Lignin-first biorefinery: A reusable catalyst for lignin depolymerization and application of lignin oil to jet fuel aromatics and polyurethane feedstock

Electronic Supplementary Information

Yong Huang,† Yijing Duan,† Shi Qiu,† Meng Wang, Chao Ju, Hui Cao, Yunming Fang*, Tianwei Tan
National Energy Research Center for Biorefinery, Beijing University of Chemical Technology, 100029, Beijing, China

* Email: fangym@mail.buct.edu.cn
† Equal contribution to this work.
Outline:

1. Additional experimental methods

2. Additional characterization results of Ru/SiC and Ru/C

3. Characterization of lignin depolymerized products in recycling runs

4. Characterization results of MoO$_3$ catalysts

5. Photograph of the jet fuel blend from lignin depolymerized product

6. Characterization results of rigid polyurethane foam produced from hexane extraction residue

7. Conceptual integration of the proposed lignin-first biorefinery with mass distribution.
1. Additional experimental methods

1.1. Determination of the Klason lignin content in apple wood

The determination of the Klason lignin content of apple wood was followed a standard Lin & Dence method. The apple wood was dried at 105 °C overnight. 2 g of each biomass sample was wet in a 2:1 toluene/ethanol mixture for 15 min followed by Soxtec extraction for 3 h at room temperature. After extraction, the liquid was removed by centrifugation. The extracted biomass samples were dried at 80 °C overnight. Extracted substrate (1 g) were loaded into 50 mL beakers with the addition of 15 mL of a 72 wt% H₂SO₄ solution with stirring for 2 h at room temperature. Subsequently, the slurry was diluted with water until the concentration reached to 3 wt%. The glass bottle was boiled for 4 h under reflux conditions. The precipitate was washed with hot water after filtration and dried at 80 °C overnight. The Klason lignin content was determined by weigh.

1.2. Hydrolytic hydrogenation of holocellulose in the recycling of Ru/SiC catalysis

The holocellulose was removed by hydrolytic hydrogenation. The solid including Ru/C was put into 500 ml high pressure autoclave with 2.5 g of tungstosilicid acid and 250 mL of deionized water. The reactor was sealed, flushed and subsequently pressurized with 5 MPa H₂ at RT. The mixture was stirred at 500 rpm and the reactor was heated to 190 °C. After 2 h reaction, autoclave was cooled to RT. The residues were filtered and dry in the oven.

1.3. Characterization of RPF

Density measurement of RPF. The apparent density of lignin oil based rigid PU foam (RPF) was measured according to ASTM D1622-03. The test specimens were cut into 30 mm × 30 mm × 30 mm (length × width × thickness). The average values of three specimens
per sample were reported.

**Water absorption measurement of RPF.** The water absorption of the RPFs was determined according to ASTM C272. The test specimens were cut into 30 mm × 30 mm × 30 mm (length × width × thickness).

**Mechanical properties measurement of RPF.** Compressive strength of the RPF was determined according to ASTM D1621-04 at ambient conditions with a universal testing machine (Chengde Jin Jian testing equipment Co., Ltd. XWW-20A). The size of the specimen was 30 mm x 30 mm x 30 mm blocks and the rate of crosshead movement was fixed at 2 mm/min for each sample. Compressive stress at 10% strain in parallel to foam rise direction. For each compressive test, three replicate specimens were tested and an average value was taken along with the standard deviation.

**Fourier transform infrared spectroscopy analysis of RPF.** The FTIR spectra of the samples were tested by MAGNA-IR750 Fourier transform infrared spectrometer from the United States Nicolet Company. The FTIR spectra of samples are illustrated in Fig. S6. According to the relevant reports in the literature, the attribution of the bands from Fig. S6 is shown in Table S1.

**Thermogravimetric analysis of RPF.** Thermogravimetric analysis (TGA) experiments were performed using a thermal analyzer (TG209C, NETZSCH Instrument). The sample was heated from room temperature to 900 °C at a heating rate of 10 °C/min under an inert atmosphere of nitrogen and the carbon residue was recorded at 850 °C. The results are shown in Fig. S7.

**Flame retardancy property of RPF.** The flame retardancy property of the lignin oil
based RPF was measured using ASTM D2863. The test sample was cut into 75mm × 10mm × 10mm strips and polished using sandpaper grit No. 60 (250 μm). The measurement was carried out using the JF-3 Oxygen Index Analyzer. Under the specified test conditions, access to 23 ± 2 °C oxygen and nitrogen mixed gas, test material to maintain the minimum oxygen concentration required for combustion.

The Limiting Oxygen Index (LOI) refers to the minimum oxygen concentration required in the mixture of oxygen and nitrogen to maintain the combustion state under the prescribed experimental conditions. In addition, according to the semi-empirical formula proposed by Ven Krevelen, the limiting oxygen index of each sample can be calculated from the char residues (CR) yield data at 850 °C.

$$LOI = 17.5 + 0.4CR$$

**Size stability measurement of RPF.** The size stability of RPF was measured according to ISO2796-1980. As per test sample requirements of size stability, PRF pieces (longitudinal) were cut into 30 mm × 30 mm × 30 mm blocks and polished using sandpaper grit no. 60 (250 μm), placed in an oven at 80 °C for 20 h, 48 h, 72 h, 96 h, 120 h, 148 h, and 168 h. The results are shown in Table S2.
2. Additional characterization results of Ru/SiC and Ru/C

Fig. S1. TEM analysis of 5%Ru/C and 5%Ru/SiC.
3. Characterization of lignin depolymerized products in recycling runs

Fig. S2. Total ion chromatograms (TICs) of liquid product obtained from depolymerization of protolignin in apple wood at 250 ºC for 3 h with 1 MPa H₂ using Ru/SiC with two recycling runs.
4. Characterization results of MoO$_3$ catalysts

![X-ray diffraction patterns of MoO$_3$ catalysts](image)

- **MoO$_3$**
- **MoO$_3$ + H$_2$ (1.5 h)**
- **MoO$_3$ (after reaction)**
- **MoO$_2$**

Intensity, a.u.

20, degree
Fig. S3. (a) XRD patterns of the spent MoO$_3$ catalysts (in comparison with fresh MoO$_3$, H$_2$ pre-reduced MoO$_3$, MoO$_3$ after reaction, MoO$_2$ samples) were measured at room temperature. (b) XPS of the Mo (3d) energy region of the spent MoO$_3$ catalyst sample after H$_2$ pre-reduction at 400 °C for 1.5 h. The numbers in parentheses are the corresponding oxidation state percentages of Mo$^{4+}$, Mo$^{5+}$ and Mo$^{6+}$, respectively. The peak area ratios: Mo$^{4+}$ : Mo$^{5+}$ : Mo$^{6+}$ = 9.3 : 83.3 : 7.4. (c) XPS of the Mo (3d) energy region of the spent MoO$_3$ catalyst sample after reaction at 400 °C for 24 h. The numbers in parentheses are the corresponding oxidation state percentages of Mo$^{4+}$, Mo$^{5+}$ and Mo$^{6+}$, respectively. The peak area ratios: Mo$^{4+}$ : Mo$^{5+}$ : Mo$^{6+}$ = 11.6 : 74.1 : 14.3.
5. Photograph of the jet fuel blend from lignin depolymerized product

![Photograph of the jet fuel blend from lignin depolymerized product](image)

**Fig. S4.** The photo of the product from HDO of lignin oil.
6. Characterization results of rigid polyurethane foam produced from hexane extraction residue

![FTIR spectra of the lignin oil based RPFs and hexane residue.](image)

Fig. S5. FTIR spectra of the lignin oil based RPFs and hexane residue.
Fig. S6. TGA curves (a) and DTG curves (b) of RPFs from different contents of lignin oil replacement.
<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Peak attribution</th>
<th>Original</th>
</tr>
</thead>
<tbody>
<tr>
<td>3333</td>
<td>Amide N-H stretching vibration</td>
<td>Amide structure in the polyurethane</td>
</tr>
<tr>
<td>2274</td>
<td>N=C=O stretching vibration</td>
<td>Isocyanate groups</td>
</tr>
<tr>
<td>1711</td>
<td>Carbonyl compound -C=O stretching vibration</td>
<td>Ester groups in the polyurethane</td>
</tr>
<tr>
<td>1516</td>
<td>Amide N-H bending vibration</td>
<td></td>
</tr>
<tr>
<td>1411</td>
<td>Amide C-H stretching vibration</td>
<td></td>
</tr>
<tr>
<td>1310</td>
<td>Aromatic amine compounds C-N stretching vibration</td>
<td>-NH- group in the polyurethane</td>
</tr>
<tr>
<td>3435</td>
<td>hexane residue -OH stretching vibration</td>
<td></td>
</tr>
<tr>
<td>2935/1458/1370</td>
<td>Aliphatic methyl group, methylene group and methine group</td>
<td></td>
</tr>
<tr>
<td>1593/1508/1461/1421</td>
<td>Aromatic ring skeleton vibration in hexane residue</td>
<td></td>
</tr>
<tr>
<td>Time, h</td>
<td>Length</td>
<td>Width</td>
</tr>
<tr>
<td>--------</td>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td></td>
<td>L0P L10P L50P U</td>
<td>L0P L10P L50P U</td>
</tr>
<tr>
<td>20</td>
<td>-0.16 -0.22 -0.47 0.03</td>
<td>-0.1 -0.5 -0.17 -0.34</td>
</tr>
<tr>
<td>48</td>
<td>-0.24 -0.38 -0.46 -0.12</td>
<td>-0.13 -0.53 -0.1 -0.32</td>
</tr>
<tr>
<td>72</td>
<td>-0.26 -0.32 -0.4 -0.18</td>
<td>-0.13 -0.6 -0.24 -0.37</td>
</tr>
<tr>
<td>96</td>
<td>-0.24 -0.29 -0.22 -0.15</td>
<td>-0.16 -0.46 -0.19 -0.23</td>
</tr>
<tr>
<td>120</td>
<td>-0.24 -0.22 -0.19 -0.15</td>
<td>-0.16 -0.46 -0.17 -0.23</td>
</tr>
<tr>
<td>148</td>
<td>0.15 -0.16 -0.15 0.06</td>
<td>-0.06 -0.46 -0.03 -0.2</td>
</tr>
<tr>
<td>196</td>
<td>-0.1 -0.1 -0.1 0</td>
<td>-0.03 -0.4 0</td>
</tr>
</tbody>
</table>
7. Conceptual integration of the proposed lignin-first biorefinery with mass distribution.

Fig. S7. Conceptual integration of the proposed lignin-first biorefinery with mass distribution.