

Unleash the Potential of Lignocellulosic Biomass with Green Solvents: Chemical Component Isolation and Mechanism

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Abstract: **【Objective】** Conversion of lignin to value-add chemicals and materials in high-efficiency is trapped in the inevitably cleavage of β -O-4 linkages and formation of highly condensed structures with deep colors during lignin isolation. The aim of this study was to develop a series of novel deep eutectic solvent to ultrafast isolate light-colored lignin with near-proto structures in a record-high yield for further application. **【Method】** The novel DES was prepared by mixing hydrogen bond acceptor with hydrogen bond donator in a molar ratio of 1:2 at 80 °C for 1 h. The preparation of control groups was the same as the abovementioned process. The liquid HBAs and DESs were placed in an NMR tube to record ^1H NMR spectra (Bruker AVIII 400 MHz, Germany), where D_2O was loaded in a capillary inside the NMR tube. A solid HBA or HBD of ^1H NMR was directly dissolved in the D_2O . The FT-IR spectra of HBAs, HBDs, and DESs were conducted employing an FT-IR spectrometer (Bruker Tensor II, Germany). The HBAs, HBDs, or DESs were mixed with KBr (1:100) and then ground, and a pellet was prepared. FT-IR spectra were recorded in the 1800–800 cm^{-1} range at a resolution of 4 cm^{-1} and 32 scans. Kamlet-Taft solvatochromic parameters (acidity α , basicity β , and polarizability π^*) of DESs were tested using a UV-Vis spectrometer (Shimadzu 2600i, Japan). Typically, 2.00 g of poplar sawdust was loaded into a preheated round-bottom flask (100 mL) with 20.00 g of DES, which was treated for a fixed time (0.5, 1.0, and 1.5 h) at specified temperatures (120, 130, and 140 °C). For the high solid loading, 4.00 g of poplar was treated with 20.00 g DES. Then 50 mL anhydrous ethanol was poured into the mixture of poplar and DES and vigorously stirred. The cellulose residue of poplar was obtained after filtering and freeze-drying. The lignin dissolved in a concentrated liquid was extracted with 20 mL THF and 10 mL water thrice, and the extracted solution was further concentrated and regenerated by carefully dripping into a saturated brine. Finally, the isolated lignin was obtained after filtering, washing, and freeze-drying. Lignin samples were characterized thoroughly. **【Result】** Both the dissolved lignin was recovered by water precipitation. The delignification efficiency of the new DES was 1.58 times higher than that of ChCl/LacA (a classical, non-functional binary, and high-efficiency DES) under the same conditions. The delignification efficiency of our method was ca. 57 times higher than that of ChCl/OA/EG (the representative ternary single functional DES) within 1 h under the same solid-liquid ratio. The contents of total β -O-4 linkages were calculated to be 29.71–31.85/100 C₉, which were 1.80–1.93 times higher than that in CLacL , i.e., 51–55% of CEL. This was also considerably higher than that in other DES systems, e.g., ChCl/OA and ChCl/AA . As the poplar loading was increased to 20%, the content of β -O-4 linkages further increased to 45.80/100 C₉, accounting for 79% of CEL. The signals of condensed structures were not observed in the spectra, even if the reaction temperature was increased to 140 °C. The S/G ratios remained comparable to that of CEL, indicating that the resulting lignin was not further condensed during isolation. The mechanism was investigated by DFT calculation. The monomer types from lignin hydrogenolysis were the same as those from reductive catalytic fractionation (RCF) of raw poplar, including 4-propyleugenol (S-3), 4-propylguaiacol (G-3), 4-propanoleugenol (S-3OH), 4-propanolguaiacol (G-3OH), 4-ethyleugenol (S-2), and 4-ethylguaiacol (S-2).

Unlike alkylation of aromatic rings by formaldehyde resulting in unselective product mixture, the hydrogenolysis of the isolated lignin led to a high selectivity (73.64%) to the propylphenols (S-3 and G-3). As expected, the isolated lignin with its uncondensed structure and abundant β -O-4 linkages, delivered a satisfactory monomer yield (up to 20.51 wt%). It was approximately 7.5 times higher than that of CPL with a poor 2.73 wt% yield owing to the extensive condensation of 43% and the trace amounts of β -O-4 linkages in CPL. The monomer yields of the DES-isolated lignin samples were approximately equivalent to the theoretical values. The monomer yield of CLacL with a low content of β -O-4 linkages was higher than its theoretical values, which was similar to that obtained in previous works. That may be attributed to α -OH groups esterified by lactic acid. The monomer yield of the isolated lignin was comparable to that of the poplar lignin isolated via the ternary diol-based functional DES (ca. 20–24 wt%) consumed within 42 h (24 h for lignin isolation and 18 h for hydrogenolysis); whereas the new DES decreased the processing time to 5 h (1 h for lignin isolation and 4 h for hydrogenolysis). **【Conclusion】** This work unleashes the valorization potential of lignin by a green and fast strategy for sustainable biorefineries.

Key words: lignin; DES; isolation; hydrogenolysis; uncondensation.