Supporting Information

A Green Process for Extraction of Lignin by the Microwave-assisted Ionic Liquid Approach: Towards Biomass Biorefinery and Lignin Characterization

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Materials and Chemicals. Eucalyptus urophylla (EU) was collected in Guangzhou province, China. The trunks were chipped into small pieces and dried in an oven at 60 ℃ for 12 h. After that, the pieces were milled in a planetary ball mill for 5 h (Fritsch GMBH, Idar-Oberstein, Germany) at room temperature. The chemical composition of EU was determined based on the analytical procedure of the National Renewable Energy Laboratory (NREL) method (Table S1).[1,2] The associated sugars were analyzed by high performance anion exchange chromatography (HPEAC) on an ICS-3000 system (Dionex, CA) equipped with an electrochemical detector and CarboPac PA 20 analytical column. IL 1-ethyl-3-methylimidazolium acetate $[C_2C_1im][OAc]$ (≥98%) and 1-butyl-3-methylimidazolium chloride $[C_4C_1im]Cl$ (≥99%) were purchased from Lanzhou Institute of Chemical Physics (Chinese Academy of Science), Lanzhou, China. All chemical reagents used were of analytical grade.

Lignin Extraction Procedure. The lignin extraction procedure is shown in Scheme 1. Starting at the beginning: the measurement of microwave absorptive by ILs was carried out with a round bottom flask which was covered by a lid and an IR temperature sensor (to detect and control the internal temperature) by using a Milestone Microsynth microwave Labstation (Germany). 10 g of IL was poured into a 50 mL of flask, which was pre-heated at 90 ℃ for 10 min to dissolve the IL. Then, 0.5 g ground powder was accurately weighed and added into the flask with stirring. After the wood powder was dispersed homogeneously in the IL, the flask was placed into the microwave reactor, and the treatment program with the desired time-temperature setting and preheating time of 6 min was started. The temperature program used consisted of a fast heating step during which power varied to maintain temperature at the target value. At the end of the reaction, samples were allowed to

cool down to room temperature. The carbohydrate-enriched material (CEM) was separated by filtration and washed with hot water (80 ℃) to remove residual IL for utilization. The obtained CEM was freeze-dried, and its amount was estimated gravimetrically. The filtrate was evaporated under vacuum to evaporate water, and deionized water was added to the concentrated filtrate to precipitate lignin.

Analytical Methods. The carbohydrate moieties associated with the lignin fractions were determined by hydrolysis with dilute sulfuric acid according to the procedure described in a previous study.[3] FT-IR spectra of the lignin were analyzed by a Thermo Scientific Nicolet iN 10-MX FT-IR chemical imaging microscope (Thermo Scientific, America) fitted with narrow-band liquid nitrogen cooled MCT detector. The weight-average (M_w) and number-average (M_n) molecular weights of the lignin fractions were determined by GPC on a PL-gel 10 mm Mixed-B 7.5 mm i.d. column according to a previously literature.[4] The 2D HSQC NMR spectra were recorded on a Bruker AVIII 400 MHz spectrometer with a 5 mm BBI probe at 25 ℃ using DMSO-d_6 as solvent. HSQC cross signals were analyzed and assigned by comparing with published literatures.[5,6] The thermal degradation of the lignin was investigated using both thermogravinetric (TGA) and differential thermal analysis (DTA) on a simultaneous thermal analyzer (DTG-60 Shimadzu, Japan) from 40 to 600 ℃.

Table S1. Chemical Composition of Eucalyptus Urophylla

Ingredient	Eucalyptus urophylla
Klason lignin	24.19%
Acid-soluble lignin	3.61%
Glucan	54.80%
Xylan	14.07%
Arabinan	1.17%
Mannan	Tr[a]
Ash	1.08%

[a]Tr: Trance.

Table S2. Assignment of Main Lignin ^{1}H-^{13}C Cross-signals in the HSQC Spectra of the Lignin Fractions

Labels	δ_H/δ_C (ppm)	Assignment
B_β	3.02/53.2	H_β-C_β in β-β' (resinol) substructures (**B**)
C_β	3.48/53.0	H_β-C_β in β-5′ (phenylcoumaran) substructures (**C**)
-OMe	3.76/55.2	H-C in methoxyls
A_γ	3.42/3.65/59.0	H_γ-C_γ in β-O-4′ substructures (**A**)
I_γ	4.15/61.2	H_γ-C_γ in *p*-hydroxycinnamyl alcohol end groups (**I**)
$(A', A'')_\gamma$	3.67/62.5	H_γ-C_γ in γ-acetylated β-O-4′ substructures (**A′**/ **A"**)
B_γ	4.19/71.0 and 3.84/71.0	H_γ-C_γ in β-β' (resinol) substructures (**B**)
A_α	4.89/71.5	H_α-C_α in β-O-4′ substructures linked to a S unit (**A**/**A′**/**A"**)
C_γ	3.40/62.1	H_γ-C_γ in β-5′ (phenylcoumaran) substructures (**C**)
B_α	4.63/84.2	H_α-C_α in β-β' (resinol) substructures (**B**)
$A_{\beta(S)}$	3.99/86.0 and 4.08/86.2	H_β-C_β in β-O-4′ substructures linked to a S unit (**A**)
$A_{\beta(G/H)}$	4.31/83.2	H_β-C_β in β-O-4′ substructures linked to a G and H units (**A**)
$S_{2,6}$	6.68/103.6	$H_{2,6}$-$C_{2,6}$ in syringyl units (**S**)
$S'_{2,6}$	7.28/106.1	$H_{2,6}$-$C_{2,6}$ in C_α-oxidized (C_α=O) phenolic syringyl units (**S′**)
G_2	6.97/109.8	H_2-C_2 in guaiacyl units (**G**)
G_5	6.94/114.8 and 6.69/114.8	H_5-C_5 in guaiacyl units (**G**)
G_6	6.81/118.8	H_6- C_6 in guaiacyl units (**G**)

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