than \$160 billion/year by 2027.[18] Thus, the potential market size of the performance-enhanced polyester using monomers from DMBP is significant. On the other hand, using biomass feedstock for chemical production has been established as a promising strategy to alleviate global warming.[19−21] It is noteworthy that polyesters could be chemically recycled or upcycled,[22,23] further reducing the overall life-cycle emission of using biomass-derived DMBP. With the increased awareness of customers to choose more environmentally friendly products, the market of sustainable DMBP from renewable sources is expected to expand.

We have previously reported a green synthesis pathway from biomass-derived 2-methylfuran (MF) to 4,4′-DMBP.[24] In this work, we propose and evaluate the industrial feasibility to produce 4,4′-DMBP using this route. Furthermore, we identify ways to improve the reaction conditions, which could make this process more commercially viable. A three-step process sequence is considered to convert furfural into 4,4′-DMBP, with MF and 5,5′-dimethylfuran (DMBF) as the intermediates. As shown in Scheme 1B, the first step is the hydrogenation of furfural to MF. The second step is the oxidative coupling of MF to 5,5′-DMBF. Finally, the third step is the tandem DA-dehydration of 5,5′-DMBF to 4,4′-DMBP, with the intermediate 2-methyl-5-(p-tolyl)furan (FP). Preliminary technoeconomic analysis (TEA) and life-cycle assessment (LCA) are performed based on the previously reported reaction conditions.[24] Improvements were made based on the minimum selling price (MSP) breakdown to increase the profitability. A toluene-based 4,4′-DMBP process proposed by ExxonMobil Chemical is also simulated and compared to biomass-based production to illustrate the pros and cons of using renewable feedstocks. To the best of our knowledge, there is no existing work on the process simulation and economic/environmental evaluation of sustainable DMBP production. This work illustrates the interplay of process system engineering tools (i.e., process design, TEA, and LCA) coupled with laboratory experimentation to improve the

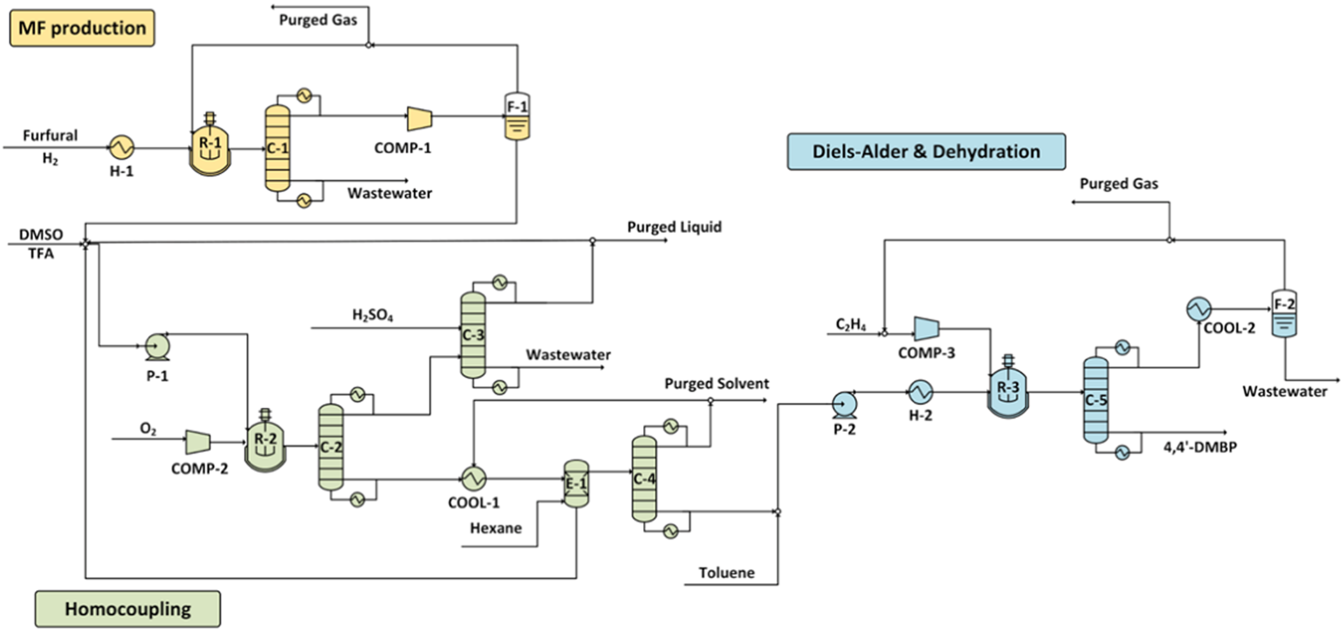


Figure 1. Process flow diagram for the conversion of furfural to DMBP via furfural hydrogenation (R-1, C-1, F-1), MF oxidative coupling (R-2, C-2, C-3, C-4, E-1), and DMBF DA-dehydration (R-3, C-5, F-2).

process economics and efficiency. Our analysis established the biomass-based DMBP production route as a profitable and environmentally friendly technology, which provides a new and attractive alternative for the furfural conversion in the integrated biorefinery operation.[20,25]

2. METHODS

2.1. Process Simulation. The flowsheets of 4,4′-DMBP production from renewable feedstock (furfural) and petrochemical raw material (toluene) are developed based on lab experiments and published patents. It was assumed that these lab-scale yields also would hold for industrial-scale production. The process simulation is performed in Aspen Plus v11 (Aspen Technology), and the non-random two-liquid (NRTL) thermodynamic model is utilized to capture the liquid−liquid and liquid−vapor phase equilibrium. Most of the compounds involved in the reactions were selected from the Aspen Plus physical property database. Chemicals not included in the database (such as DMBP isomers) were defined by their structures and boiling points,[26] and missing physical properties were retrieved from NIST Thermo Data Engine (TDE) or estimated using the Aspen Plus Property Constant Estimation System (PCES). The RStoic reactor model with experimental conversions was used in the process simulation. More detailed reaction kinetics could be incorporated based on future scale-up experiments to better capture the reactor behavior.

2.2. Technoeconomic Analysis. Aspen Process Economic Analyzer V11 was used to determine the capital and operating cost and perform economic evaluations. Despite being a promising intermediate for value-added products, the market of DMBP is still developing. Accurate market price estimation at the early stage is challenging. Thus, economic criteria that involve product selling prices are less reliable, including the net present value (NPV) and return on investment (ROI). Discounted cash flow analysis was conducted, and the MSP, defined as the selling price of the product when the net present value is zero, was calculated. Heat integration was conducted using Aspen Energy Analyzer (Aspen Technology 2019) to reduce the utility usage and cost. Sensitivity analysis was performed on the critical process parameters to account for the effects of uncertainties. Additional TEA assumptions could be found in Section 3 of the Supporting information.

2.3. Life-Cycle Assessment. The SimaPro software with Ecoinvent 3.3 data is used for the life-cycle assessment (LCA).[27] A "cradle-to-gate" system boundary is defined for all 4,4′-DMBP production processes, which comprises the biomass growth, extraction of raw material, upstream utility generation, and production stage. This study utilized the Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI) 2.1 method for impact assessment.[28] As one of the most commonly used environmental metrics, the global warming potential (GWP) is chosen as the environmental impact of interest.[29] For biomass-based DMBP production, the furfural feedstock is mainly produced from corn cob, which absorbs carbon dioxide during plant growth. Thus, the carbon sequestration effects are considered based on the corn cob usage and carbon content in the database. Since multiple isomers and an MCHT intermediate are generated from the process, mass allocation is performed on 3,4′-DMBP isomers to avoid the influence of price fluctuations.[30] The "avoided burden" method is deployed to give credit for selling 2,*X*′-DMBP and unreacted MCHT as refinery feedstock.[31] More details regarding LCA are outlined in Section 4 of the Supporting information.

3. RESULTS AND DISCUSSION

3.1. UD 1.0 Process: Preliminary Technoeconomic Analysis. *3.1.1. Process Description.* The furfural-based 4,4′-DMBP production is designed on the basis of Cho et al.[24] to assess the industrial feasibility of this synthesis route. It is named as the UD 1.0 process, and the process flowsheet is shown in Figure 1.

The process comprises three stages, as shown in Figure 1: (1) hydrogenation of furfural to MF and water, (2) MF oxidative coupling to 5,5′-DMBF and water, along with the associated separations and recycle, and (3) DA-dehydration of 5,5′-DMBF to 4,4′-DMBP and water, followed by 4,4′-DMBP purification. Furfural and hydrogen gas were sent to the hydrogenation reactor R-1 to produce MF at 238 °C and ambient pressure. These reaction conditions lead to an MF yield of 98.5%, and the remaining byproduct is assumed to be furfuryl alcohol.[32] Next, a distillation column C-1 and a flash drum F-1 were used to separate wastewater and unreacted raw material from the MF stream. The MF stream was then mixed with dimethyl sulfoxide (DMSO) and trifluoroacetic acid (TFA) and pressurized in P-1 to 10 bar. The solution was fed into the 45 °C reactor R-2 with the addition of oxygen gas to perform the homogeneous oxidative coupling reaction catalyzed by palladium acetate. The major side reaction in R-2 is the hydrolysis of MF into 4-oxopentanal.[24] Then, distillation column C-2 is used to recycle most of the TFA and MF from the product mixture. As suggested by a Goodyear patent,[33] sulfuric acid was added to column C-3 to break the water/TFA azeotrope and recover most of the TFA. Next, the bottom stream of C-2 containing DMBF was extracted by hexanes at a concentration of 0.07 M, while the palladium acetate stayed in the DMSO phase and was recycled back to the reactor because of its high solubility in DMSO.[24] Efficient technologies have been developed to effectively recover precious metals from homogeneous systems[34−36] or oxidize deactivated Pd nanoparticles back to palladium acetate.[37] Consequently, it is assumed that only 1% of the homogeneous catalyst is lost due to deactivation every 6 months. A sensitivity analysis is performed in Section 3.4 to study the effects of this assumption. The solvent was then recycled by distillation column C-4. Next, 5,5′-DMBF was dissolved in toluene as 0.15 M solution, pressurized, and heated before feeding into the Diels−Alder-dehydration reactor R-3 at 250 °C and 34 bar. After this reaction, the 4,4′-DMBP product was isolated by distillation column C-5, and flash drum F-2 is utilized for recycling the unreacted raw material and solvent. Part of the 4,7-dimethylbenzofuran (benzofuran) byproduct and water were removed from the bottom of F-2 to avoid accumulation in the recirculation.

Based on the Aspen Plus process simulation, 6717 kg/h 4,4′-DMBP was produced from 8000 kg/h furfural (83 kmol/h). The cost breakdown of the UD 1.0 process is illustrated in Figure 2a.

Because of the long reaction times and relatively low 5,5′-DMBF concentration, large reactor volumes and thus high equipment costs are unavoidable. The minimum selling price (MSP) from discounted cash flow calculation is thus calculated to be \$4008/t for the UD 1.0 process, with equipment and other capital investment taking up a significant portion (\$1525/t). Thus, priority should be given to reducing the reaction time and solvent usage in both reactions for cost reduction. Moreover, furfural cost accounts for \$1088/t of the raw material cost, suggesting that the 4,4′-DMBP production cost is sensitive to the furfural market prices.

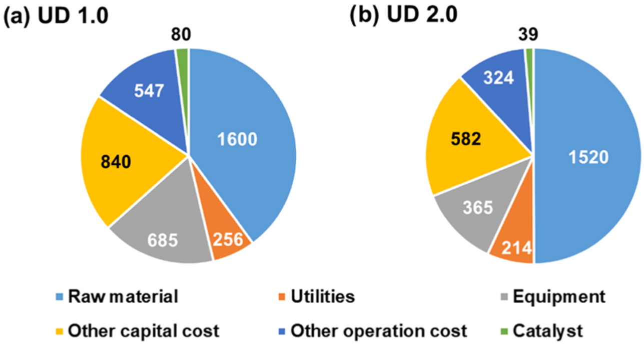


Figure 2. Minimum selling price breakdown for 1 metric ton 4,4′-DMBP produced by the (a) UD 1.0 and (b) UD 2.0 process.

Based on the initial process design, several changes are to be made in the synthesis route. First of all, due to the high equipment and other capital costs caused by long reaction times (Table 1), we considered the following scenario of decreasing the reaction times. High reaction yields and selectivity are typically favored in batch experiments, but it is essential to consider recycling solvent and unreacted feedstock in continuous productions. Thus, reactions with lower conversions but a shorter reaction time may lead to reduced costs than their batch process counterparts when recycling streams are implemented in the continuous process operation. Some industrial processes, such as adipic acid production from cyclohexane oxidation, have been developed and operated under very low conversion (e.g., 1−8 mol %) and large recycle streams.[38] Although there have been various control structures and strategies proposed for such recycle reactor systems in the literature, they are still more difficult to control due to the time-scale separation.[39−42] Future reduction of the recycling streams, including lower solvent usage and higher conversion in a short residence time, is needed to improve the controllability of the UD 2.0 process.

Table 1. Oxidative Coupling Reaction of MF to Produce 5,5′-DMBF[a]

process	UD 1.0	UD 2.0
T (°C)	45	30
time (h)	3	1
MF conv. (%)	62.9	27.8
5,5′-DMBF yield (%)	59.1	27.8

[a] Reaction conditions: 2.67 mol % $Pd(OAc)_2$, 3 M TFA, 3 M MF in DMSO (total volume 4.5 mL), 10 bar O_2.

Apart from the economic viability, other technical issues also pose challenges to the UD 1.0 process feasibility. In reactor R-2, for example, the decomposition of DMSO is noticeable at 45 °C and should be avoided to increase the solvent recyclability. Also, the separation of 4,4′-DMBP with the benzofuran byproduct is very challenging in the UD 1.0 process. Due to the high boiling point of benzofuran (216 °C), a significant amount of benzofuran is still present in the recirculation stream. Hence, it is necessary to improve the selectivity further to avoid the presence of benzofuran. Moreover, the surface area of P-SiO_2 (DA-dehydration catalyst) decreases from 275 to 262 m^2/g after three cycles. It would be desirable to have a more stable catalyst that can lead to a higher selectivity in reactor R-3.[24]

3.2. Improved UD 2.0 Process and Technoeconomic Analysis.

After identifying the major cost contributors as described in Section 3.1, the most efficient way to cut the production cost is to reduce the reactor volumes. Hence, a set of new reaction conditions are proposed and implemented in the updated UD 2.0 process.

Table 1 shows the changes in the reaction conditions of reactor R-2. The decrease of reaction temperature from 45 to 30 °C avoids the decomposition of DMSO under an acidic environment.[43,44] The reaction time is also reduced from 3 to 1 h to reduce the reactor volume and catalyst loading, which leads to smaller investment on the reactors and catalyst. The improvements of reactor R-3 are listed in Table 2. γ-Al_2O_3, which has high Lewis acid density,[45−47] is able to catalyze both Diels−Alder and dehydration reactions (Figure S1 and Table S1).[48,49] The replacement of P-SiO_2 with γ-Al_2O_3 leads to a higher selectivity towards FP and 4,4′-DMBP at 8 h, with a carbon balance of 96.3%. The thermogravimetric analysis (TGA) of the spent γ-Al_2O_3 catalyst (Figure S2) shows that about 3.6 wt % of carbon deposits formed on the catalyst during the reaction (~2.3% carbon loss of the carbon balance). Furthermore, γ-Al_2O_3 is a stable and robust solid catalyst, which is widely used in the industry because of its high surface area and thermal stability.[45] The characterization of the regenerated catalyst after the third cycle demonstrates that the physical and chemical properties remain similar (Table S1). Meanwhile, the regenerated catalyst shows similar catalytic performance to the fresh catalyst, as displayed in Figure S3, confirming its recyclability. The reaction time is set at 8 h to minimize the reactor size, while the unreacted 5,5′-DMBF and the FP intermediate are recycled to reactor R-3 to undergo further conversion.

Table 2. Diels−Alder (DA) and Dehydration Reactions of 5,5′-DMBF to Produce 4,4′-DMBP

process	UD 1.0[a]		UD 2.0[b]	
catalyst	P-SiO_2		γ-Al_2O_3	
time (h)	24	48[c]	8	16[d]
5,5′-DMBF conv. (%)	96.9	100.0	56.2	88.9
FP (%)	46.4	0.0	51.1	72.8
4,4′-DMBP yield (%)	36.1	83.4	1.3	13.0
benzofuran (%)	8.2	9.8	0.0	0.0

[a] Reaction conditions: 0.15 M 5,5′-DMBF in toluene (total volume 6 mL), 80 mg of P-SiO_2 (DMBF/P = 19), 34 bar C_2H_4 (at room temperature (RT)).[24] [b] Reaction conditions: 0.15 M 5,5′-DMBF in hexanes (total volume 6 mL), 94 mg of γ-Al_2O_3, 34 bar C_2H_4 (at RT). [c] After 24 h of reaction, the reaction mixture separated from the spent catalyst underwent DA-dehydration over a fresh P-SiO_2 for 24 h.[24] [d] After 8 h of reaction, the reaction mixture separated from the spent catalyst underwent DA-dehydration over a fresh γ-Al_2O_3 for 8 h.

The updated UD 2.0 process used hexanes for both extraction and reaction, which avoided the use of toluene solvent and simplified the process. This UD 2.0 process generated 6600 kg/h 4,4′-DMBP from 8000 kg/h furfural. Its cost breakdown is shown in Figure 2b. The calculated MSP using the improved process is \$3044/t, which corresponds to a \$964/t reduction from the former UD 1.0 process. As expected, this is a result of smaller reactor sizes and thus lower capital investment. There is still room for improvement in the R-3 reactor to increase the reaction rate and reduce the solvent usage further. However, DA-dehydration optimization with a higher reactant concentration will be necessary to achieve high selectivity and carbon balance.

3.3. XOM Process and Technoeconomic Analysis.

As a comparison, the process of DMBP isomer production from petroleum resources (toluene) is modeled based on a series of patents by ExxonMobil Chemical. The reaction conditions are listed in Table 3.

Figure 3 depicts the conceptual plant configuration. Toluene was pressurized and co-fed with hydrogen gas before heating and sent to the hydroalkylation reactor R-1 under 180 °C and 12 bar, where toluene was converted to (methylcyclohexyl)-toluene (MCHT) isomers with different regioselectivity.[3,50] Using the Pd-loaded MCM-49 catalyst, the main byproduct from this process was the fully hydrogenated methylcyclohexane (MCH) with 23% selectivity.[50] An ambient-pressure distillation column (C-1) removed the heavy impurities from the product mixture in the top stream. Additional hydrogen gas was added to the mixture and pressurized again to 7.9 bar. Next, this mixture of different MCHT isomers, MCH, and unreacted toluene was sent to reactor R-2 for the dehydrogenation reaction under 425 °C and 7.9 bar, where the extra hydrogen gas was regenerated and supplied to R-1. It is assumed that MCH could also undergo dehydrogenation with the same 80% conversion as the MCHT intermediates to regenerate toluene in R-2.[51] Flash drum F-1 condensed the liquid-phase product from the hydrogen gas and sent it to distillation column C-2 to isolate 3,*X*′-DMBP and 4,4′-DMBP isomers from the bottom stream. Next, the distillate was conveyed to flash drum F-2 and distillation column C-3 to collect toluene from the top, and unreacted MCHT and 2,*X*′-DMBP from the bottom. This bottom stream mixture could be sent to a different refinery for further processing, while the top toluene stream was cooled in COOL-1 and sent back to pump P-1.[52]

Table 3. Reaction Conditions for Toluene-Based DMBP Synthesis

reaction	hydroalkylation	dehydrogenation	isomerization
T (°C)	180	425	200
P (bar)	12	7.9	14.8
WHSV (h^{-1})	2	2	1
H_2:hydrocarbon	2	5	0
catalyst	0.3% Pd/MCM-49	1% Pt/0.15% Sn/SiO_2	80% USY
conv. (%)	37	80	56

The average crude oil cost was taken as the surrogate of the byproduct stream price. The fact that 3,*X*′-DMBP and 4,4′-DMBP have close boiling points prevents efficient separation through distillation.[26,53] Therefore, the 3,*X*′-DMBP and 4,4′-DMBP streams were cooled to −5 °C in COOL-2 and crystallized in CRYS-1 to obtain nearly pure 4,4′-DMBP. The mother liquid stream was sent to distillation in C-4 to reduce the 4,4′-DMBP concentration. Next, the 3,4′-DMBP-rich stream was cooled again to −18 °C in COOL-2 and subjected to another crystallization in CRYS-2 to yield the 3,4′-DMBP solid. More information regarding DMBP solubility at different temperatures and operating conditions could be found in a recent patent.[52] The remaining 3,3′-DMBP-rich stream was heated to 200 °C and pressurized to 14.8 bar before being sent to the isomerization reactor R-3 packed with the USY catalyst.[52,54] This isomerization step is designed to convert lower-valued isomers, such as 3,3′-DMBP, into more valuable ones. After this reaction, the outlet stream has a higher 3,4′-DMBP and 4,4′-DMBP isomer ratio. This stream was then fed to flash drum F-1 for separation.

When the feedstock toluene flow rate is 83 kmol/h (7648 kg/h), 1419 kg/h 4,4′-DMBP, 1780 kg/h 3,4′-DMBP, and 3806 kg/h 2,*X*′-DMBP, and an MCHT-enriched stream are generated. Thus, the selectivity of the most valuable 4,4′-DMBP product is low, and the process’ economic performance will not be satisfactory if only the 4,4′-isomer is sold.

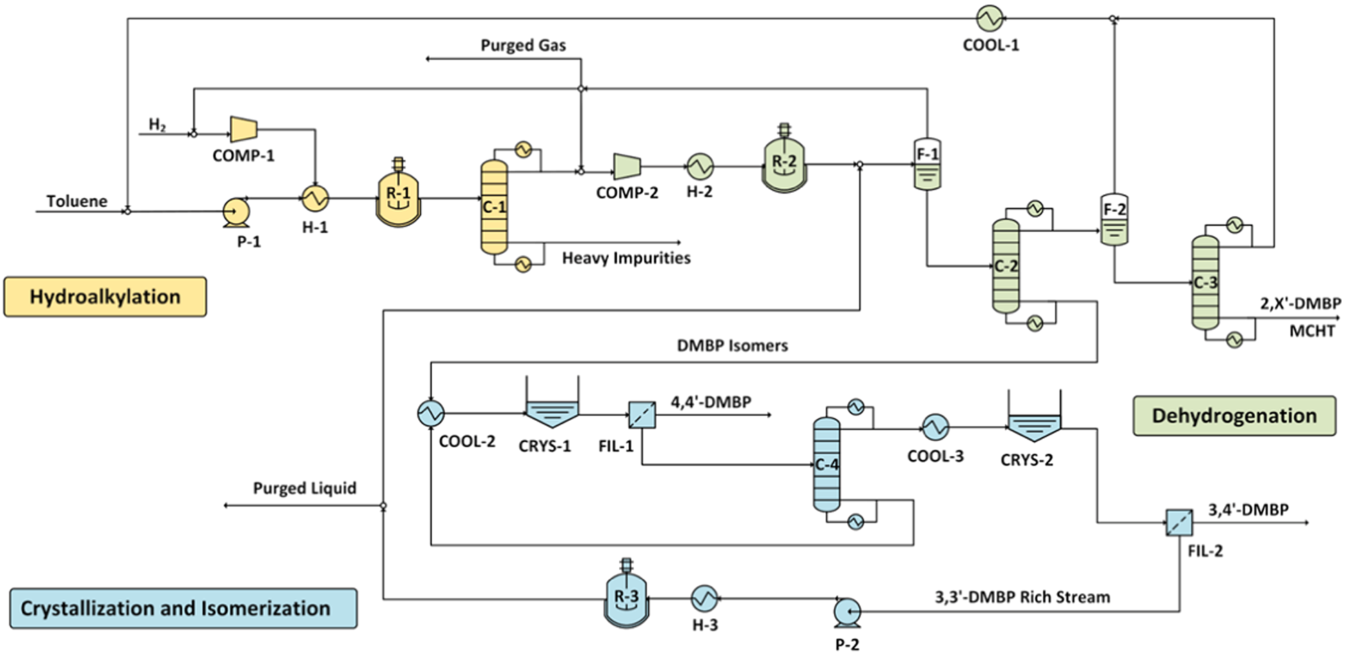


Figure 3. Process flow diagram for the conversion of toluene to DMBP via toluene hydroalkylation (COMP-1, P-1, H-1, R-1, C-1), MCHT dehydrogenation (COMP-2, H-2, R-2, F-1, C-2, F-2, C-3, COOL-1), and DMBP crystallization and isomerization (COOL-2, CRYS-1, FIL-1, C-4, COOL-3, CRYS-2, FIL-2, P-2, H-3, R-3).

Since a large quantity of 3,4′-DMBP is generated and has significant economic value, it is important to sell this byproduct to improve the process profitability and reduce waste. Consequently, a weighting factor was assigned to lower-valued co-product streams to represent the ratio between the selling prices of the 3,4′-DMBP isomer and the targeted 4,4′-DMBP isomer. The polyesters using 4,4′-DMBP demonstrate excellent performance, while 3,4′-DMBP could be used in polyester or plasticizer production at a lower cost. Therefore, in the base-case scenario, the price ratio of mixed xylene to *p*-xylene (0.71) is used as a surrogate for the 3,4′-DMBP to 4,4′-DMBP price ratio because of the similarities in molecular structure and applications. A sensitivity analysis is later performed to account for market price uncertainty for this emerging chemical product.

The MSP of 4,4′-DMBP by the toluene-based XOM process is \$2488/t for the base-case scenario, but this value is highly sensitive to the isomer price ratio and byproduct cost assumptions. Figure 4 compares the MSP breakdown between XOM and UD processes. One reason for the XOM process to have lower MSP than the UD processes is the revenue by selling the 2,*X*′-DMBP and MCHT mixture to other refineries. The XOM process also has the edge over the UD processes because of its fast reaction rate, leading to smaller equipment sizes and capital investment. This process could achieve better performance if the 2,*X*′-DMBP isomers from the byproduct stream are separated, isomerized, and sent back to the XOM process to increase 3,4′-DMBP and 4,4′-DMBP yields.[54] Nevertheless, an unfavorable market for the MCHT/2,*X*′-DMBP mixture or limited processing ability of the downstream refinery will lead to the deteriorated economic performance of the XOM process. However, after the reaction improvement, the UD 2.0 process has a noticeable decrease in the capital investment compared to UD 1.0 and shows comparable production cost to the XOM process if the byproduct cost is not considered (\$3082/kg). Moreover, the UD process is still at its early stage of development. When the solvent usage and reaction time are further reduced, the UD process economic performance is expected to improve.

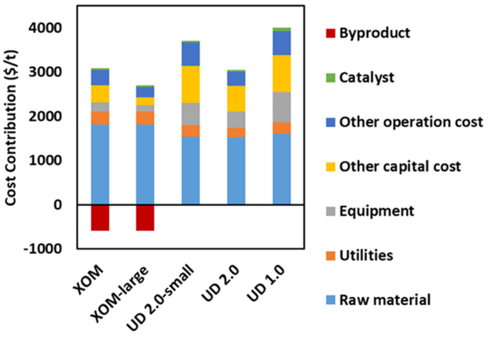


Figure 4. Cost comparison between XOM and UD processes (XOM and UD 2.0 both use 83 kmol/h feedstock; XOM-large and UD 2.0 both produce 6600 kg/h 4,4′-DMBP; XOM, and UD 2.0-small both produce 1420 kg/h 4,4′-DMBP).

Another essential assumption in the XOM process is the byproduct prices. Since 4,4′-isomers are produced in relatively small quantities, most of the profit comes from less valuable 3,4 and 2,*X*′ isomers. If the demand for the 4,4′-isomer is more urgent, the XOM process with merely 20.3% 4,4′-DMBP selectivity is apparently disfavored.

3.4. Sensitivity Analysis.

Although the preliminary economic evaluation indicates that the XOM process has an advantage over the UD process in the base case, this comparison largely depends not only on the assumptions made but also on the uncertainties in the parameters considered in the modeling. As mentioned in Section 3.4, the price ratio between the 4,4′-DMBP and 3,4′-DMBP could drastically change the final selling price of the targeted 4,4′ isomer. It is also widely acknowledged that processes with large production capacities benefit from economy-of-scale. Another source of uncertainty comes from the highly dynamic chemical market and subsidies for biomass-based feedstocks. Thus, a sensitivity analysis is performed to study the effects of these uncertainties.

The minimum selling prices of DMBP by XOM and UD 2.0 processes at different scales are first compared. When the feedstock's mole flow rates are kept constant, the UD process produces much more 4,4′-DMBP isomers than the XOM process (6600 vs 1420 kg/h) due to its high 4,4′-isomer regioselectivity. Two additional cases are considered in which the UD process produces 1420 kg/h 4,4′-DMBP (UD 2.0-small) and the XOM process generates 6600 kg/h 4,4′-DMBP (XOM-large). As illustrated in Figure 5, after scaling the capacity up by a factor of 4.6, the MSP for the XOM-large process reduces by merely \$384/kg to \$2104/kg. The UD 2.0-small process, on the other hand, has a more significant cost rise of \$655/kg to \$3699/kg. It is noteworthy that the XOM process in the base case already has a relatively low capital cost and fixed operating costs, leaving little room to improve through the expansion of plant scales.

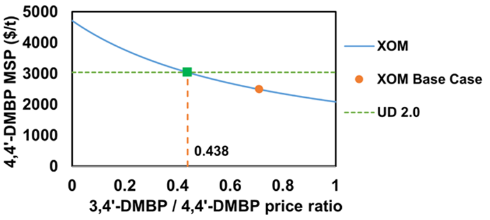


Figure 5. Minimum selling price (MSP) of 4,4′-DMBP under different isomer price ratio (Green square represents the critical isomer price ratio of 0.438).

Next, the 4,4′-DMBP minimum selling price of the XOM process as a function of the isomer price ratio is depicted in Figure 5. This price ratio also reflects the relative importance of different DMBP isomers. When the need for 4,4′-DMBP is urgent, more emphasis should be given to its production, causing the 3,4′-DMBP to 4,4′-DMBP price ratio to drop. If the 3,4′-DMBP isomer price is lower than 0.438 of the 4,4′-DMBP price, the UD 2.0 process will outperform the XOM process.

The effects of other uncertain parameters on the UD 2.0 and XOM processes' MSPs are illustrated in Figure 6. For both processes, the feedstock prices are the biggest contributor to the overall MSP variations. One vital assumption for the UD 2.0 process is the homogeneous catalyst loss during the continuous operation. Even if the Palladium acetate catalyst loss increases by ten folds (from 1 to 10% every 6 months), the final MSP only increases by \$140/t. Moreover, the XOM process relies heavily on the byproduct revenue for cost reduction. Thus, a slight fluctuation of the byproduct cost would trigger noticeable changes in the 4,4′-DMBP's minimum selling price.

3.5. Life-Cycle Assessment.

Life-cycle assessment has been widely used for the comprehensive evaluation of different processes' environmental impacts, which enables sustainable decision-making.[55] Since the mass allocation is performed on the 3,4′-DMBP byproduct, the underlying assumption is that 1 kg of 3,4′-DMBP will bear the same emission burden as 1 kg of 4,4′-DMBP. Another common method to treat byproducts is economic allocation, which is based on the total values of the product streams and is more susceptible to price fluctuation. The global warming potentials (GWPs) of producing 1 kg DMBP by both processes are compared in Figure 7.

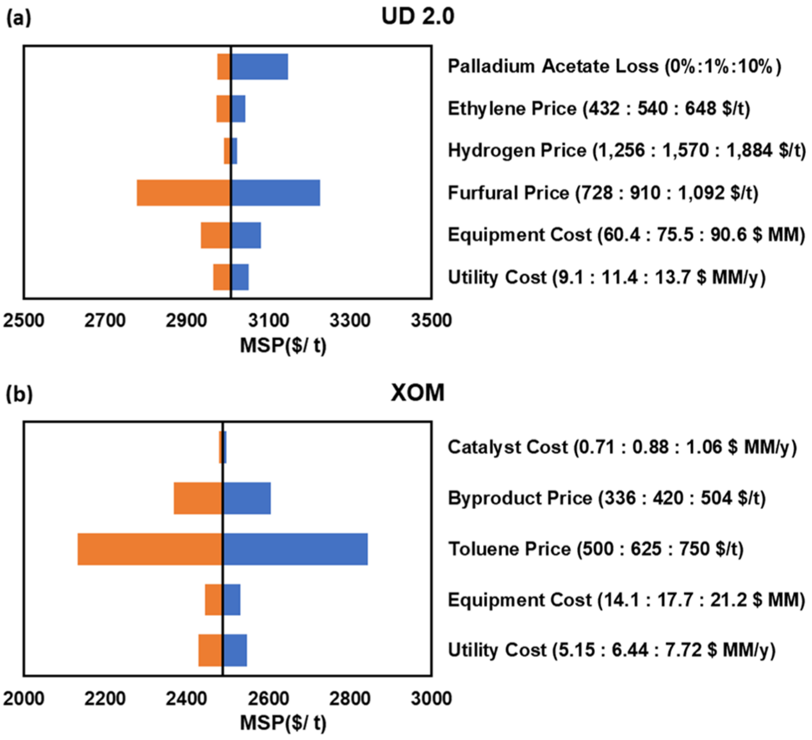


Figure 6. Sensitivity of the MSP of 4,4′-DMBP to feedstock and byproduct price, equipment investment, utility cost, and catalyst loss. Parameters were varied ±20% relative to the base-case design, except for the palladium acetate catalyst loss every 6 months. Blue indicates the high parameter value, and orange indicates the low parameter value. The solid black line shows the baseline cost.

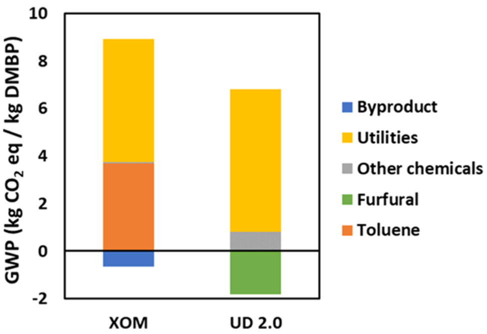


Figure 7. Global warming potential (GWP) breakdown of 1 kg DMBP produced by XOM and UD 2.0 processes.

The life-cycle assessment shows that the GWP associated with utilities in UD 2.0 (5.99 kg CO_2 equiv/kg DMBP) is close to that of the XOM process (5.20 kg CO_2 equiv/kg DMBP). Moreover, the utility usage leads to the highest CO_2 emissions for both processes, although its contribution to the cost is modest. This is because steam, electricity, and other heating sources are supplied primarily from burning fuels. Not surprisingly, the UD 2.0 process has lower greenhouse gas emissions than the XOM process, primarily because of its use of biomass-based furfural feedstock instead of fossil-based toluene. Furfural is manufactured industrially through the use of corn cob, an agricultural waste. Thus, carbon dioxide is stored and converted to organic components during the biomass growth stage, leading to the negative emission factor (−1.82 kg CO_2 equiv/kg DMBP). On the other hand, toluene is produced from petroleum, which inevitably causes greenhouse emissions (3.70 kg CO_2 equiv/kg DMBP). In addition to toluene, the XOM process only uses hydrogen gas as its feedstock. Since the majority of the hydrogen gas produced from the second-step dehydrogenation reaction was recycled and fed back to the hydroalkylation reactor, only a minimal amount of makeup hydrogen stream was needed. It is assumed that the excess hydrogen gas is supplied by the methane steam reforming process. Consequently, the XOM process has a relatively low GWP from the use of other chemicals as compared to the UD 2.0 process. Overall, 1 kg of DMBP produced by the UD 2.0 process has a cradle-to-gate GWP of 5.00 kg CO_2 equiv, only 60.3% of that produced by the XOM process (8.28 kg CO_2 equiv).

4. CONCLUSIONS

Two 4,4′-DMBP production routes using different feedstocks are designed and simulated based on experimental results and patent information. Then, the economic and environmental performance of the furfural-based process (UD 1.0 and UD 2.0) is benchmarked against the toluene-based process (XOM). The cost breakdown provides insight into the path toward economic viability by optimizing the reaction conditions, such as shorter reaction times and a more robust catalyst. The XOM process benefits from small equipment sizes and cheap toluene feedstock, showing a lower MSP ($2488/t) than the UD 2.0 process ($3044/t) in the base case. Nevertheless, various byproduct and 3,4′-DMBP price scenarios could still render it less appealing economically than the UD 2.0 process.

On the other hand, the UD 2.0 process has a higher regioselectivity towards the most valuable DMBP isomer, making it a carbon-efficient method to produce and separate the valuable 4,4′-DMBP in larger quantities.[54] The carbon efficiency of the furfural-based route is nominally 1 as no other DMBP positional isomers are formed, although this value may be slightly lower in reality due to the byproduct formation and coke accumulation. Consequently, a smaller plant size is enough to cater to the same demand of 4,4′-DMBP as the toluene-based process. It is also less sensitive to the market price fluctuation of isomers that have different applications. From the process operation point of view, the XOM process requires heating to as high as 425 °C for the dehydrogenation reaction and cooling to as low as −18 °C for isomer crystallization, making the product quality more challenging to control than the UD process. The furfural feedstock, hexane solvents, catalysts, and other chemicals in the proposed UD route are commonly used in the chemical industry with abundant supply. Reaction conditions have been optimized to give good conversions and avoid unwanted side reactions. Although scale-up and careful engineering design remain the focus of our future work, our analysis has emphasized the need to reduce solvent usage and reaction time, which is typically achieved in technology development and scale-up.[56−58] These process improvements will further increase the financial and operational feasibility of the biomass-based routes. Environmentally, the use of renewable feedstock (furfural) significantly reduces the greenhouse gas emissions of the 4,4′-DMBP production, encouraging customers to choose this process with the increasing awareness of global warming.

Overall, the novel furfural-based 4,4′-DMBP process proposed and optimized in this work has the potential to produce polyesters with higher quality, lower emission, and reasonable costs. As indicated by the sensitivity analysis, the process economics will benefit significantly with decreased furfural prices or subsidies for decreased CO_2 emission. Future research efforts that can further cut the cost include reduced solvent usage and residence time for extraction and reaction and a more efficient recycling method of the homogeneous Pd(II) catalyst.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.2c00398.

> Catalyst characterization (Table S1, Figures S1−S3); experimental procedure; additional technoeconomic analysis and life-cycle assessment assumptions (Table S2, Figure S4); cost summary of each scenario (Tables S3−S7) (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is financially supported by the U.S. Department of Energy's RAPID Manufacturing Institute for Process Intensification (DE-EE000788-7.6), Catalysis Center for Energy Innovation (DE-SC0001004), the National Science Foundation's Growing Convergence Research program (NSF GCR CMMI 1934887), and Grant No. OIA − 2119754. The authors also acknowledge Yong Yuan for measuring the Lewis acid density.

■ REFERENCES

(1) Browne, A.; McIntyre, J. Solid State Manufacture of Polyesters. U.S. Patent US3,842,041A, October 15, 1974.

(2) Mazoyer, E.; Lanci, M. P. Preparation and Use of Biphenyldicarboxylic Acids. U.S. Patent US20,200,361,845A1, November 19, 2020.

(3) Salciccioli, M.; Dakka, J. M.; De Smit, E.; Sangar, N.; Weigel, S. J.; Raman, S.; Helton, T. E.; DeCaul, L. C.; Elia, C. N.; Bai, C. Production and Use of Dialkylbiphenyl Isomer Mixtures. U.S. Patent US20,150,361,011A1, December 17, 2015.

(4) Morris, J. C.; Jackson, W. J., Jr. Copolyesters of 4, 4′-Biphenyldicarboxylic Acid, 1, 4-Butanediol and Ethylene Glycol. U.S. Patent US5,081,220A, January 14, 1992.

(5) Luo, R.; Xu, H.; Gu, H.-X.; Wang, X.; Xu, Y.; Shen, X.; Bao, W.; Zhu, D.-R. Four MOFs with 2, 2′-dimethoxy-4, 4′-biphenyldicarboxylic acid: syntheses, structures, topologies and properties. *CrystEngComm* **2014**, *16*, 784−796.

(6) Wang, H.-H.; Jia, L.-N.; Hou, L.; Shi, W.-J.; Zhu, Z.; Wang, Y.-Y. A new porous MOF with two uncommon metal−carboxylate−pyrazolate clusters and high CO_2/N_2 selectivity. *Inorg. Chem.* **2015**, *54*, 1841−1846.

(7) Wang, X.-Z.; Zhu, D.-R.; Xu, Y.; Yang, J.; Shen, X.; Zhou, J.; Fei, N.; Ke, X.-K.; Peng, L.-M. Three novel metal-organic frameworks with different topologies based on 3, 3′-dimethoxy-4, 4′-biphenyldicarboxylic acid: syntheses, structures, and properties. *Cryst. Growth Des.* **2010**, *10*, 887−894.

(8) Kaplan, G. Preparation of Biphenols by Oxidative Coupling of Alkylphenols Using a Recyclable Copper Catalyst. U.S. Patent US6,689,921B2, 2004.

(9) Eckardt, M.; Greb, A.; Simat, T. J. Polyphenylsulfone (PPSU) for baby bottles: a comprehensive assessment on polymer-related non-intentionally added substances (NIAS). *Food Addit. Contam., Part A* **2018**, *35*, 1421−1437.

(10) Dakka, J. M.; DeCaul, L. C.; Costello, C. A.; Mozeleski, E. J.; Osterrieth, P.; Zushma, S.; Goodwin, A. D.; Smirnova, D.; Faler, C. A.; DeFlorio, V. Alkyl Aromatic Hydroalkylation for the Production of Plasticizers. U.S. Patent US9,085,669B2, July 21, 2015.

(11) Sun, Y.; Li, X.; Sun, H. Arylation of non-activated C−Cl bond with Grignard reagents catalyzed by pincer [PCP]-nickel complexes. *Inorg. Chim. Acta* **2014**, *415*, 95−97.

(12) Savanur, H. M.; Kalkhambkar, R. G.; Laali, K. K. $Pd(OAc)_2$ catalyzed homocoupling of arenediazonium salts in ionic liquids: synthesis of symmetrical biaryls. *Tetrahedron Lett.* **2016**, *57*, 663−667.

(13) Dakka, J. M.; DeCaul, L. C.; Kuechler, K. H.; Sangar, N.; Salciccioli, M.; Galuska, A. A.; Mohr, G. D. Production and Use of 3, 4′and 4, 4′-Dimethylbiphenyl Isomers. U.S. Patent US20,150,080,545A1, March 19, 2015.

(14) Vercammen, J.; Bocus, M.; Neale, S.; Bugaev, A.; Tomkins, P.; Hajek, J.; Van Minnebruggen, S.; Soldatov, A.; Krajnc, A.; Mali, G.; et al. Shape-selective C−H activation of aromatics to biarylic compounds using molecular palladium in zeolites. *Nat. Catal.* **2020**, *3*, 1002−1009.

(15) Ramineni, K.; Liu, K.; Zhang, C.; Chen, X.; Hou, G.; Gao, P.; Balaga, R.; Marri, M. R.; Yan, P.; Guan, X.; et al. Synchronized C−H activations at proximate dinuclear Pd^{2+} sites on silicotungstate for oxidative C−C coupling. *ACS Catal.* **2021**, *11*, 3455−3465.

(16) Cioc, R. C.; Crockatt, M.; van der Waal, J. C.; Bruijnincx, P. C. A. The interplay between kinetics and thermodynamics in huran Diels−Alder chemistry for sustainable chemicals production. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202114720.

(17) Dakka, J. M.; Patel, B. A.; Salciccioli, M.; Zushma, S. Oxidation of Methyl-Substituted Biphenyl Compounds. U.S. Patent US20,200,325,096A1, October 15, 2020.

(18) The Polyester Fiber Market valuation would reach over USD 160 billion by 2027. 2021, https://www.globenewswire.com/fr/news-release/2021/09/22/2301185/0/en/The-Polyester-Fiber-Market-valuation-would-reach-over-USD-160-billion-by-2027-says-Global-Market-Insights-Inc.html (accessed Jan 3, 2022).

(19) Athaley, A.; Annam, P.; Saha, B.; Ierapetritou, M. Techno-economic and life cycle analysis of different types of hydrolysis process for the production of p-Xylene. *Comput. Chem. Eng.* **2019**, *121*, 685−695.

(20) Athaley, A.; Saha, B.; Ierapetritou, M. Biomass-based chemical production using techno-economic and life cycle analysis. *AlChE J.* **2019**, *65*, No. e16660.

(21) Ye, M.; Kuo, M. J.; Lobo, R. F. Oxidative coupling of 2-methyl furoate: A scalable synthesis of dimethyl 2,2′-bifuran-5,5′-dicarboxylate. *Appl. Catal., A* **2021**, *619*, No. 118138.

(22) Rorrer, N. A.; Nicholson, S.; Carpenter, A.; Biddy, M. J.; Grundl, N. J.; Beckham, G. T. Combining reclaimed PET with bio-based monomers enables plastics upcycling. *Joule* **2019**, *3*, 1006−1027.

(23) Singh, A.; Rorrer, N. A.; Nicholson, S. R.; Erickson, E.; DesVeaux, J. S.; Avelino, A. F. T.; Lamers, P.; Bhatt, A.; Zhang, Y.; Avery, G.; Tao, L.; Pickford, A. R.; Carpenter, A. C.; McGeehan, J. E.; Beckham, G. T. Techno-economic, life-cycle, and socioeconomic impact analysis of enzymatic recycling of poly(ethylene terephthalate). *Joule* **2021**, *5*, 2479−2503.

(24) Cho, H. J.; Kuo, M. J.; Ye, M.; Kurz, Y.; Yuan, Y.; Lobo, R. F. Selective synthesis of 4,4′-dimethylbiphenyl from 2-methylfuran. *ACS Sustainable Chem. Eng.* **2021**, *9*, 3316−3323.

(25) Huang, K.; Brentzel, Z. J.; Barnett, K. J.; Dumesic, J. A.; Huber, G. W.; Maravelias, C. T. Conversion of furfural to 1,5-pentanediol: Process synthesis and analysis. *ACS Sustainable Chem. Eng.* **2017**, *5*, 4699−4706.

(26) Lanci, M. P.; Paek, C.; Dorsi, C. M. Production and Separation of Dimethyl Biphenyl Isomers. U.S. Patent US20,190,300,457A1, October 3, 2019.

(27) Wernet, G.; Bauer, C.; Steubing, B.; Reinhard, J.; Moreno-Ruiz, E.; Weidema, B. The ecoinvent database version 3 (part I): overview and methodology. *Int. J. Life Cycle Assess.* **2016**, *21*, 1218−1230.

(28) Bare, J. TRACI 2.0: the tool for the reduction and assessment of chemical and other environmental impacts 2.0. *Clean Technol. Environ. Policy* **2011**, *13*, 687−696.

(29) Guest, G.; Cherubini, F.; Strømman, A. H. Global warming potential of carbon dioxide emissions from biomass stored in the Anthroposphere and used for bioenergy at end of life. *J. Ind. Ecol.* **2013**, *17*, 20−30.

(30) Svanes, E.; Vold, M.; Hanssen, O. J. Effect of different allocation methods on LCA results of products from wild-caught fish and on the use of such results. *Int. J. Life Cycle Assess.* **2011**, *16*, 512−521.

(31) Anastasopoulou, A.; Keijzer, R.; Patil, B.; Lang, J.; van Rooij, G.; Hessel, V. Environmental impact assessment of plasma-assisted and conventional ammonia synthesis routes. *J. Ind. Ecol.* **2020**, *24*, 1171−1185.

(32) Liu, Z.; Zhu, D.; Jin, W.; Shwn, Q.; Hou, M.; Yang, X. Catalyst for Furfural Gas-Phase Hydrogenization Synthetizing 2-Methyl Furan. CN Patent CN1047100C, December 8, 1995.

(33) Hahn, B. R.; Maier, T. R.; Chawla, S. K. Separation Process. U.S. Patent US5,240,566A, August 31, 1993.

(34) Livingston, J. R., Jr.; Mozeleski, E. J.; Sartori, G. Method for Separating Water Soluble Noble Metal Catalyst from a Noble Metal Catalyzed Hydroformylation Reaction. U.S. Patent US5,215,667A, June 1, 1993.

(35) Demopoulos, G. P.; Pouskouleli, G.; Prud'Homme, P. J. A. Direct Recovery of Precious Metals by Solvent Extraction and Selective Removal. U.S. Patent US4,654,145A, March 31, 1987.

(36) Jasra, R. V.; Ghosh, P. K.; Bajaj, H. C.; Boricha, A. B. Process for Recovery of Palladium from Spent Catalyst. U.S. Patent US7,473,406B2, January 6, 2009.

(37) Chang, B.-H.; Goel, A. B. Manufacture of Palladous Carboxylates. U.S. Patent US4,465,635A, August 14, 1984.

(38) Oppenheim, J. P.; Dickerson, G. L.Updated by Staff. Adipic Acid. In *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons, Inc., 2000.

(39) Kanadibhotla, R. S.; Riggs, J. B. Nonlinear model based control of a recycle reactor process. *Comput. Chem. Eng.* **1995**, *19*, 933−948.

(40) Reyes, F.; Luyben, W. L. Design and control of a gas-phase adiabatic tubular reactor process with liquid recycle. *Ind. Eng. Chem. Res.* **2001**, *40*, 3762−3774.

(41) Kumar, A.; Daoutidis, P. Nonlinear dynamics and control of process systems with recycle. *J. Process Control* **2002**, *12*, 475−484.

(42) Baldea, M.; Daoutidis, P.; Kumar, A. Dynamics and control of integrated networks with purge streams. *AlChE J.* **2006**, *52*, 1460−1472.

(43) Yang, X.-W.; Zhang, X.-Y.; Guo, Z.-C.; Bai, W.-S.; Hao, L.; Wei, H.-Y. Effects of incompatible substances on the thermal stability of dimethyl sulfoxide. *Thermochim. Acta* **2013**, *559*, 76−81.

(44) Deguchi, Y.; Kono, M.; Koizumi, Y.; Izato, Y.-I.; Miyake, A. Study on autocatalytic decomposition of dimethyl sulfoxide (DMSO). *Org. Process Res. Dev.* **2020**, *24*, 1614−1620.

(45) DeWilde, J. F.; Chiang, H.; Hickman, D. A.; Ho, C. R.; Bhan, A. Kinetics and mechanism of ethanol dehydration on γ-Al2O3: the critical role of dimer inhibition. *ACS Catal.* **2013**, *3*, 798−807.

(46) Gafurov, M. R.; Mukhambetov, I. N.; Yavkin, B. V.; Mamin, G. V.; Lamberov, A. A.; Orlinskii, S. B. Quantitative analysis of Lewis acid centers of γ-alumina by using EPR of the adsorbed anthraquinone as a probe molecule: comparison with the pyridine, carbon monoxide IR, and TPD of ammonia. *J. Phys. Chem. C* **2015**, *119*, 27410−27415.

(47) Zuo, Z.; Huang, W.; Han, P.; Gao, Z.; Li, Z. Theoretical studies on the reaction mechanisms of AlOOH-and γ-Al_2O_3-catalysed methanol dehydration in the gas and liquid phases. *Appl. Catal., A* **2011**, *408*, 130−136.

(48) Rohling, R. Y.; Tranca, I. C.; Hensen, E. J. M.; Pidko, E. A. Mechanistic Insight into the [4 + 2] Diels−Alder Cycloaddition over First Row d-Block Cation-Exchanged Faujasites. *ACS Catal.* **2019**, *9*, 376−391.

(49) Nikbin, N.; Feng, S.; Caratzoulas, S.; Vlachos, D. G. p-Xylene formation by dehydrative aromatization of a Diels−Alder product in Lewis and Brønsted acidic zeolites. *J. Phys. Chem. C* **2014**, *118*, 24415−24424.

(50) Dakka, J. M.; DeCaul, L. C.; Tang, W. (Methylcyclohexyl) Toluene Isomer Mixtures, Their Production and Their Use in the Manufacture of Plasticizers. U.S. Patent US9,580,572B2, February 28, 2017.

(51) Dakka, J. M.; Bai, C.; Tanke, J. J.; De Martin, G. J.; Van Nostrand, M. T.; Salciccioli, M.; Kheir, A. A.; Sangar, N. Methyl-Substituted Biphenyl Compounds, their Production and their Use in the Manufacture of Plasticizers. U.S. Patent US9,688,602B2, June 27, 2017.

(52) Bokis, C. P.; Gazman, J.; Lotz, M. D.; Lanci, M. P.; Dorsi, C. M.; Weigel, S. J. Production and Use of 3, 4′and 4, 4′-Dimethylbiphenyl Isomers. U.S. Patent US20,210,053,890A1, February 25, 2021.

(53) Dakka, J. M.; DeCaul, L. C.; Kuechler, K. H.; Sangar, N.; Salciccioli, M.; Galuska, A. A.; Mohr, G. D. Production and Use of 3, 4′and 4, 4′-Dimethylbiphenyl Isomers. U.S. Patent US2,0150,080,545A1, March 19, 2015.

(54) Salciccioli, M.; Dakka, J. M.; De Smit, E.; Sangar, N.; Weigel, S. J.; Raman, S.; Helton, T. E.; DeCaul, L. C.; Ella, C. N.; Bai, C.; Ghose, R. Production and Use of Dialkylbiphenyl Isomer Mixtures. U.S. Patent US20,160,176,785A1, June 23, 2016.

(55) Luo, Y.; Ierapetritou, M. Comparison between different hybrid life cycle assessment methodologies: a review and case study of biomass-based p-xylene production. *Ind. Eng. Chem. Res.* **2020**, *59*, 22313−22329.

(56) Piccinno, F.; Hischier, R.; Seeger, S.; Som, C. From laboratory to industrial scale: a scale-up framework for chemical processes in life cycle assessment studies. *J. Cleaner Prod.* **2016**, *135*, 1085−1097.

(57) Bergesen, J. D.; Suh, S. A framework for technological learning in the supply chain: A case study on CdTe photovoltaics. *Appl. Energy* **2016**, *169*, 721−728.

(58) Walser, T.; Demou, E.; Lang, D. J.; Hellweg, S. Prospective environmental life cycle assessment of nanosilver T-shirts. *Environ. Sci. Technol.* **2011**, *45*, 4570−4578.

https://doi.org/10.1021/acs.iecr.2c00398
Ind. Eng. Chem. Res. 2022, 61, 8963−8972