Supporting Information

Hydrogenation of fourteen biomass-derived phenolics in water and in methanol: Their distinct reaction behaviours

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Experimental

All the chemicals used in this study are analytical grade and were used without any further treatment. Pd/C catalyst (Pd loading: 5 wt%) were purchased from Sigma-Aldrich. Pd/SiO$_2$ catalyst was prepared via an impregnation method. Palladium nitrate was used as a precursor and the loading to Pd to SiO$_2$ was 5 wt%. The bio-oil used here was produced from pyrolysis of poplar wood at 550°C with an Auger reactor. The configuration of the reactor was shown below in Figure S1. The residence time of biomass inside the Auger reactor was around 3 min. The feeding rate of the feedstock was 500 g per h. The first condenser use water as the coolant while the second use dry ice as the coolant. The gaseous products were further condensed with a mixture of methanol/chloroform (volumetric ratio: 1 : 4) as the sorbent. The typical yield of bio-oil from the pyrolysis of poplar wood with the Auger reactor was ca. 55%. The yield of the char was ca. 30% while the yield of gases product was ca. 15%. The elemental composition of the bio-oil has been characterized and the results were shown in Table S1. The composition of the products were analyzed with GC-MS. The peak area percentage of some typical compounds were summarized in Table S2.

Hydrogenation of bio-oil and the phenolic compounds were conducted in an autoclave reactor with the maximum operating temperature and pressure of 380°C and 250 bar. In a typical experiment, 1 g of bio-oil or the phenolic compound was mixed with water or methanol and then loaded into the autoclave reactor at room temperature. After assembly of the reactor, the residual air inside the reactor was purged with high-purity nitrogen via pressurizing the reactor to 40 bar and then the gases were released slowly. Same operation was repeated for three times and then the reactor was pressurized with high-purity hydrogen to 40 bar. It needs to note that 40 bar hydrogen was fed in at room temperature. When the temperature of the reactor was increased to 200°C, more hydrogen was fed to the reactor to maintain the working pressure of 70 bar throughout the experiment. The holding time at 200°C was 100 min, while the stirring rate was 600 rpm. No sampling was conducted during the whole process of the experiment. At the end of the test, the reactor was taken out of the furnace to quench the reaction. The liquid product and the catalyst were collected and filtered for further analysis.

Analysis of the liquid products were performed with a GCMS-QP2020 (Shimadzu). An INNOWax capillary column was used for separation of liquid products. Briefly, the
samples were diluted to a concentration of 0.5 wt% in acetone before the analysis. Helium was used as the carrier gas (gas flow rate: 5 ml/min) and the temperature of the injection pot was set at 250°C. Temperature of the oven was set at 45°C initially and was then increased to 250°C at a ramping rate of 10°C/min and the holding time at 250°C was 5 min. Identification of the products was achieved via the spectral library (NIST 2010) and were further analyzed via manual analysis of the mass spectrum. It is very difficult to find the commercial standards for products as many of the products are the mixture of isomers. Thus, their relative proportion (normalized peak area to the total peak area) were used to represent their relative abundance in the products. The conjugated π-bonds structures were analyzed with a UV-fluorescence spectrometer (Shimadzu RF-6000). The wavelength indicates sizes of the aromatic ring structures while the peak intensity is an indicator of the abundance. The liquid samples were diluted to 600 ppm before the analysis, which was in a linear range with the concentration of the aromatic compounds in the products.
Table S1 Elemental composition of the bio-oil produced

<table>
<thead>
<tr>
<th>Elemental composition (wt%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
<td>O</td>
<td>N</td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>54.3</td>
<td>7.1</td>
<td>38.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.1</td>
<td>ND&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Concentration of oxygen was calculated by difference.

<sup>b</sup>“ND” stands for “Not Detected”.
Table S1 Composition of the bio-oil

<table>
<thead>
<tr>
<th>Compounds in bio-oil</th>
<th>Percentage of peak area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>25.7&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>12.6</td>
</tr>
<tr>
<td>2-Propanone, 1-hydroxy-</td>
<td>7.32</td>
</tr>
<tr>
<td>1-Hydroxy-2-butanone</td>
<td>0.24</td>
</tr>
<tr>
<td>Butyric acid</td>
<td>0.16</td>
</tr>
<tr>
<td>3-Ethyl-2-hydroxy-2-cyclopenten-1-one</td>
<td>0.15</td>
</tr>
<tr>
<td>2-methoxy-4-methyl-phenol</td>
<td>0.61</td>
</tr>
<tr>
<td>3-Pentanone, 2-methyl-</td>
<td>0.71</td>
</tr>
<tr>
<td>Propanoic acid</td>
<td>1.96</td>
</tr>
<tr>
<td>1,2-Ethanediol</td>
<td>1.21</td>
</tr>
<tr>
<td>1-(2-Furanyl)-ethanone,</td>
<td>0.19</td>
</tr>
<tr>
<td>Acetaldehyde, hydroxy-</td>
<td>3.12</td>
</tr>
<tr>
<td>2-Methoxy-4-vinylphenol</td>
<td>0.46</td>
</tr>
<tr>
<td>3-Methyl-2(5H)-furanone,</td>
<td>0.36</td>
</tr>
<tr>
<td>2-Cyclopenten-1-one</td>
<td>2.13</td>
</tr>
<tr>
<td>1,2-Cyclopentanedione</td>
<td>1.01</td>
</tr>
<tr>
<td>2(5H)-Furanone</td>
<td>0.19</td>
</tr>
<tr>
<td>1,2-Ethanediol, diacetate</td>
<td>0.23</td>
</tr>
<tr>
<td>Phenol, 2,6-dimethoxy-</td>
<td>1.67</td>
</tr>
<tr>
<td>Furfural</td>
<td>3.79</td>
</tr>
<tr>
<td>Phenol, 4-ethyl-2-methoxy-</td>
<td>0.14</td>
</tr>
<tr>
<td>Furfuryl alcohol</td>
<td>0.96</td>
</tr>
<tr>
<td>5-Methyl-2(5H)-furanone,</td>
<td>0.67</td>
</tr>
<tr>
<td>Benzene, 1,2,3-trimethoxy-5-methyl-</td>
<td>1.37</td>
</tr>
<tr>
<td>1,2,4-Trimethoxybenzene</td>
<td>3.11</td>
</tr>
<tr>
<td>levoglucosan</td>
<td>14.23</td>
</tr>
<tr>
<td>2-methoxy-phenol</td>
<td>3.21</td>
</tr>
<tr>
<td>Ethanone, 1-(3,4-dimethoxyphenyl)-</td>
<td>1.23</td>
</tr>
<tr>
<td>2-Methoxy-5-methylphenol</td>
<td>1.43</td>
</tr>
<tr>
<td>Phenol</td>
<td>1.79</td>
</tr>
<tr>
<td>Phenol, 2,6-dimethoxy-4-(2-propenyl)-</td>
<td>2.26</td>
</tr>
<tr>
<td>Vanillin</td>
<td>1.31</td>
</tr>
<tr>
<td>3,4,5-trimethoxy-Phenol,</td>
<td>1.73</td>
</tr>
<tr>
<td>4-Hydroxy-3,5-dimethoxy-benzaldehyde,</td>
<td>0.24</td>
</tr>
</tbody>
</table>

<sup>a</sup>The unit is wt% for water concentration in bio-oil.
Table S3: Hydrogenation of vanillin in water and in methanol with Pd/SiO$_2$ catalyst$^a$

<table>
<thead>
<tr>
<th>Reaction conditions</th>
<th>Yield of creosol</th>
<th>Conversion of vanillin</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C, 7 MPa, t =120 min, solvent: water</td>
<td>46.3%</td>
<td>99.9%</td>
</tr>
<tr>
<td>200°C, 7 MPa, t =120 min, solvent: methanol</td>
<td>71.6%</td>
<td>92.5%</td>
</tr>
<tr>
<td>160°C, 6 MPa, t =120 min, solvent: water</td>
<td>28.3%</td>
<td>83.1%</td>
</tr>
<tr>
<td>160°C, 6 MPa, t =120 min, solvent: methanol</td>
<td>70.9%</td>
<td>86.1%</td>
</tr>
</tbody>
</table>

$^a$Another main product, 2-methoxy-4-methylcyclohexanol, was not presented in the table as it was not quantified due to the unavailability of the standard.
Figure S1 Configuration of the reactor for production of the bio-oil used in this study.
Figure S2 Constant energy (−2800 cm⁻¹) synchronous spectra of the products after hydrogenation of vanillin in water and metha
**Figure S3** Conversion of vanillin and yields of creosol versus the different loading of vanillin during the hydrogenation. Experimental conditions: $T = 200^\circ C$, $t = 120$ min, $P_{H_2} = 70$ bar, Pd/C: 0.25 g, solvent: 40 ml.
Figure S4 Distribution of the products in acid catalysis/hydrogenation of guaiacol in methanol. Experimental conditions: T = 200°C, t = 120 min, P_{H2} = 70 bar, Pd/C: 0.25 g, Amberlyst 70 (A70): 0.5 g, guaiacol: 1 g, solvent: 40 ml.
**Figure S5** TPR profile of the Pd/SiO$_2$ catalyst prepared via impregnation method. The loading of Pd to SiO$_2$ was 5%. 
**Figure S6** Distribution of the products in hydrogenation of the phenolics in methanol and in water. T = 200°C, t = 120 min, P_{H2} = 70 bar, Pd/C: 0.25 g, phenolic compound: 1 g, solvent: 40 ml.
Figure S7 Distribution of the isomers in hydrogenation of vanillin in methanol and in water.
Figure S8 Distribution of the isomers in hydrogenation of guaiacol in methanol and in water.
Figure S9 Distribution of the isomers in hydrogenation of 1,2,4-trimethoxybenzene in methanol and in water.
Figure S10 Distribution of the isomers in hydrogenation of syringaldehyde in methanol and in water.
Full name of the compounds in Figure 2, 3, 5, 6 in the manuscript and Figure S2 and S4 in Supporting information

1. 4-Hydroxymethyl-2-methoxy-phenol  
2. 2-Methoxy-4-methyl-phenol  
3. 6-Methoxy-4-methylcyclohex-1-enol  
4. 2-Methoxy-4-methylcyclohexanone  
5. 2-Methoxy-4-methylcyclohexanol  
6. 1,2-Dimethoxy-4-methylcyclohexane  
7. 1-Methoxy-4-methylcyclohexane  
8. 2-Methoxy-4-(methoxymethyl)phenol  
9. 4-Methylcyclohexane-1,2-diol  
10. 2-Methoxycyclohexanone  
11. 2-Methoxycyclohexanol  
12. 1,2-Dimethoxycyclohexane  
13. 1,2-Cyclohexanediol  
14. Cyclohexanol  
15. 2-Methoxycyclohexanone  
16. 2-methoxycyclohexanol  
17. 1,2-Dimethoxycyclohexane  
18. Cyclohexane-1,2-diol  
19. Cyclohex-1-enol  
20. Cyclohexanol  
21. 2-Hydroxycyclohexanone  
22. Methoxybenzene  
23. 1-Methoxycyclohexane  
24. 1-Methoxycyclohexane  
25. 1,1-Dimethoxycyclohexane  
26. 2-Methyl-1-cyclohexanone  
27. 4-Propyl-2-methoxyphenol  
28. 2-Methoxy-4-propylcyclohexanol  
29. 1,2-Dimethoxy-4-propylcyclohexane  
30. 1-Methoxy-3-propylcyclohexane  
31. 4-Propylecyclohexane-1,2-diol  
32. 3-Propylecyclohexanol  
33. Propylbenzene  
34. Propylecyclohexane  
35. Cyclohexanepropanol  
36. 1,1-Dimethoxy-4-methylcyclohexane  
37. 1-Methoxy-4-methylcyclohexane  
38. 4-Methylcyclohexanol  
39. Cyclohexane, methyl-  
40. 2-Methylecyclohexanone  
41. 1,1-Dimethoxy-2-methylcyclohexane
42 1-Methoxy-2-methylcyclohexane
43 2-Methylcyclohexanol
44 1,1-Dimethoxy-3-methylcyclohexane
45 3-Methylcyclohexanol
46 1-Methoxy-3-methylcyclohexane
47 5-Methylcyclohex-1-enol
48 Cyclohexanone, 3-methyl-
49 3-Methylcyclohexanol
50 6-Methylcyclohex-1-enol
51 2-Methyl-1-cyclohexanone
52 3,4,5-Trimethylcyclohexanol
53 3-Ethylcyclohexanol
54 4-Ethylcyclohexanol
55 4-Ethyl-2-methoxycyclohexanol
56 4-Ethylcyclohexane-1,2-diol
57 2-Methoxy-4-propylcyclohexanol
58 2-Methoxycyclohexanol
59 Cyclohexanol
60 3-Propylcyclohexanol
61 4-sec-Butylcyclohexanol
62 sec-Butylcyclohexane
63 Toluene, 3,4,5-trimethoxy-
64 1,2,3-Trimethoxy-5-methyl-cyclohexane
65 1,2-Dimethoxy-4-methylcyclohexane
66 1-Methoxy-3-methylcyclohexane
67 Cyclohexanol
68 3,4-Dimethoxytoluene
69 3,5-Dimethoxytoluene
70 1,2,3-Trimethoxybenzene
71 Guaiacol
72 Benzoic acid, 3,4,5-trimethoxy-, methyl ester
73 2-Methoxy-4-methylcyclohexanone
74 2-Methoxy-4-methylcyclohexanol
75 3-Methylcyclohexanone
76 2,6-Dimethoxy-4-methylphenol
77 2,6-Dimethoxy-4-methylcyclohexanol
78 1,3-Dimethoxy-5-methylcyclohexane
79 Phenol, 2-methoxy-4-methyl-
80 Phenol, 3-methyl-
81 4-Methylcyclohexane-1,2-diol
82 Cyclohexane, 1,2,4-trimethoxy
83 1,2-Dimethoxycyclohexane
84 1,4-Dimethoxy-cyclohexane
85 Benzene, 1,3-dimethoxy-
86 Benzene, 1,2-dimethoxy-
87 Cyclohexanol, 4-methoxy-
88 2-Methoxycyclohexanol
89 Cyclohexanol
90 1,2,3-trimethoxy-5-methylcyclohexane
91 3-Methylcyclohexanol