

Supplementary Information for Selective Conversion of Lignin in Corncob Residue to Monophenols with High Yield and Selectivity

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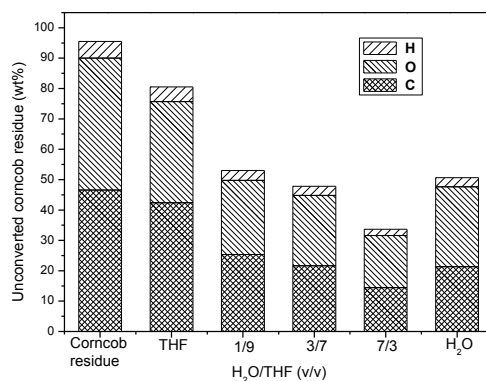


Fig. S1. Elemental analysis of the reaction residue from the reaction system with different ratio of H₂O/THF.

After treatment in THF system, the percentage of C and H in reaction residue decreased slightly, while the percentage of O significantly decreased. This confirmed that THF system was unfavorable for the conversion of corn cob residue. With the addition of H₂O in THF system (H₂O/THF, 1:9), the percentage of C, H, and O had a sharp decrease, which implied that the conversion of corn cob residue could be improved in H₂O/THF co-solvent system. When corn cob residue was treated in H₂O/THF (3:7) co-solvent system, the percentage of C and H continuously decreased. However, the percentage of O had only a little reduction, which suggested that the conversion of corn cob residue was dominated by the degradation of lignin component, because of the relative lower percentage of O in lignin than that in cellulose. With continuously increasing ratio of H₂O/THF (7:3), the percentage of C, H, and O in reaction residue all sharply decreased again, which was ascribed to the conversion of cellulose component in corn cob residue. However, in H₂O system, the percentage of C, H, and O slightly increased. All these results were consistent with the results of chemical titration.

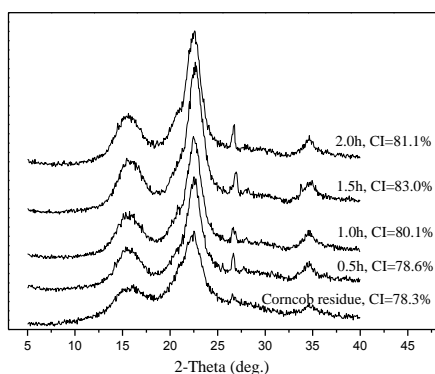


Fig. S2. X-ray diffraction of corncob residue and reaction residues at different times.

The crystalline form of corncob residue and the residues after liquefaction at different reaction time was examined by XRD measurements on DANDONG FANGYUAN DX-1000 instrument. The diffracted intensity of Cu K_{α} radiation ($k = 0.1540$ nm; 40 kV and 25 mA) was measured over the 2θ range from 5° to 40° , and the crystallinity index (CI) of cellulose in samples was calculated. Four characteristic peaks at $2\theta = 14.6^{\circ}$, 16.5° , 22.4° , and 34.6° corresponding to the diffraction of cellulose I were apparently observed. The crystal structure of reaction residue after treatment gained a sharper diffraction peak than raw material, which suggested that crystalline structure of cellulose remained excellently. A slight increase in crystallinity index from 78.3% for the original material to 83.0% at 1.5 h was observed, which indicated that the cellulosic crystal structure become neater after the removal of lignin and some cellulose existed in amorphous regions. With increasing reaction time from 1.5 to 2.0 h, the crystallinity index of reaction residue decreased with time, which implied the damage of crystalline cellulose. This result agreed well with that of chemical titration.

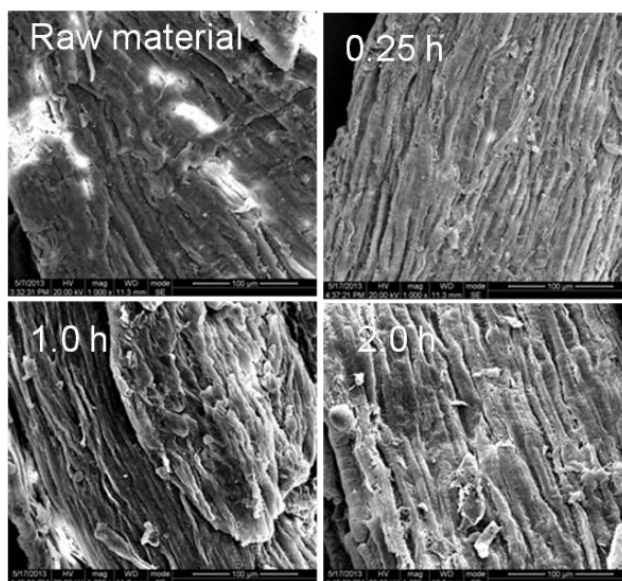


Fig. S3. SEM micrographs of residues at different reaction time.

Compared to the smooth surface of raw material, the bundle structure of cellulose was still remained after treatment, which proved that the crystalline structure of cellulose was not damaged by treatment. However, the surface of reaction residues after treatment became rougher with increasing reaction time to 1.0 h, which implied the dropping of lignin fraction from corncob residue. It indicated that H₂O/THF (3:7, v:v) co-solvent promoted the conversion of lignin. At 2.0 h, the bundle structure of cellulose was observed to be damaged, because of the exposure of cellulose in reaction solvent after removal of lignin. The results corresponded to those of the chemical titration and XRD measurement.

Table S1

Assignment of main lignin ^{13}C - ^1H correlation signals in HSQC spectra of liquid fraction according to literature.

Labels	$\delta_{\text{C}}/\delta_{\text{H}}$ (ppm)	Assignment
OMe	56.0/3.74	C-H in methoyls
A $_{\gamma}$	59.8/3.61	C $_{\gamma}$ -H $_{\gamma}$ in β -O-4' structures (A)
A' $_{\gamma}$	63.5/4.15	C $_{\gamma}$ -H $_{\gamma}$ in β -O-4' structures (A')
I $_{\gamma}$	61.2/4.15	C $_{\gamma}$ -H $_{\gamma}$ in β -O-4' structures (I)
G $_2$	111.5/6.80	C $_2$ -H $_2$ in guaiacyl units (G)
G' $_2$	111.4/7.4	C $_2$ -H $_2$ in oxidized (C $_{\alpha}$ =O) guaiacyl units (G)
G $_5$	115.3/6.68-6.99	C $_5$ -H $_5$ in guaiacyl units (G)
G $_6$	119.8/6.60	C $_6$ -H $_6$ in guaiacyl units (G)
S $_{2,6}$	104.3/6.71	C $_{2,6}$ -H $_{2,6}$ in syringyl units (S)
S' $_{2,6}$	106.5/7.26	C $_{2,6}$ -H $_{2,6}$ in (C $_{\alpha}$ =O) syringyl units (S)
H $_{2,6}$	128.2/7.19	C $_{2,6}$ -H $_{2,6}$ in <i>p</i> -hydroxyphenyl units (H)
HB $_{2,6}$	130.8/7.56	C $_{2,6}$ -H $_{2,6}$ in oxidized (C $_{\alpha}$ =O) <i>p</i> -hydroxyphenyl units (HB)