

Production of Terephthalic Acid from Corn Stover Lignin

Song Song[†], Jianguang Zhang[†], Gökalp Gözaydın and Ning Yan^{*}

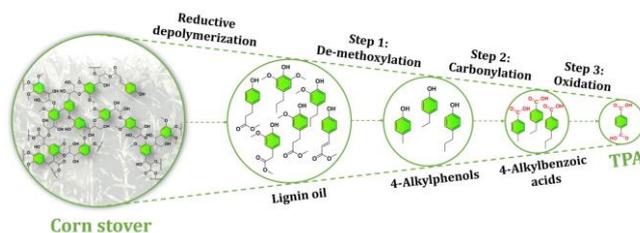
Abstract: Funneling and functionalization of a mixture of lignin-derived monomers into a single high-value chemical is fascinating. Herein, we report a three-step strategy for the production of terephthalic acid (TPA) from lignin-derived monomer mixtures, in which redundant, non-uniform substitutes such as methoxyl groups are removed and the desired carboxyl groups are introduced. This strategy begins with the hydro-treating of corn stover-derived lignin oil over supported molybdenum catalyst to selectively remove methoxyl groups. The generated 4-alkylphenols are converted into 4-alkylbenzoic acids via carbonylation with carbon monoxide. The Co-Mn-Br catalyst then oxidizes various alkyl chains into carboxyl groups, transforming the 4-alkylbenzoic acids mixture into a single product: TPA. Based on this route, the overall yields of TPA based on lignin content of corn stover could reach 15.5 wt%, and importantly, TPA with >99% purity was obtained simply by first decanting the reaction mixture, followed by washing the solid product with water.

Lignocellulose as an abundant and renewable source for various chemicals has attracted substantial attention over the last decade.^[1] Terephthalic acid (TPA), consumed primarily in polyethylene terephthalate manufacturing for making clothing and plastic bottles, is a critical commodity chemical with an expected market value of 110.66 billion USD by 2025.^[2] In industry, TPA is produced by the oxidation of *p*-xylene, which is derived from catalytic reforming of petroleum feedstock.^[3] Production of TPA from renewable biomass feedstock has been attracting much research interest.^[4] In recent years, the ongoing shift from naphtha to lighter feed slates (ethane in particular) in the crackers considerably compromise the production of heavier products such as *p*-xylene,^[5] making the development of alternative ways to prepare TPA a more pressing issue.

Previous studies mainly focus on the utilization of cellulose or hemicellulose-based platform molecules as substrates to produce *p*-xylene and/or TPA.^[4] As the most abundant aromatic biopolymer on earth, lignin has been proven as a suitable renewable resource to produce certain aromatic chemicals,^[1b, 1d, 1e] such as phenol^[6]. Recently, a report claims to convert vanillic acid and syringic acid to TPA with an overall yield of 39%.^[7] Although these two acids are in principle available via lignin oxidation, their combined yields are typically below 5 wt%^[8] making the route impractical. Compared to the oxidation treatment of lignin, reductive lignin depolymerization affords a much higher yields of aromatic monomers.^[1c, 1e] Starting from

birch wood, for instance, the total monomer yields reached up to 46%, with guaiacyl- and syringyl- type compounds as the main components.^[9] Even higher yields (78%) of monomers comprising mainly guaiacyl and syringyl monomers with 4-propyl- and 4-ethyl- substitutions have been more recently achieved from poplar wood lignin with the addition of formaldehyde as a stabilizer.^[10] From an engineering perspective, the flowthrough reductive catalytic fractionation technology, which enables the continuous production of lignin monomers, has also become viable.^[11]

Despite these advances, efficient transformation of the monomeric mixtures derived from reductive depolymerisation of lignin into an easily purifiable, single-component, value-added chemical remains a challenge. Inspired by the recent exciting achievement to convert complex lignin degradation products via a biological funneling strategy,^[12] herein, we communicate a route for the chemical transformation of corn stover-derived lignin oil mixtures into TPA (Scheme 1). In the first step, the methoxyl groups in the lignin-derived phenolics are removed by de-methoxylation, simplifying the stream into a mixture of 4-alkylphenols (step 1). These substituted phenols are further converted into a mixture of 4-alkylbenzoic acids by carbonylation to introduce the first -COOH group (step 2). Oxidation of the alkyl groups affords the second -COOH group, further narrowing down the stream to a single product TPA (step 3). Corn stover was used as the raw lignocellulose to demonstrate the feasibility of this strategy. For each step, simple model substrates were used first to identify effective catalysts and suitable reaction conditions, and then real lignin oil from corn stover (for step 1), or a mixture of substrates obtained from the previous step (for steps 2-3) was tested to ensure the feasibility of the entire route.



Scheme 1. Chemical funneling and functionalization of lignin derived phenolic stream into terephthalic acid (TPA).

Hydro-treating of lignin-derived phenolic model compounds (e.g. guaiacol and eugenol) over supported metal catalysts have been extensively investigated, but various products including phenols, alkanes and arenes, are all possible.^[13] To make the strategy viable, the key for step 1 is to identify a suitable catalyst that can selectively remove the methoxyl group while keeping the phenolic hydroxyl group and benzene ring untouched. We explored the de-methoxylation performance of a series of supported molybdenum oxide catalysts^[14] ($\text{MoO}_x/\text{TiO}_2$,

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MoO_x/CeO₂, MoO_x/SiO₂, MoO_x/AC and MoO_x/Al₂O₃) using 4-propylguaiacol as a model compound (Figure 1a). The highest yield of the target product 4-propylphenol (51%) was obtained over MoO_x/AC among all screened catalysts at 593 K, 30 bar H₂ after 2 h, possibly due to the inert nature and high surface area of activated carbon support. Time-on-stream performance for the de-methoxylation of 4-propylguaiacol over MoO_x/AC catalyst is shown in Figure 1b. Under applied reaction conditions, the direct de-methoxylation of 4-propylguaiacol to 4-propylphenol appears to be the dominant pathway. The yields of 4-propylphenol reached 71% with full conversion after 4 h. 2-methyl-4-propylphenol, 1,2-dimethoxy-4-propylbenzene and propylbenzene were detected as the main side products. Methanol originating from the hydrogenolysis of methoxyl group, had reacted with the remaining substrate to become 1,2-dimethoxy-4-propylbenzene, which was further transformed into propylbenzene over the MoO_x/AC catalyst *via* de-methoxylation. Thus, the yield of 1,2-dimethoxy-4-propylbenzene increased initially but then decreased after 4 h. Additionally, alkylation of 4-propylphenol afforded another side product, 2-methyl-4-propylphenol. An overall reaction network over MoO_x/AC catalyst is depicted in Scheme S1.

Next, MoO_x/AC catalyzed de-methoxylation of corn stover-derived lignin oil was conducted. Corn stover is produced at 216 and 220 million tons every year in the US and China, respectively,^[15] and its efficient utilization is a matter that has implications on both environment and economy. Lignin oil was obtained from corn stover by reacting with H₂ in methanol over a Ru/C catalyst (see SI for experimental details). A GC spectrum of the product is shown in Figure 1c (black line), where 4-ethylphenol, 2-methoxy-4-propylphenol, methyl 3-(4-hydroxyphenyl) propionate, 2,6-dimethoxy-4-propylphenol, methyl 3-methoxy-4-hydroxyphenylacetate, methyl 3-(3-methoxy-4-hydroxyphenyl) propionate and methyl coumarate were detected as the main monomers, with a total yield of 34.6 wt% based on the lignin content (13.5 wt%) (Table S1). The monomer yields were comparable to the reference (maximum yield: 38 wt%).^[16] MoO_x/AC catalyzed de-methoxylation of the lignin oil obtained from corn stover was then performed. As shown in Figure 1c (red line), the percentage of methoxyl group containing substrates that are the prevailing fraction in lignin oil (black dash rectangle in Figure 1c) dropped drastically to below 10% after the reaction.

Interestingly, the MoO_x/AC catalyst not only catalyzed the cleavage of the methoxyl group but also removed the oxygen in para-substituted ester groups on the phenolic monomers, probably due to the oxygen vacancy on the surface of MoO_x/AC catalyst that is known to be active in ester deoxygenation. This is a significant advantage, since the carboxyl group containing compounds, which are the dominant fraction in corn stover lignin oil, can be converted into 4-alkylphenols after the reaction. Results for the de-methoxylation of 2,6-dimethyl-4-propylphenol monomer are unsatisfactory, in accordance with the previous reports,^[6c, 17] but it is not a significant issue since it only accounts for 10 wt% in monomers. Three alkyl phenols, including 4-methylphenol, 4-ethylphenol and 4-propylphenol are the dominant fractions after de-methoxylation, which are ideal for further transformation (red dash rectangle in Figure 1c and Table S2).

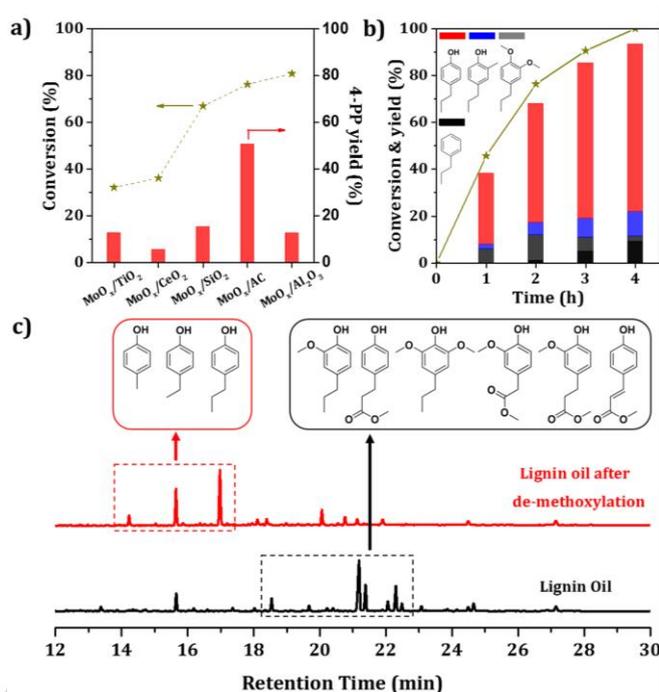


Figure 1. a) De-methoxylation of 4-propylguaiacol over molybdenum oxide catalysts (4-propylphenol was denoted as 4-PP). Reaction conditions: 4-propylguaiacol 1 mmol, catalyst 0.1 g, octane (internal standard) 0.07 g, toluene 3 mL, H₂ = 30 bar, T = 593 K, t = 2 h; b) Time-on-stream performance of de-methoxylation of 4-propylguaiacol over MoO_x/AC catalyst. Reaction conditions: same as in a); c) Black line: A GC spectrum of the obtained lignin oil from corn stover. Reaction conditions: corn stover 1.0 g, 5% Ru/C 0.1 g, methanol 250 mL, H₂ = 30 bar, T = 513 K, t = 3 h; Red line: A GC spectrum of lignin oil after de-methoxylation. Reaction conditions: lignin oil 0.11 g, MoO_x/AC 0.2 g, toluene 3 mL, H₂ = 30 bar, T = 593 K, t = 10 h.

Insertion of CO into the C-OH bond in 4-alkylphenols is the second step. We used Pd-based catalyst to promote the reaction, and 4-propylphenol was chosen as a model substrate. Due to the inert nature of the phenolic hydroxyl group, 4-propylphenol was first mixed with triflic anhydride to form 4-propylphenol triflate (Figure S1 & 2), and then the triflate was converted into 4-propylbenzoic acid (Figure S3 & 4) over Pd catalysts with nine phosphine ligands (as shown in Figure 2). Several diphosphine ligands, like Xantphos (**L1**), dcpp (**L2**), dppe (**L3**) and dppp (**L4**), as well as SPhos (**L5**), a typical Buchwald ligand, exhibited no activity. 12% yield of 4-propylbenzoic acid was obtained with monodentate phosphine ligand, PPh₃ (**L6**), after 12 h at 60 °C. BINAP-type ligands exhibited much better activity, with yields of 21% and 42% yield being obtained for BINAP (**L7**) and Tol-BINAP (**L8**) respectively. The best performance (47%) was observed with ferrocene-type phosphine ligands, dppf (**L9**). The yield of 4-propylbenzoic acid further increased to 78% using the **L9** ligand at a reaction time of 24 h. Different solvents including DMSO, DMA, NMP, CH₃CN and DMF, were tested but no activity was observed except reactions in DMSO, which may have formed strong complexes with Pd (II) during the reaction.

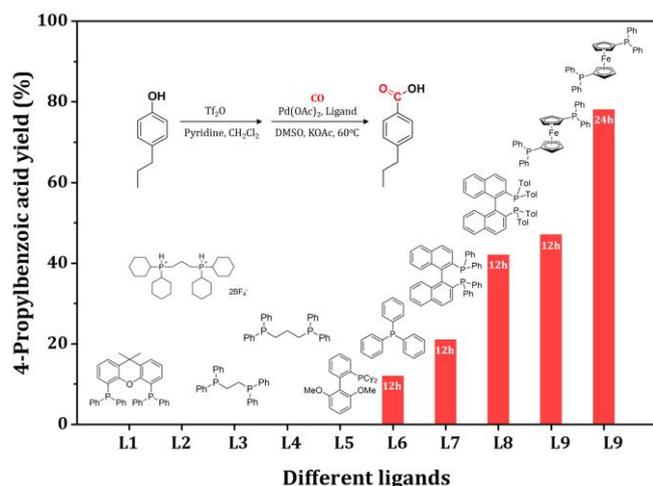


Figure 2. Carbonylation of 4-propylphenol to 4-propylbenzoic acid over different phosphine ligands. Reaction conditions: (1) 4-propylphenol 10 mmol, DCM 50 mL, pyridine 20 mmol, triflic anhydride 12 mmol; (2) 4-propylphenol triflate 2 mmol, Pd(OAc)₂ 5 mol%, ligand 20 mol%, KOAc 8 mmol, DMSO 25 mL, CO balloon, T = 60 °C.

A mixture of 4-methylphenol, 4-ethylphenol and 4-propylphenol, in the same portions as obtained after the demethoxylation of lignin oil, was used as the substrate for the carbonylation reaction. To our delight, close to 75% average yields of 4-alkylbenzoic acids (4-methyl benzoic acid 72%, 4-ethylbenzoic acid 75% and 4-propylbenzoic acid 76%) were obtained, demonstrating that the carbonylation protocol developed in the study is applicable to the transformation of various lignin derived alkyl phenols into the corresponding alkyl benzoic acids in one-pot.

In the last step, 4-alkylbenzoic acids are converted into TPA (step 3). Compared to stoichiometric oxidants (such as KMnO₄ or K₂Cr₂O₇), oxidants like H₂O₂ or O₂ are preferred due to their economic and environmental benefits. The Co-Mn-Br system is one of the most active and selective catalysts for aerobic oxidation reactions, such as in the oxidation of *p*-xylene,^[3] and therefore, it was selected to convert 4-propylbenzoic acid. The reaction didn't occur in the presence of Co(OAc)₂, Mn(OAc)₂ or KBr as catalysts (Table S3, entries 1 to 3), and no activity was observed with the combined use of Co(OAc)₂ + Mn(OAc)₂ (Table S3, entry 4). 6% and 11% yields of TPA were obtained when Co(OAc)₂ + KBr and Mn(OAc)₂ + KBr were used as catalysts, respectively (Table S3, entries 5 and 6). When all three components were added, the yield of TPA reached 60% under the same reaction conditions (Table S3, entry 7). Replacing KBr by KCl or KI completely quenched catalytic activity, suggesting the crucial role of Br (Table S3 entries 8 and 9). The reaction activity of various cobalt precursors follow the order: Co(OAc)₂>Co(acac)₃>CoCl₂>Co(NO₃)₂ (Table S3, entries 1, 8, 9 and 10). Similarly, Mn(OAc)₂ exhibited higher activity compared to MnSO₄ and MnCl₂ (Table S3, entries 11 and 12). We also performed the reaction using Ni(OAc)₂, Zn(OAc)₂ or Cu(OAc)₂ in the presence of Mn(OAc)₂ and KBr (Table S3, entries 15-17), but the yield of TPA was much lower (< 10%).

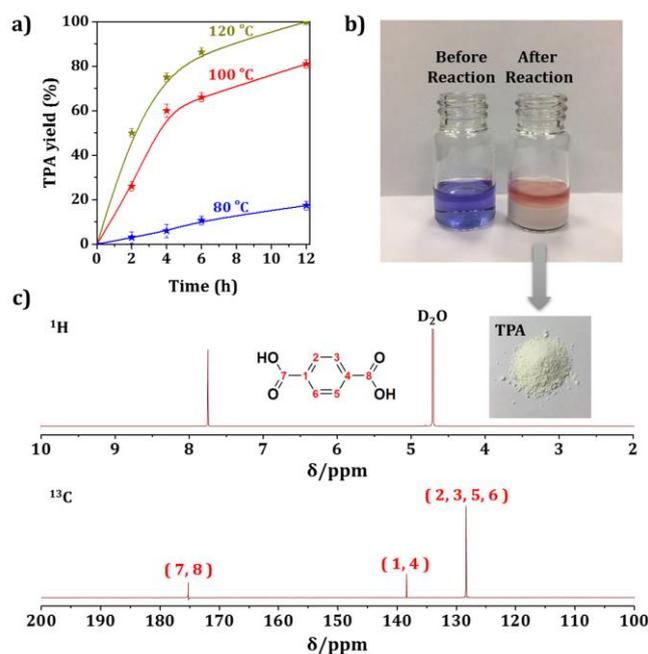


Figure 3. a) Time-on-stream performance for oxidation of 4-propylbenzoic acid over Co-Mn-Br catalyst at different reaction temperature. Reaction conditions: 4-propylbenzoic acid 2 mmol, Co(OAc)₂ 2.5 mol%, Mn(OAc)₂ 2.5 mol%, KBr 5.0 mol%, acetic acid 3 mL, O₂ = 10 bar; b) Pictures before reaction versus after reaction for oxidation of mimetic mixture over Co-Mn-Br catalyst. Reaction conditions: 4-methylbenzoic acid 0.1 mmol, 4-ethylbenzoic acid 0.7 mmol, 4-propylbenzoic acid 1.2 mmol, Co(OAc)₂ 2.5 mol%, Mn(OAc)₂ 2.5 mol%, KBr 5.0 mol%, acetic acid 3 mL, O₂ = 10 bar, T = 120 °C, t = 12 h; c) ¹H and ¹³C NMR spectra for the obtained product from Figure 3b.

From above, the co-existence of Co(OAc)₂, Mn(OAc)₂ and KBr were essential for the high activity. Time-on-stream curves at different reaction temperatures (Figure 3a) suggest that the reaction proceeded smoothly at 80 °C with 17% yield of TPA after 12 h. The yield increased significantly to 81% after raising the temperature to 100 °C. Further increasing the temperature to 120 °C enabled quantitative formation of TPA. Encouraged by the effectiveness of the system on the model compound, a mixture of 4-methylbenzoic acid, 4-ethylbenzoic acid and 4-propylbenzoic acid, obtained after the carbonylation step, was converted over Co(OAc)₂ + Mn(OAc)₂ + KBr catalyst with 10 bar O₂ at 120 °C. All the three substrates were converted into TPA in close to 100% yield within a single reaction vessel.

Before starting the reaction, the reaction media containing substrates, catalyst (Co(OAc)₂ + Mn(OAc)₂ + KBr) and acetic acid was a transparent homogeneous solution with a deep blue color (Figure 3b). After the reaction, the color of the solution changed to light red. Notably, large amounts of TPA in the form of white powder appeared at the bottom of the reactor, facilitating its purification from the reaction mixture. TPA was obtained simply by filtering and then washing with water. The NMR spectrum of the as-obtained white powder, dissolved in NaOH/D₂O, is shown in Figure 3c. Single ¹H signal (δ_{1H}=7.83 ppm) and three characteristic ¹³C signal (δ_{13C}=175.30, 138.51, and 128.49 ppm) belonging to TPA were detected, while no other peak is observable indicating the high purity of the product.

Purification of products from the reaction media is often a major challenge in biorefinery. Precipitation of the desired product from the solution with close to 100% purity is uncommon in biomass valorization, and this feature will significantly facilitate post-treatment and reduce the process cost.

The three chemical reactions developed above bridge corn stover lignin with TPA. On a lignin basis, 16.1 wt% of 4-alkylphenols were obtained after the de-methoxylation step, which can be converted into 14.8 wt% of 4-alkylbenzoic acids via carbonylation, and finally to 15.5 wt% TPA after oxidation (Figure S5). Of note, the yields of the 4-alkylbenzoic acids in our study were obtained from a mimetic mixtures of 4-alkylphenols). Based on this, we propose a conceptual design for the full utilization of corn stover for polyethylene terephthalate and other value-added applications (Figure S6). Lignin is converted into lignin oil via reductive depolymerization and then transformed into TPA based on the strategy developed in the current work. Acid catalysis of polysaccharide offers a series of high-value biomass platform molecules, such as glucose, xylose, 5-hydroxymethylfurfural, furfural, levulinic acid, etc. Hydrogenolysis of sugars affords ethylene glycol (EG) and propylene glycol, which copolymerize with TPA to access 100% bio-based polyethylene terephthalate (PET) and other plastics.

To summarize, we developed a new chemical route that could be used to produce TPA from corn stover-derived lignin oil via de-methoxylation, carbonylation and oxidation steps. A salient feature is that TPA precipitates from the solution in the final step in an almost pure form, avoiding any complex purification process. This work provides an example of chemical funneling and functionalization of complex lignin-derived monomers into a single, value-added compound.

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Keywords: carbonylation • de-methoxylation • lignin • renewable chemical • terephthalic acid

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Layout 1:

COMMUNICATION

Renewable PET: Terephthalic acid (TPA) with high yield and purity from corn stover lignin is achieved through a three-step conversion strategy.



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