Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

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

Electronic Supplementary Information

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Outline:

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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

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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 15min followed by Soxtec extraction for 3h 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% H_2SO_4 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 500ml high pressure autoclave with 2.5 g of tungstosilicic acid and 250 mL of deionized water. The reactor was sealed, flushed and subsequently pressurized with 5 MPa H_2 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

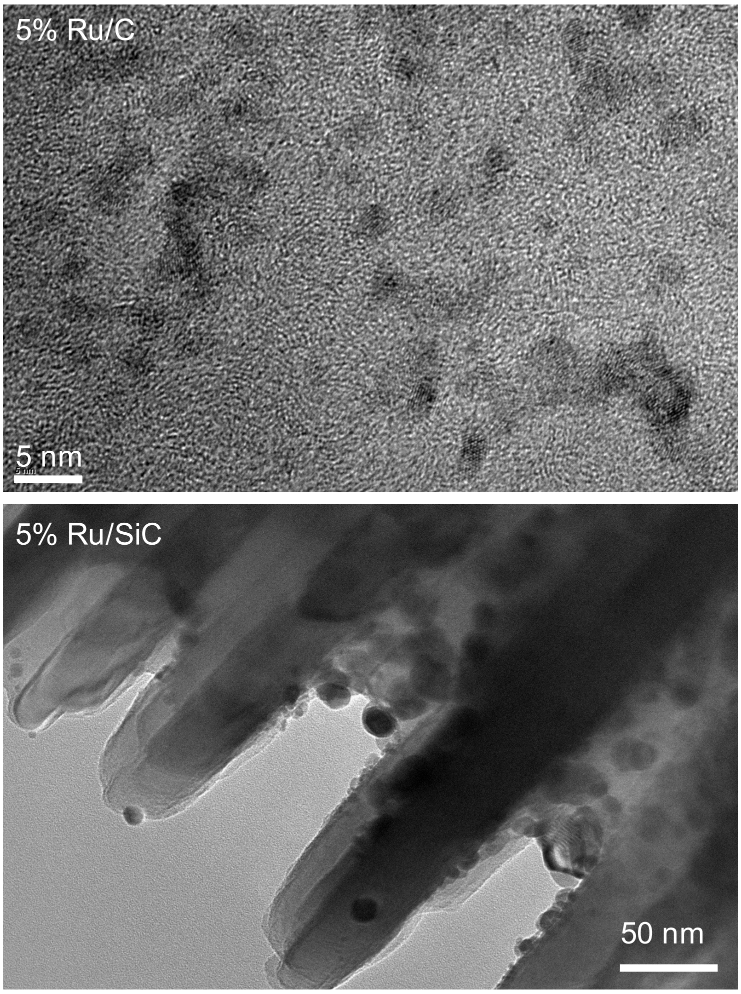


Fig. S1. TEM analysis of 5%Ru/C and 5%Ru/SiC.

3. Characterization of lignin depolymerized products in recycling runs

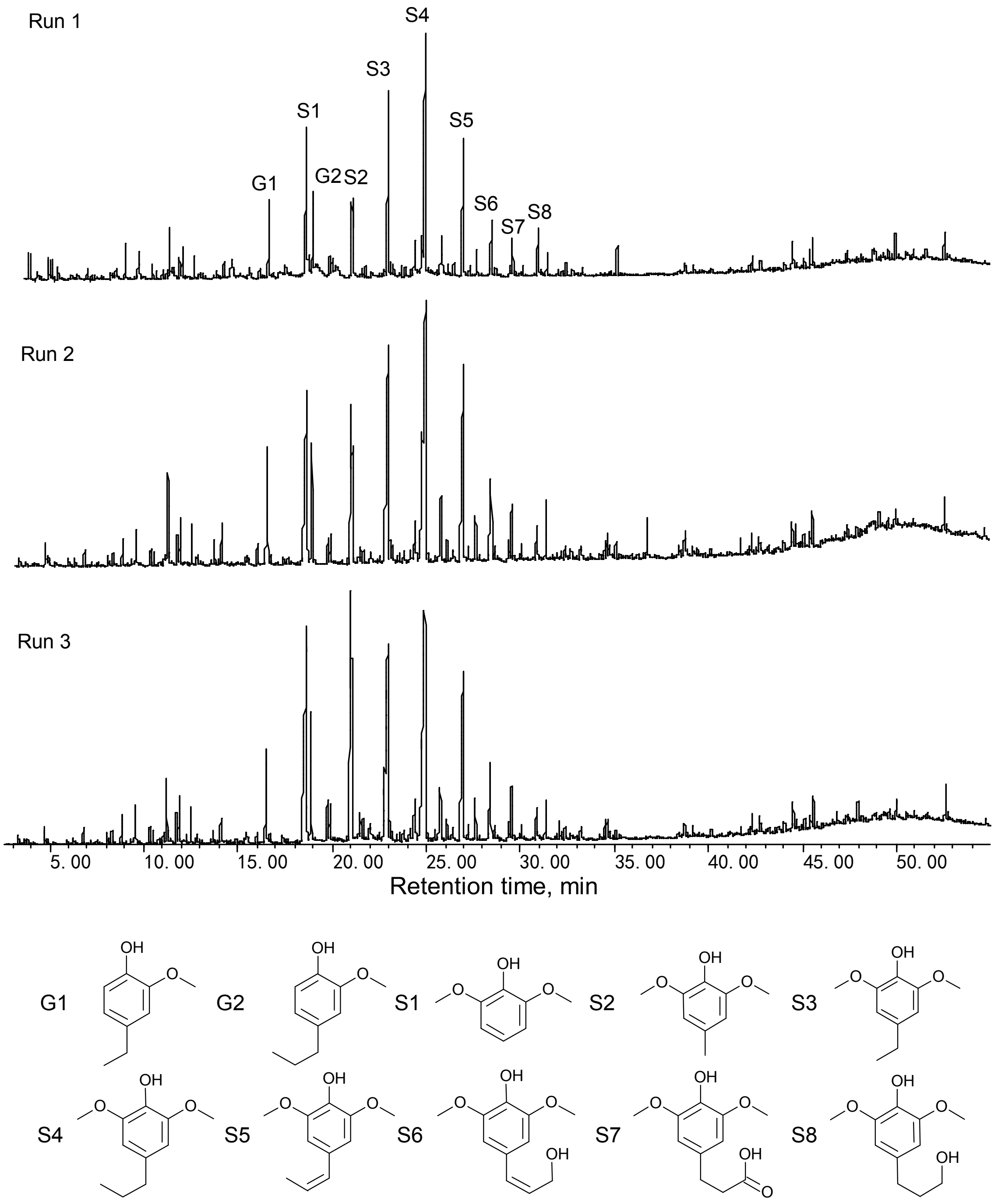
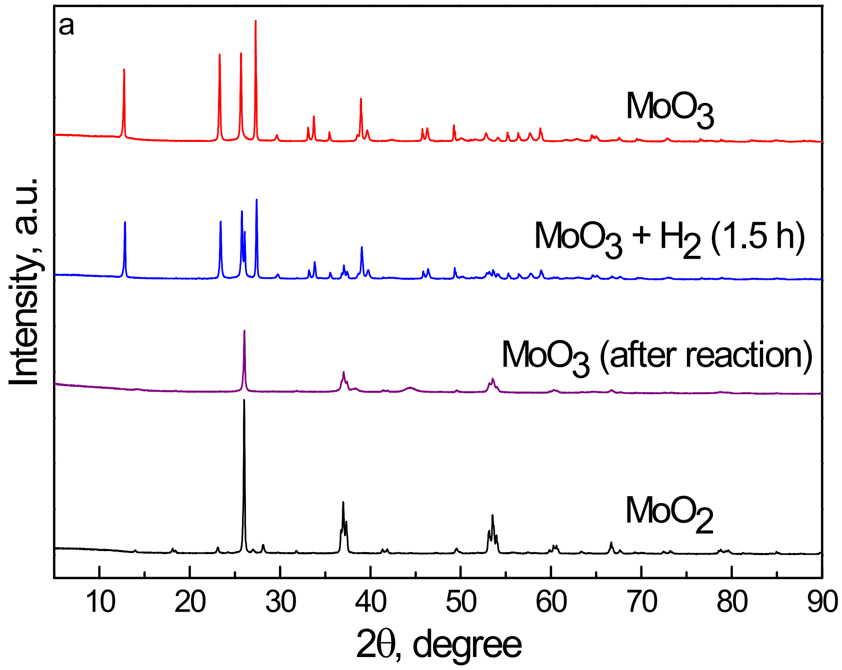
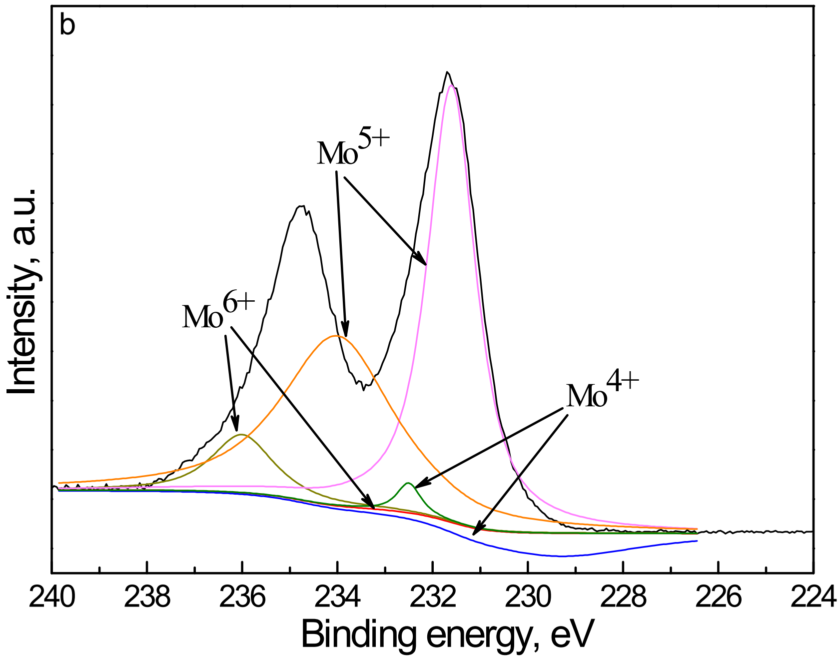


Fig. S2. Total ion chromatograms (TICs) of liquid product obtained from depolymerization of protolignin in apple wood at 250 °C for 3 h with 1 MPa H_2 using Ru/SiC with two recycling runs.

4. Characterization results of MoO_3 catalysts





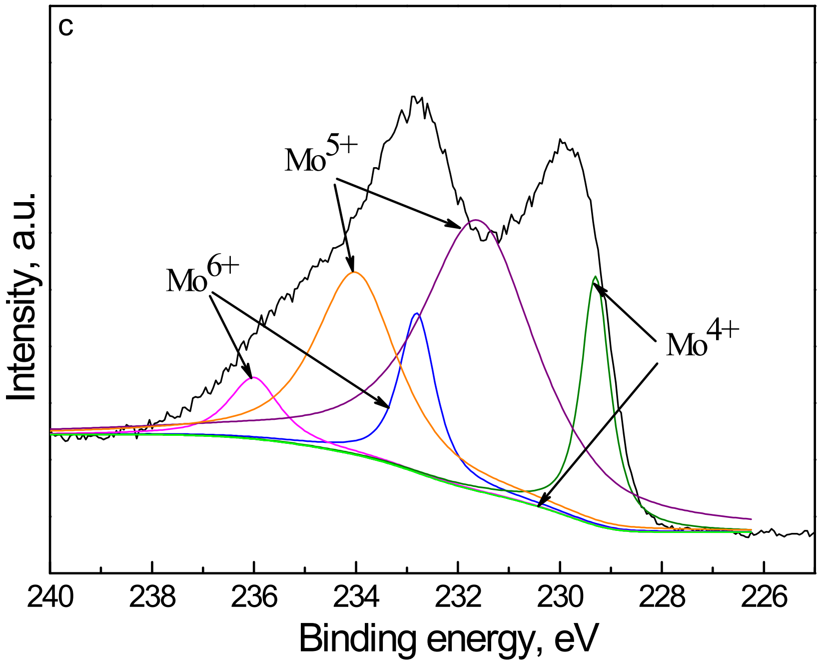


Fig. S3. (a) XRD patterns of the spent MoO_3 catalysts (in comparison with fresh MoO_3, H_2 pre-reduced MoO_3, MoO_3 after reaction, MoO_2 samples) were measured at room temperature. (b) XPS of the Mo (3d) energy region of the spent MoO_3 catalyst sample after H_2 pre-reduction at 400 °C for 1.5 h. The 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

Fig. S4. The photo of the product from HDO of lignin oil.

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

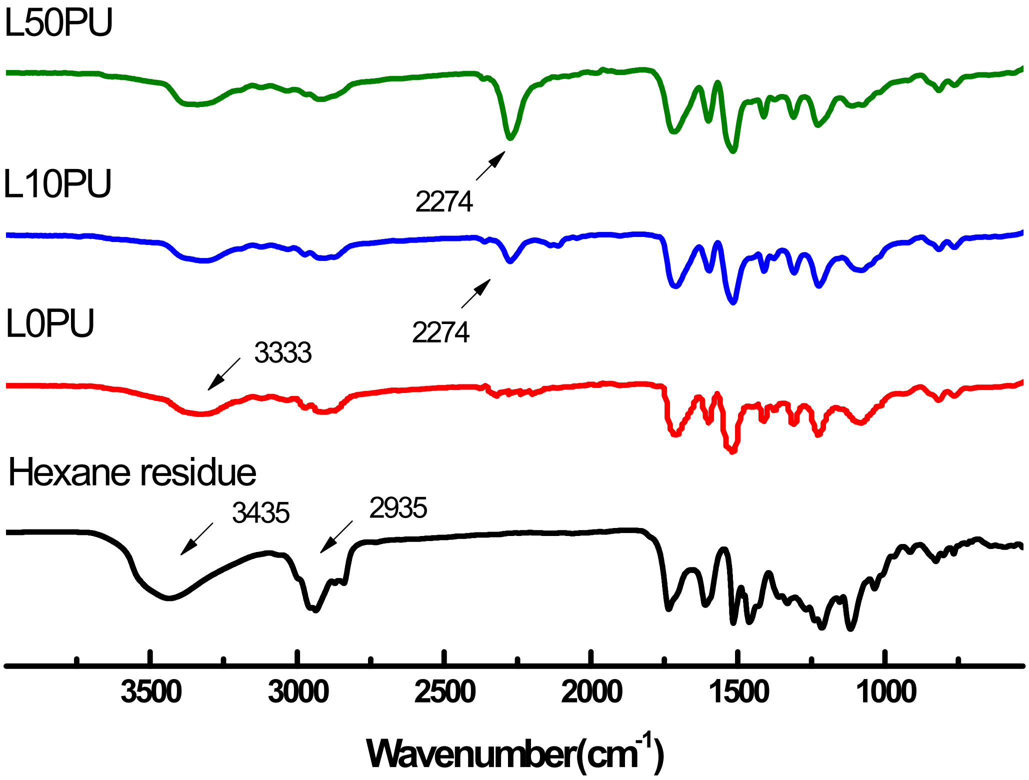


Fig. S5. FTIR spectra of the lignin oil based RPFs and hexane residue.

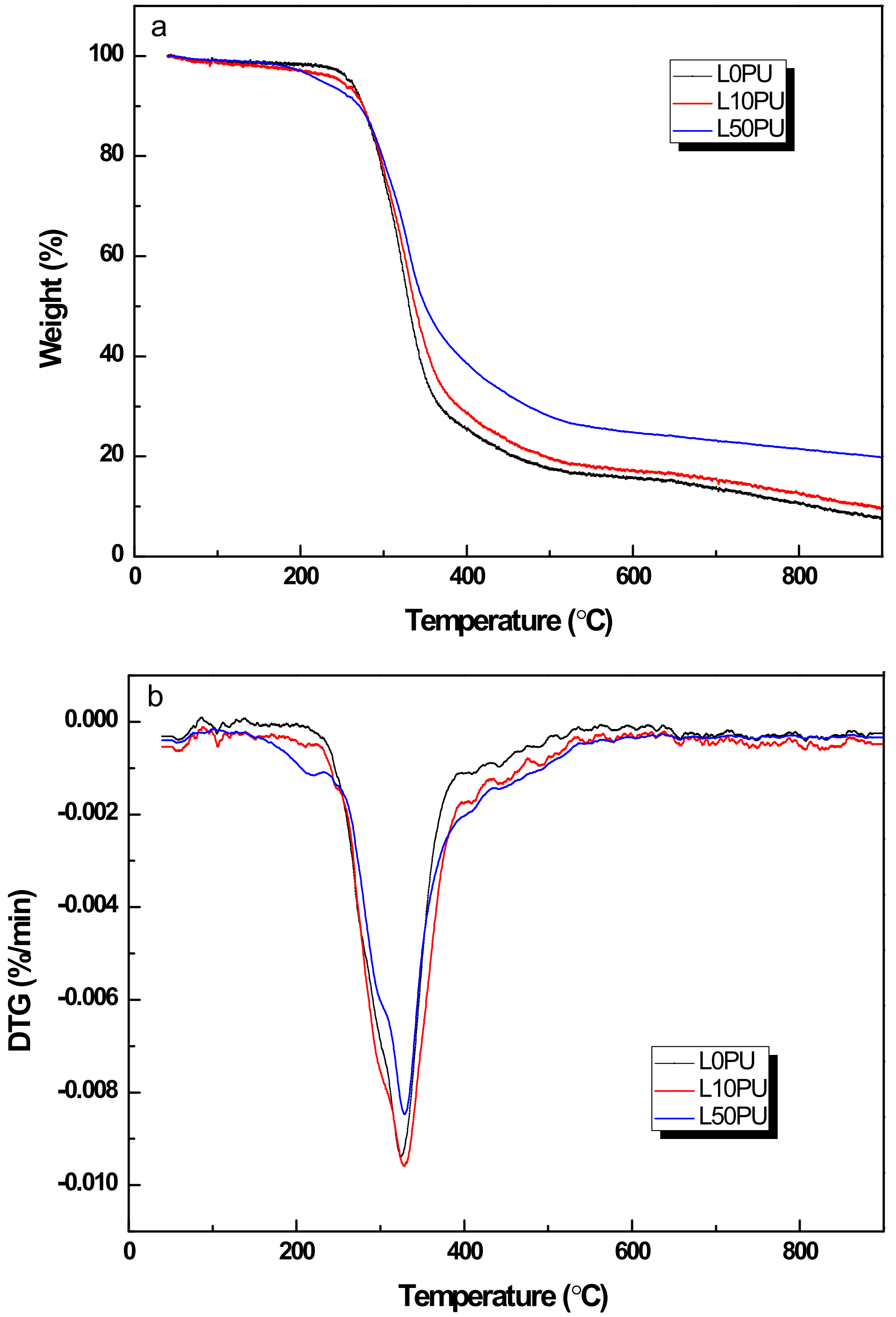


Fig. S6. TGA curves (a) and DTG curves (b) of RPFs from different contents of lignin oil replacement.

Table S1. Attribution of the infrared band of the lignin oil based RPFs and hexane residue

Wavenumber (cm^{-1})	Peak attribution	Original
3333	Amide N-H stretching vibration	Amide structure in the polyurethane
2274	N=C=O stretching vibration	Isocyanate groups
1711	Carbonyl compound -C=O stretching vibration	Ester groups in the polyurethane
1516	Amide N-H bending vibration	
1411	Amide C-H stretching vibration	
1310	Aromatic amine compounds C-N stretching vibration	-NH- group in the polyurethane
3435	hexane residue -OH stretching vibration	
2935/1458/1370	Aliphatic methyl group, methylene group and methine group	
1593/1508/1461/1421	Aromatic ring skeleton vibration in hexane residue	

Table S2. The dimensional stability of lignin oil based RPF

Time, h	Length			Width			Height		
	L0PU	L10PU	L50PU	L0PU	L10PU	L50PU	L0PU	L10PU	L50PU
20	-0.16	-0.22	-0.47	0.03	-0.1	-0.5	-0.17	-0.34	-0.62
48	-0.24	-0.38	-0.46	-0.12	-0.13	-0.53	-0.1	-0.32	-0.62
72	-0.26	-0.32	-0.4	-0.18	-0.13	-0.6	-0.24	-0.37	-0.44
96	-0.24	-0.29	-0.22	-0.15	-0.16	-0.46	-0.19	-0.23	-0.28
120	-0.24	-0.22	-0.19	-0.15	-0.16	-0.46	-0.17	-0.23	0
148	0.15	-0.16	-0.15	0.06	-0.06	-0.46	-0.03	-0.2	-0.09
196	-0.1	-0.1	-0.1	0	-0.03	-0.4	0	-0.18	-0.06

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

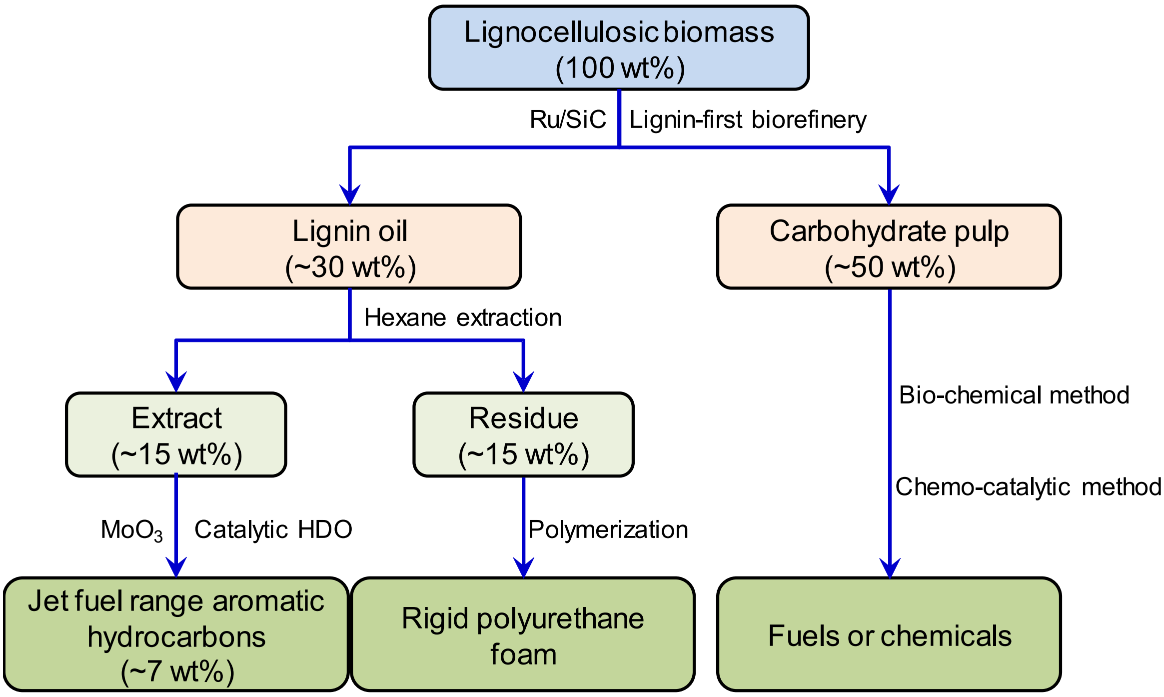


Fig. S7. Conceptual integration of the proposed lignin-first biorefinery with mass distribution.