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Catalytic Conversion of Lignin in Woody Biomass into Phenolic Monomers in Methanol/Water Mixtures without External Hydrogen

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Supporting Information

ABSTRACT: The valorization of lignin in renewable lignocellulosic biomass is an important target in the transition to a more sustainable production of fuels and chemicals. We present here a modification of the "lignin-first" approach that does not hinge on the use of external hydrogen. Instead, we use methanol/water mixtures as a suitable solvent that can be partly reformatted into hydrogen. We propose a one-step process in which in planta lignin (wood sawdust) is converted to phenolic monomers over a Pt-based catalyst in an inert atmosphere. The role of the methanol/water mixture is not only to supply hydrogen but also to extract lignin fragments from the biomass matrix. Pt catalyzes methanol reforming to obtain hydrogen and the stabilization of reactive lignin intermediates by hydrogenation of reactive bonds. The latter aspect is crucial to avoid unfavorable condensation of fragments. Under optimized conditions, a yield of phenolic monomers of nearly 50% can be obtained from birch wood at a temperature of 230 °C in 3 h.

KEYWORDS: Lignin, Aromatics, Lignin first, Hydrogen, Reforming, Catalysis

INTRODUCTION

Nearly all fuels and bulk and specialty chemicals are currently produced from fossil resources. This practice cannot be sustained due to the negative impact on the environment of the use of nonrenewable feedstocks with global warming as the greatest concern. Replacing petroleum feedstock by nonfood lignocellulosic biomass is widely considered as a promising alternative for the production of chemical building blocks in a sustainable manner. The main components contained in lignocellulose are cellulose, hemicellulose, and lignin. Cellulose and hemicellulose are polymers of carbohydrates, while lignin is made up from the phenylpropanoids p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) derived from the respective monolignols p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. Efficient fractionation of these three main components of lignocellulose is important when the aim is to obtain value-added products of the monomers contained in them.

While many processes have been developed to convert the carbohydrate fractions of woody biomass into useful intermediate chemicals, the upgrading of lignin is at a much more infant stage. It is however increasingly recognized that lignin is a very interesting source of sustainable aromatics. Moreover, biorefining concepts that traditionally focus on sugar upgrading can only be cost competitive when as much as possible of the lignocellulosic biomass is valorized. Accordingly, many researchers have explored possibilities to convert lignin into aromatic monomers. An important corollary of these investigations so far is that technical lignins, which are obtained by first removing the cellulose part from woody biomass, are very unreactive. The main cause is that most of the reactive ether-type lignin intralinkages in the original woody biomass have been condensed into more recalcitrant carbon—carbon bonds. This explains the attractiveness of "in planta" fractionation of lignin as compared to the valorization of "ex planta" (technical) lignin. Selective removal of lignin fragments can be achieved under much milder conditions by reductive depolymerization of the original woody biomass than by upgrading of lignin. In the in planta approach the ester and ether bonds between the lignin and hemicellulose can be cleaved by solvolysis, releasing lignin oligomers. These reactive lignin fragments can be stabilized and converted to more stable aromatic monomers by reductive depolymerization using metal catalysis and hydrogen. These lignin-first approaches typically yield about 50% aromatic monomers from the lignin fraction of woody biomass. Reductive lignin depolymerization comprises the extraction of lignin fragments from biomass followed depolymerization into phenolic monomers in a one-pot approach. A wide range of solvents has been evaluated with the aim to optimize the delignification step. As lignin contains both nonpolar and polar moieties, solvents with intermediate polarity such as methanol and ethanol are preferred for lignin extraction.

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Lignin fragments are converted to phenolic monomers through metal-catalyzed hydrogenolysis in the presence of hydrogen. For instance, a hydrogen pressure of 30 bar was used to convert lignin in birch wood to a range of phenolic monomers using a Ru/C catalyst. Delignification and lignin depolymerization can also be performed in a two-stage fixed-bed reactor.

### Table 1. Comparison of Different Approaches for Reductive Lignin Depolymerization Involving Hydrogen-Donor Solvents and Methanol/Water Mixtures

<table>
<thead>
<tr>
<th></th>
<th>Ref. 24</th>
<th>Ref. 26</th>
<th>Ref. 28</th>
<th>This work</th>
</tr>
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<tr>
<td>Feedstock</td>
<td>0.2 g of birch sawdust</td>
<td>2.0 g of birch sawdust</td>
<td>2.0 g of poplar sawdust</td>
<td>2.0 g of birch sawdust</td>
</tr>
<tr>
<td>Catalyst</td>
<td>30 mg 1 mol% Co on phenanthroline/carbon</td>
<td>100 mg of 10 wt% Ni/C</td>
<td>200 mg of Pd/C</td>
<td>500 mg 1 wt% Pt/γ-Al2O3</td>
</tr>
<tr>
<td>Monomer yield</td>
<td><img src="" alt="Monomer 1" /></td>
<td><img src="" alt="Monomer 2" /></td>
<td><img src="" alt="Monomer 3" /></td>
<td><img src="" alt="Monomer 4" /></td>
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<tr>
<td></td>
<td>15 wt%</td>
<td>48 wt%</td>
<td>35.5 wt%</td>
<td>46.1 wt%</td>
</tr>
<tr>
<td></td>
<td><img src="" alt="Monomer 5" /></td>
<td><img src="" alt="Monomer 6" /></td>
<td><img src="" alt="Monomer 7" /></td>
<td><img src="" alt="Monomer 8" /></td>
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<tr>
<td></td>
<td>11 wt%</td>
<td>0.5 wt%</td>
<td>5.0 wt%</td>
<td>0.3 wt%</td>
</tr>
<tr>
<td></td>
<td><img src="" alt="Monomer 9" /></td>
<td><img src="" alt="Monomer 10" /></td>
<td><img src="" alt="Monomer 11" /></td>
<td><img src="" alt="Monomer 12" /></td>
</tr>
<tr>
<td></td>
<td>8 wt%</td>
<td>5.4 wt%</td>
<td>2.9 wt%</td>
<td>3.1 wt%</td>
</tr>
<tr>
<td>Pressure a</td>
<td>-</td>
<td>1 bar Ar</td>
<td>20 bar H₂</td>
<td>30 bar N₂</td>
</tr>
<tr>
<td>Temperature</td>
<td>200 °C</td>
<td>200 °C</td>
<td>200 °C</td>
<td>230 °C</td>
</tr>
<tr>
<td>Solvent</td>
<td>6 ml ethanol/water (1/1, v/v)</td>
<td>Pure methanol</td>
<td>40 ml methanol/water (7/3, v/v)</td>
<td>40 ml methanol/water</td>
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<td>H₂ source</td>
<td>Formic acid and sodium formate</td>
<td>Methanol</td>
<td>External H₂</td>
<td>Methanol and water</td>
</tr>
<tr>
<td>Influence of water addition</td>
<td>Improving delignification</td>
<td>Decreasing monomer yield</td>
<td>Increasing solubilization lignin and hemicellulose</td>
<td>Improving hydrogen generation and delignification</td>
</tr>
<tr>
<td>Carbohydrate retention</td>
<td>Glucans 58 wt% - Xylans 4 wt%</td>
<td>Cellulose c &gt;90 wt% Hemicellulose d &gt;60 wt%</td>
<td>Glucans 41 wt% Xylans &lt;1 wt%</td>
<td></td>
</tr>
</tbody>
</table>

*aPressure at room temperature. *bMethanol/water is 10/9 (v/v). *cCellulose fraction: glucose. *dHemicellulose fraction: xylose, arabinose, galactose, mannose.
which allows independent control of lignin extraction and hydrogenolysis, the kinetic studies of each step, and facile separation of the heterogeneous catalyst.\textsuperscript{19,20} Lignin in poplar wood was extracted by methanol in the first bed and converted into phenolic monomers (18% yield) using Ni/C in the presence of 6 MPa hydrogen.\textsuperscript{21} Hydrogen is currently mainly produced from the steam reforming of natural gas.\textsuperscript{21} In a more sustainable scenario, hydrogen should be obtained from alternative sources. The aqueous-phase reforming of biomass-derived alcohols can provide a source of hydrogen.\textsuperscript{22} Another approach is to use hydrogen-donor solvents that can later be rehydrogenated. In the context of lignin upgrading, Rinaldi et al. described a catalytic hydrogen transfer strategy in which the isopropanol solvent was converted to acetone and hydrogen in the presence of a Raney Ni catalyst. The obtained lignin oil is a complex mixture of aromatics and other low molecular weight products. The hydrogenation of acetone byproduct to isopropanol is required to recycle the solvent.\textsuperscript{23} Samec et al. used a heterogeneous cobalt catalyst for lignin depolymerization and hydrogen transfer hydrogenolysis using formic acid/formate as a hydrogen donor in a mixture of ethanol and water, producing 34% monophenolic compounds based on the initial lignin content.\textsuperscript{24} Moreover, hemicellulose released from birch wood was used as hydrogen donor for hydrogenolysis of lignin, and in this way, a 37% yield of phenolic monomer was obtained in a continuous-flow system.\textsuperscript{25} Xu et al. reported that pure methanol can be a source of hydrogen during depolymerization of lignin: high yields (54%) of propyguaiacyl and propylysyringol were obtained using a Ni-based catalyst during the conversion of birch wood. An interesting phenomenon observed was that the lignin monomer yield dropped to 22% when water was added to the reaction.\textsuperscript{26} Besides in planta lignin conversion, a similar hydrogen-free strategy has also been used for valorization of technical lignin. Weckhuysen and coauthors reported a two-step method in which kraft, organosolv, and sugar cane bagasse lignins were dissolved in an ethanol/water mixture in the first step followed by the liquid-phase reforming of dissolved lignin to monoaromatics (17% yield) over a Pt/Al₂O₃ catalyst in a He atmosphere, which helped generate hydrogen in the second step.\textsuperscript{27}

Inspired by previous work on lignin depolymerization without external hydrogen, here we present for the first time an alternative catalytic approach that combines in planta lignin depolymerization with methanol reforming using a commercial Pt/γ-Al₂O₃ catalyst.\textsuperscript{23,24,26,27} A comparison is made in Table 1 to emphasize the results of this work. The use of Pt as a catalyst not only stabilizes lignin monomers but also contributes to the hydrogen generation through the methanol reforming reaction (\(	ext{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2\)). The use of methanol/water mixtures has several advantages over other hydrogen-donor solvent strategies: addition of water to pure organic solvent decreases the economic cost, unsaturated byproducts such as acetone in isopropanol transfer hydrogenation are avoided, water enhances the hydrogen generation and also the extraction efficiency of lignin fragments from the lignocellulosic matrix. We found that the type of aromatic monomers can be controlled between 4-propenyl-syringol and 4-propyl-syringol by adjusting the methanol/water ratio and the reaction temperature. Up to 49% of phenolic monomers with 82% selectivity to 4-propyl-syringol can be obtained from birch wood lignin under optimized conditions (methanol–water molar ratio 1/2, 230 °C, 30 bar N₂, 3 h).

### EXPERIMENTAL SECTION

#### Chemicals and Materials.

Birch wood sawdust was obtained from Staatsbosbeheer in The Netherlands. Anhydrous methanol, H₂SO₄ (95–97%), ethyl acetate, tetrahydrofuran (THF), and d₆-DMSO (dimethyl sulfoxide) were purchased from Merck. n-Dodecane was purchased from Alfa Aesar. Guaiacylglycerol-β-guaiacyl ether and 4-n-propanol-guaiacol were purchased from TCI. One weight percent Pt/γ-Al₂O₃, 5 wt % Pt/C, and 5 wt % Pd/C catalysts were purchased from Sigma-Aldrich. The preparation of Mo₅C/AC (AC = activated carbon), Cu/CeO₂, and Cu/ZnO/Al₂O₃ catalysts is given in the Supporting Information (Supporting Information section 1.2).

#### Feedstock Pretreatment.

The birch wood sawdust was milled and sieved to a particle size of 125–300 μm and pretreated to remove extractives with water (24 h) and ethanol (24 h) in a Soxhlet extractor. The pretreated birch sawdust was dried at 105 °C overnight. A standard two-step hydrolysis procedure in sulfuric acid was used to determine the Klason lignin content in birch wood (Supporting Information section 2.1).

#### Catalytic Activity Measurements.

In a typical reaction, 2.0 g of pretreated birch sawdust (20.1 wt % Klason lignin), 500 mg of 1 wt % Pt/γ-Al₂O₃, and 40 mL of solvent were loaded into a 100 mL Parr autoclave. The autoclave was sealed and flushed with nitrogen. After leak testing, the autoclave was pressurized to 30 bar with nitrogen at room temperature. The mixture was stirred at 500 rpm and heated to the reaction temperature at a rate of 10 °C/min. After reaction, the autoclave was cooled in ice water. For the model compound experiments, 50 mg of guaiacylglycerol-β-guaiacyl ether, 20 mL of methanol/water solvent, and 50 mg of Pt/γ-Al₂O₃ was loaded in a Parr autoclave (100 mL). After sealing and leak check, the autoclave was heated to the reaction temperature for 3 h. After reaction, the monomers were extracted by ethyl acetate and analyzed by the procedures below.

#### Product Analysis and Characterization.

The lignin products were separated from the solid residue by filtration. Methanol was removed from the filtrate by rotary evaporation. The lignin oil was extracted by 40 mL of ethyl acetate, and the sugar-derived products were kept in the water phase. To this end, 30 μL of n-dodecane was added as an external standard to the lignin ethyl acetate solution to determine the lignin monomer yield. The lignin monomers were analyzed by a Shimadzu 2010 gas chromatograph with mass spectrometry and flame ionization detection equipped with a TRX-1701 column. The degree of delignification was determined by the weight of lignin oil after the evaporation of ethyl acetate.\textsuperscript{18} The delignification degree and lignin monomer yield were calculated as follows:

\[
\text{delignification degree (\%)} = \frac{\text{weight of lignin oil}}{\text{weight of sawdust} \times \text{Klason lignin content}} \times 100% \tag{1}
\]

\[
\text{lignin monomer yield (\%)} = \frac{\text{weight of lignin monomers}}{\text{weight of sawdust} \times \text{Klason lignin content}} \times 100% \tag{2}
\]

The lignin oil was dissolved in THF (2 mg mL⁻¹) and d₆-DMSO (100 mg mL⁻¹) for gel permeation chromatography and 2D ¹H–¹³C heteronuclear single-quantum coherence (HSQC) NMR analysis. Gel permeation chromatography analysis was performed on a Shimadzu apparatus equipped with a Mixed-C and Mixed-D columns in series and a UV–vis detector operated at 254 nm. The molecular weight was determined at 25 °C using THF as the eluent at a flow rate of 1 mL min⁻¹. 2D HSQC NMR spectra were recorded on a Bruker 400 MHz spectrometer. The spectral widths were 5000 and 20000 Hz for the ¹H and ¹³C dimensions. A total of 16 scans with a 2 s relaxation delay and 256 time increments were used in the ¹³C dimension. Data processing was performed by the MestReNova software. The gaseous products were collected by a gas sample cylinder and then analyzed by
an Interscience Compact gas chromatograph equipped with Mol sieve 5 Å and Porabond Q columns connected to thermal conductivity detectors and an Al₂O₃/KCl column equipped with a flame ionization detector.

Results and Discussion

We investigated the approach to use methanol/water mixtures in a nitrogen atmosphere of 30 bar by comparing different reaction temperatures, methanol/water ratios, and catalysts. Optimization of the reaction temperature and solvent composition was carried out using a commercial Pt/γ-Al₂O₃ catalyst with a metal loading of 1 wt %. Such supported Pt catalysts are known to be active for aqueous phase reforming of alcohols and carbohydrates and also the valorization of organosolv lignin. Although γ-Al₂O₃ is not stable under hydrothermal conditions, it has been shown that the interaction with lignin fragments can slow down the conversion to boehmite. We studied the mechanism in more detail by using guaiacylglycerol-β-guaiacyl ether as a model compound. Finally, we discuss the benefits of our approach and the implications for aromatics production from lignocellulosic biomass.

Influence of Temperature. Catalytic upgrading of birch wood was carried out in methanol/water mixtures under a nitrogen atmosphere using Pt/γ-Al₂O₃ as a catalyst. In our process, the catalyst is involved in the depolymerization of lignin, reforming of methanol to produce hydrogen, and possibly in the extraction of lignin from the biomass matrix. Reductive lignin-first processes are typically performed in the 170–250 °C temperature range, depending on the heterogeneous catalyst, addition of cocatalysts, solvent, and biomass resource. The aqueous reforming of light alcohols occurs at 150–350 °C.

Figure 1a shows the delignification degree and lignin monomer yield in an equimolar mixture of methanol and water after a reaction time of 3 h. At 210 °C, about 84% of lignin is removed from birch wood sawdust and 98% of cellulose remains intact in the carbohydrate residue. Only 17% of hemicellulose was left, the ease of degradation being due to its amorphous structure, which allows for easy contact with the reagents. Analysis of sugar-derived products revealed that part of hemicellulose was converted to xylose (7.0 wt %), ethylene glycol (1.3 wt %), 1,2-propanediol (1.2 wt %), and 1,2-butandiol (0.10 wt %) (Table S1). Under the present conditions we also expect the formation of humins due to the xylose oligomerization.35 The birch wood mass balance after reaction at 210 °C is 83% (Table S2). The highest delignification degree (99%) is observed at 230 °C. However, carbohydrate retention in the obtained solid residue decreases with increasing temperature (Figure S1). The lignin monomers obtained in these experiments are mainly 4-propyl-guaiacol, 4-propenyl-syringol, and 4-propyl-syringol. While lignin monomer yield is only 17% at 170 °C, it increases to 43% at 230 °C. The delignification degree at 250 °C is substantially lower than that at the optimum temperature of 230 °C. The product distribution depends strongly on the reaction temperature. At low temperature the main products were syringol-derived monomers, while the selectivity to guaiacol-derived monomers increases at higher temperature. The lignin part of birch wood, which is a hardwood, contains mainly syringyl (S) units and a relatively small amount of guaiacyl (G) units. Thus, our results show that the extraction and depolymerization of S-type lignin fragments is easier than those of G-type lignin fragments. While 4-propenyl-syringol was the main product at 170 °C, the double bond in the side chain was increasingly hydrogenated with increasing temperature. Samec et al. also reported that the monomer selectivity in lignin conversion toward the unsaturated product (4-propenyl-syringol) can be increased by using hemicellulose as the hydrogen donor using a Pd/C catalyst.36 At 230 °C, 4-propyl-syringol was the main product in the lignin oil. We attribute this to the higher partial pressure of hydrogen with increasing temperature as a result of more extensive methanol reforming. To verify this hypothesis, we also analyzed the gas-phase products in these experiments (Figure 1b). The main components in the gas phase were hydrogen, carbon monoxide, and carbon dioxide. A small amount of hydrocarbons, mostly methane, was obtained as a byproduct (Figures S2 and S3). Figure 1b confirms that the hydrogen yield increases with temperature due to increased methanol reforming, thus providing a good explanation for the
The yield significantly increased to 37% when the molar methanol/water ratio was 2. The addition of water to methanol (methanol–water volume ratio 1/3) decreased the monomer yield in the birch wood lignin conversion using a Ni/C catalyst in an earlier report. We found that the optimum yield of 49% was obtained when the methanol/water ratio was 1/2. The increased lignin monomer yield is attributed to the higher hydrogen yield obtained when the methanol/water ratio is lower (Figure 2b). Hydrogen can effectively hydrogenate the reactive functional groups in dissolved lignin fragments through catalytic reduction, e.g., the hydrogenation of unsaturated side chains and the hydrodeoxygenation of ketones and aldehydes. This reduction essentially prevents undesirable lignin repolymerization and results in a high yield of stable phenolic monomers. The highest monomer yield (49 wt %) was obtained for a molar methanol/water ratio of 1/2 at 230 °C. Compared to lower temperatures, these reaction conditions resulted in relatively lower cellulose/hemicellulose retention and lower mass balance closure (73 wt %), presumably due to secondary reactions involving solubilized carbohydrates (Table S3). In pure water, the lignin monomer yield dropped to 6%, which is most likely due to a lack of hydrogen. The lignin monomer yield in pure water is lower than in an organic solvent–water mixture and strongly influenced by the use of different catalysts (Ru/C, Pd/C, Rh/C, and Pt/C) even in the presence of external hydrogen.37 Gas product analysis (Figure 2b) also shows that hydrogen cannot be effectively obtained by reforming of carbohydrates released from the biomass matrix under these conditions in pure water. Furthermore, a control experiment was performed under identical conditions in the presence of Pt-base catalyst but without birch wood. An amount of 14.7 mmol of hydrogen is produced from the methanol–water mixture (molar ratio 1/2), which corresponds to 0.8 mol % of the starting methanol (Table S4). This further confirms that hydrogen is mainly generated from Pt-catalyzed methanol reforming. An earlier study found that formic acid, which acts as the hydrogen donor, is released during the pulping process in birch wood lignin depolymerization in an ethanol/water mixture. It was also established that ethanol did not act as the hydrogen donor under the reaction conditions.35 Regarding the products obtained, unsaturated 4-propenyl-syringol is the main product in the absence of water. Due to the increased production of hydrogen, the selectivity shifts from 4-propenyl-syringol to 4-propyl-syringol when the water content is increased. The addition of water to methanol not only changes the lignin yield and monomer selectivity but also decreases the operating cost of whole process. Thus, we conclude that the production of hydrogen by reforming of methanol has a positive effect on the reductive fractionation of lignocellulosic biomass into phenolic monomers.

**Influence of the Catalyst.** We next investigated the role of the catalyst. Extraction of the lignin fragments involves the cleavage of lignin–carbohydrate interlinkages, which are typically comprised of phenyl glycoside, γ-ester, and benzyl ether bonds.39 Given that the substrate to be converted during extraction is a large polymer, accessibility of the reactive bonds is limited for heterogeneous catalysts. Nevertheless, it has been
reported that a heterogeneous metal catalyst can promote the cleavage of ether bonds under mild reaction conditions.40

Table 2 shows that the delignification degree without catalyst is comparable to the case where Pt/γ-Al2O3 is used as the catalyst. The high delignification degree is therefore mainly due to solvolysis of the indicated chemical bonds, which benefits from the relatively high reaction temperature of 230 °C. The slightly higher than expected delignification degree is due to the formation of a small amount of condensation products of carbohydrate-derived compounds (humins) and other condensation products between carbohydrate-derived compounds and lignin fragments.41

After release into the solution, the dissolved lignin fragments are depolymerized to aromatic monomers through cleavage of the dominant β−O−4 bonds. The chemical structure of the main components in the lignin oil was investigated by 2D HSQC NMR spectroscopy (Figure 3). A lignin oil obtained by delignification in methanol under mild conditions without a catalyst (Supporting Information section 6.1) exhibits characteristic signals of β−O−4, α−O−4/β−5, and β−β bonds in the NMR spectra shown in Figure 3a. The characteristic cross-signals of the guaiacol (G) and syringol (S) units of the lignin oil can be clearly seen in the spectra (Figure 3e−h). Notably, we found the cross-signals of coniferyl/sinapyl alcohol (structure I) and oxidized syringyl unit (structure S′) in the lignin oil obtained under mild delignification conditions (Figure 3e). The use of Pt/γ-Al2O3 as the catalyst in an inert

Table 2. Results of Birch Wood Upgrading under Various Conditions^a

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
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<th>delignification (%)</th>
<th>monomer yield (%)</th>
<th>H2 yield (mmol)</th>
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<tr>
<td>1</td>
<td>Pt/γ-Al2O3</td>
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<td>49</td>
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<tr>
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<td>Pt/γ-Al2O3</td>
<td>H2</td>
<td>102</td>
<td>43</td>
<td></td>
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<tr>
<td>3</td>
<td>N2</td>
<td></td>
<td>95</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Pt/γ-Al2O3</td>
<td>N2</td>
<td>101</td>
<td>7</td>
<td>0.4</td>
</tr>
</tbody>
</table>

^aExperimental conditions: 2.0 g of pretreated birch wood (Klason lignin content 20.1 wt %), 40 mL of methanol/water (1/2 mol/mol), 230 °C, 3 h. ^b500 mg of 1 wt % Pt/γ-Al2O3. ^c250 mg of 1 wt % Pt/γ-Al2O3.

Figure 3. Aliphatic side-chain (top, a–d) and aromatic (bottom, e–h) regions of 1H−13C HSQC NMR spectra of the lignin oils obtained by treatment of sawdust of birch wood (a, e) under mild organosolv conditions (methanol, 30 bar N2, 170 °C, 2 h) and in the presence of (b, f) 30 bar N2 and Pt/γ-Al2O3, (c, g) 30 bar H2 and Pt/γ-Al2O3, and (d, h) 30 bar N2 without catalyst.
naphthyl, and its conversion to monomers. The use of external hydrogen (Figure 3c and 3g) shows similar results to those with nitrogen. It is interesting to note that the \( \beta-O-4 \) bonds were also not observed without the Pt/\( \gamma \)-Al\(_2\)O\(_3\) catalyst (Figure 3d). These findings indicate that cleavage of \( \beta-O-4 \) bonds does not require a catalyst and mainly occurs via thermal solvolysis. Nevertheless, the lignin monomer yield in this approach is very low due to the condensation of reactive lignin groups. The disappearance of coniferyl/sinapyl alcohol and unsaturated syringyl units in Figure 3d and 3h might be caused by the condensation of these reactive unsaturated groups.\(^{42,43}\) The delignification in alcohol/water mixtures as employed here draws similarities with organosolv processes in which lignin is released from the native biomass structure due to solvolysis of lignin–carbohydrate bonds and also cleavage of \( \beta-O-4 \) bonds. The mechanism of \( \beta-O-4 \) bond cleavage in the organosolv pulping process has been studied in some detail.\(^{35}\) The formation of unstable lignin intermediates, such as benzylic cations and unsaturated monomers, will result in condensation into less reactive lignin oligomers.\(^{44,45}\)

The lignin monomer yields are shown in Table 2. Using Pt/\( \gamma \)-Al\(_2\)O\(_3\) as the catalyst in a nitrogen atmosphere, up to 49% of lignin monomers can be obtained. This shows that condensation is suppressed by hydrogenation of the reactive groups formed upon solvolysis of the \( \beta-O-4 \) bonds. Analysis of the gaseous products showed that 3.1 mmol of hydrogen was formed. When external hydrogen gas was used, a slightly lower lignin monomer yield of 43% was obtained (entry 2). A similar phenomenon was observed in the transfer hydrogenolysis of lignin to monomers over Ni/C catalyst.\(^{26}\) A possible explanation is a more intense gas/liquid contact when hydrogen is generated close to the sites where also hydrodeoxygenation/hydrogenation of unstable lignin monomer takes place.\(^{26}\) Without a catalyst (entry 3) the lignin monomer yield was very low (1%), showing that the lignin monomers obtained by \( \beta-O-4 \) cleavage rapidly condense. When we decrease in entry 4 the Pt/\( \gamma \)-Al\(_2\)O\(_3\) loading to one-half of the amount used in entry 2 we find a much lower hydrogen yield of 0.4 mmol and consequently also a decreased lignin monomer yield (7%).

The catalytic results in Table 2 and the \(^{1}H-^{13}C\) HSQC NMR spectra in Figure 3 point to the critical role of the Pt/\( \gamma \)-Al\(_2\)O\(_3\) catalyst for obtaining a high monomer yield in the current process. To further support this role, gel permeation chromatography (GPC) was applied to determine the molecular weight distribution of obtained lignin oils (Figure 4). Without a catalyst the peak of monomers is not observed and the lignin oil is mainly composed of dimers and oligomers. This is in line with the low monomer yield (entry 3, Table 2). In the presence of Pt/\( \gamma \)-Al\(_2\)O\(_3\) and hydrogen, a monomer feature appears in the chromatograms, indicative that the dimers and oligomers are converted into monomers. Using Pt/\( \gamma \)-Al\(_2\)O\(_3\) in a nitrogen atmosphere, the molecular weight distribution of the lignin oil is very similar to the one obtained in an hydrogen atmosphere. This indicates that hydrogen generated by methanol reforming has a comparable effect to applying an external hydrogen pressure with respect to reductive depolymerization of lignin fragments.

We also evaluated whether the Pt-based catalyst can be replaced by other supported metal catalysts (Table 3). These catalysts were selected because of their high activity in hydrogenation or methanol reforming. The delignification degree was not influenced by the type of catalyst, which is in line with the results in Table 2, emphasizing that delignification is a solvolysis process. In the use of Pt/\( \gamma \)-Al\(_2\)O\(_3\), the formation of Boehmite was confirmed by XRD analysis of spent Pt/\( \gamma \)-Al\(_2\)O\(_3\), which indicates the instability of Al\(_2\)O\(_3\) support in methanol reforming conditions (Figure S4). Carbon as a support is argued to be more stable than \( \gamma \)-Al\(_2\)O\(_3\) in an earlier study.\(^{32}\) Therefore, we replaced Pt/\( \gamma \)-Al\(_2\)O\(_3\) with Pt/C and achieved a nearly similar lignin monomer yield at complete delignification (entry 1). Pt/C has been successfully used in the hydrogenolysis of ether bonds of lignin.\(^{46}\) Entry 2 shows that Pt/C can yield up to 22% lignin monomers. The lower yield is likely due to a lower activity of the catalyst in methanol reforming, as evident from the lower hydrogen yield. Entry 3 shows that Cu/ZnO/Al\(_2\)O\(_3\) which is a known catalyst for methanol synthesis, can form hydrogen from the solvent mixture in line with earlier reports.\(^{27}\) However, the lignin monomer yield for this catalyst was very low because of the relatively low hydrogenation activity of Cu.
similar for Cu/CeO₂ (entry 4). On the basis of an earlier report that Mo₂C/C is a suitable catalyst for Kraft depolymerization and methanol reforming,37,48 we also evaluated this catalyst prepared by carbothermal reduction (Supporting Information section 1.2). The relatively low lignin monomer yield is most likely due to the relatively low reaction temperature compared to the literature in which harsh conditions (300–400 °C) were used to upgrade technical lignin.

**Model Compound Study.** The above results show the importance of the methanol/water solvent and a metal catalyst to our process. Lignin is extracted from the lignocellulosic matrix by solvolysis and depolymerized into unstable monomers in methanol/water through solvolysis. The use of Pt/γ-Al₂O₃ promotes methanol reforming reactions which provide hydrogen and also prevent undesired lignin fragment repolymerization, thereby increasing the monomer yield. To understand these aspects in more detail, we also performed a similar set of experiments by using a representative lignin dimer model compound, namely, guaiacylglycerol-β-guaiacyl ether as the substrate. The main products are guaiacol, propylguaiacol, ethylguaiacol, and methylguaiacol, and their yields are shown in Figure 5. In the use of Pt/γ-Al₂O₃ catalyst under 30 bar of nitrogen, the β-O-4 bonds were efficiently cleaved and up to 77% of guaiacol was obtained (Figure 5). A small amount of methylyguaiacol was detected due to the methylation of obtained guaiacol with methanol in the reaction. The formation of propyl- and ethylguaiacol can be taken as an indication that the mechanism of β-O-4 bond cleavage involves the acidolysis or the solvolysis. The acidolysis of the β-O-4 bond involves two pathways: one is the Hibbert ketone pathway that leads to the phenolic C3-ketones; the other one involves decarbonylation resulting in a C2-aldehyde.99 Pt/γ-Al₂O₃ promotes the hydrogenation of the unsaturated C3-ketone and C2-aldehyde to propyl- and ethyl-guaiacol, respectively. The high yield of propyl guaiacol in the model experiment shows that the Hibbert ketone (C3) pathway might be the main route for β-O-4 bond cleavage. Another possible mechanism is that the coniferyl alcohols are formed as the main intermediates in the solvolysis process.25,42 These intermediates are hydrogenated to propanol/propyl guaiacol in the presence of Pt-based catalyst. The ethyl-substituted monomer is formed due to cleavage of the CH₂OH group from the propanol guaiacol.50 From the observation that the propyl/ethylguaiacol and guaiacol ratio was lower than one, we infer that a small amount of monomers was polymerized to high molecular weight products, even in the presence of the catalyst. The use of external hydrogen leads to similar results, suggesting that some polymerization is inevitable. Without catalyst in a nitrogen atmosphere cleavage of the β-O-4 bond still occurs, resulting in a considerable yield of guaiacol as the only product. The disappearance of propyl- and ethylguaiacol is likely due to the polymerization involving the unsaturated monomers.

**Proposed Mechanism.** In the reductive lignin depolymerization the roles of each step, namely, lignin extraction, depolymerization, and monomer stabilization, have already been well investigated for the case that external hydrogen gas is present.14 Our results clearly show that effective hydrogen generation for monomer stabilization is also important to obtain a high lignin monomer yield from birch sawdust in our approach. Lignin fragments are extracted from the lignocellulosic biomass matrix through solvolysis, and these fragments are further converted into phenolic monomers. Acidolysis/solvolysis underlies the removal of lignin fragments from the biomass matrix as well as its depolymerization, primarily resulting in unsaturated monomers. Without catalyst these reactive intermediates condense into high molecular weight products, explaining the low monomer yield in the absence of a hydrogenation function. The use of a Pt-based catalyst is crucial to obtain a high lignin monomer yield. A methanol/water solvent can be used to provide hydrogen through methanol reforming. The Pt-based catalyst also promotes hydrogenation reactions of the unsaturated side chains to stabilize the reactive intermediates, contributing to a high lignin monomer yield.

**CONCLUSIONS**

We developed an alternative strategy for the reductive depolymerization of in planta lignin into phenolic monomers using a Pt-based catalyst with methanol/water as a safe and effective hydrogen source. In this study, the influence of temperature and methanol/water ratio is investigated. Nearly complete delignification (94%) and a high yield of aromatic monomers (49%) can be obtained from birch sawdust under optimized conditions (230 °C, 30 bar N₂, 3 h, methanol/water molar ratio 1/2). The product selectivity can be tuned between 4-propenyl-syringol and 4-propyl-syringol by changing the hydrogenation formation rate through methanol reforming. Model compound experiments and HSQC NMR analysis of lignin oil reveal the solvolytic cleavage of the dominant β-O-4 bond and the importance of monomer stabilization in the present process. Lignin is extracted from the lignocellulosic matrix and depolymerized to an unstable intermediate through β-O-4 bond cleavage. The Pt-based catalyst essentially catalyzes the methanol reforming for hydrogen generation and also the reductive stabilization of unstable lignin intermediates. The latter aspect is important to prevent
unfavorable lignin condensation. Overall, this approach provides an effective strategy for the lignin catalytic conversion without using external hydrogen.

**ASSOCIATED CONTENT**

 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b01497.

Details of Cu/ZnO/Al2O3, Cu/CoO, Mo2C/AC catalysts preparation; carbohydrate retention in solid residue; birch wood mass balance; water phase products; gaseous products in the methanol reforming; XRD of spent Pt/γ-Al2O3. (PDF)

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Notes

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