Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

$ZnCl_2$ Induced Catalytic Conversion of Softwood Lignin to Aromatics and Hydrocarbons

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1. Experimental details

1.1 Raw material and technical lignin preparation

The beetle-killed lodgepole pine wood chips were purchased from Forest Concepts, LLC. The feedstock is 2 mm crumbles from chips from standing dead, needless trees cut within 100 feet of US Forest Service Land 615.1 Road 1/2 mile (GPS location N. 40* 35.959' W. 106* 36.250', elevation 8,740 feet, Teal Lake, watershed named Grizzly Creek Drainage near Walden, CO), 2-4 years after death. The trees are about 56' 9" tall with diameter breast height 10" DBH or 35" circumference. The feedstock contains 37.89±0.59% of glucan, 5.25±0.15% of xylan, 29.95±0.78% of lignin, 3.62±0.29% of galactan, 2.25±0.42% of arabinan and 9.89±0.12% of mannan according to NREL K-lignin analysis (NREL LAP “Determination of structural carbohydrates and lignin in biomass).[1] The technical lignin was recovered from the hydrolysate of 0.05 wt.% sulfuric acid flowthrough pretreatment of beetle-killed lodgepole pine wood chips with particle size of 40-60 mesh at 240°C with flow rate of 25mL/min for 8 min. It was collected by settling pretreatment liquid at pH 2-3 overnight to precipitate solid lignin at the bottom followed by fast filtration to collect lignin solids, avoiding filter paper clogging. Lignin was prepared through 0.05 wt. % sulfuric acid flowthrough pretreatment of beetle-killed lodgepole pine wood chips with particle size of 40-60 mesh at 240°C with flow rate of 25mL/min for 8 min.[2]

1.2 Lignin purity analysis

Both NREL K-lignin analysis procedure (see NREL LAP “Determination of structural carbohydrates and lignin in biomass)[1] and the improved acetyl bromide procedure were used to analyze the purity of the prepared lignin (technical lignin).[3] Following the improved acetyl bromide procedure, 1-2 mg of lignin was dissolved in 2.5 ml of 25 wt. % acetyl bromide (AcBr) in acetic acid solution in a 15 ml vial. The vial was then sealed with a PTEFE-coated silicone cap and put in an oven at 70±0.2 °C for 30 min. The vial was shaken every 10 min to improve diffusion. Then the mixture was cooled down and transferred to a 50 mL volumetric flask, where 2.5 mL of 2 $mol \cdot L^{-1}$ NaOH and 0.5 mL of 7.5 $mol \cdot L^{-1}$ $NH_2OH \cdot HCl$ were added. The mixture was then diluted to 50 mL with acetic acid. The absorptions of the solutions at 280 nm against a blank control without lignin sample were recorded and analyzed using the equation of Morrison as following:

$$\text{Lignin (\%)} = 3.37 \times \text{absorbance/sample concentration } (\text{g}\cdot\text{L}^{-1}) - 1.05$$

1.3 Characterization of pine wood lignin by 2D NMR

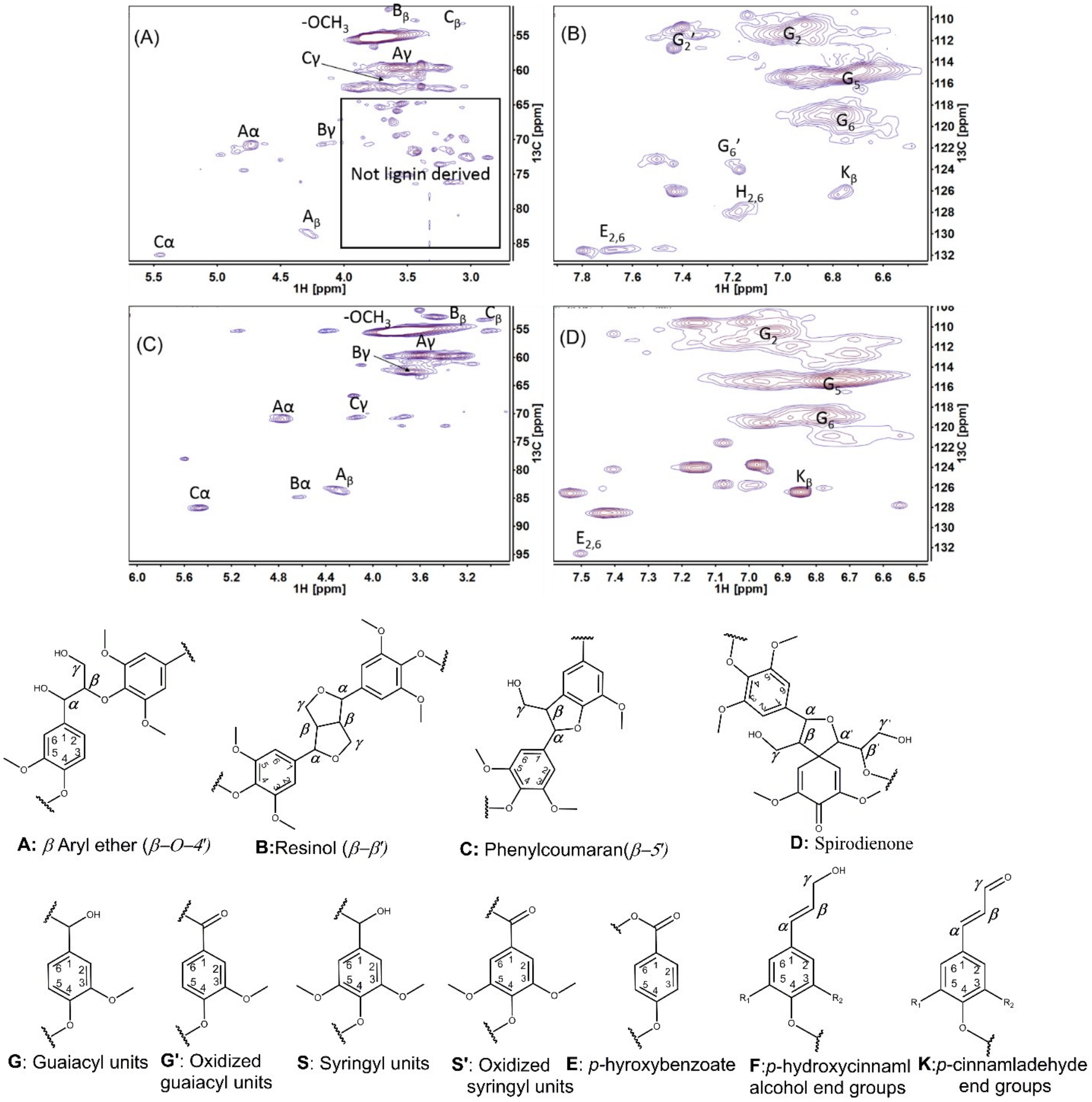
50 mg lignin was dissolved in 600 µL deuterated DMSO (Cambridge Isotope Laboratories). The resulting liquid sample was placed in 5 mm Wilmad 535-PP NMR tubes. NMR spectra were collected at 25° C on 500 and 600 MHz Agilent (Varian) Inova NMR spectrometers equipped with z-axis pulsed-field triple-resonance HNCP probes. Samples contained 0.05% (v/v) TMS for chemical shift referencing. Two-dimensional ^{1}H-^{13}C HSQC spectra of the aliphatic and aromatic regions were collected separately using the BioPack gchsqc pulse sequence, with ^{1}H spectral width of 17 ppm and ^{13}C spectral widths of 100 or 60 ppm for the aliphatic or aromatic regions, respectively. Spectra were collected with 1024 points (Varian parameter np) and 61 ms acquisition time with 128 or 256 transients and 128 or 96 complex points (Varian parameter ni in States-TPPI mode) in the indirect dimension, for aliphatic and aromatic spectra, respectively. Adiabatic WURST decoupling was applied during acquisition. Delay times tCH and lambda for 1/4*JCH, were 1.8 ms and 1.6 ms for aliphatic spectra, and 1.45 ms and 1.3 ms for aromatic spectra, respectively. Reference one-dimensional ^{1}H spectra were collected with 32k points and 128 transients. HSQC spectra were processed and analyzed with Felix 2007 (FelixNMR, Inc) or MestReNova 6.0.4 (Mestrelab Research), with matched cosine-bell apodization in both dimensions, 2X zero filling in both dimensions, and forward linear prediction of 30% more points in the indirect dimension. One-dimensional 1H spectra were processed with no apodization or linear prediction and 2X zero filling. Relative peak integrals were measured in MestReNova.[2]

1.4 Characterization of pine lignin by ATR-IR

The spectra (4000-800 cm^{-1}) were obtained with a Bruker Fourier transform infrared spectrophotometer using about 2 mg of each sample. Spectra were obtained using the triangular apodization, resolution of 4 cm^{-1}, and interval of 1 cm^{-1}. 64 scans were conducted for each background and sample spectra. Baseline and ATR corrections for penetration depth and frequency variations were applied using the Opus software supplied with the equipment. The pretreated lignin as well as native ball milled lignin was analyzed by FTIR to understand the modification of lignin functional groups resulting from pretreatment under tested conditions.[4]

2. Additional results

2.1 Two dimensional (2D) HSQC NMR spectroscopic analysis of technical lignin



A: *β* Aryl ether (*β–O–4′*)
B:Resinol (*β–β′*)
C: Phenylcoumaran(*β–5′*)
D: Spirodienone
G: Guaiacyl units
G': Oxidized guaiacyl units
S: Syringyl units
S': Oxidized syringyl units
E: *p*-hyroxybenzoate
F:*p*-hydroxycinnaml alcohol end groups
K:*p*-cinnamladehyde end groups

Figure S1. ^{13}C-^{1}H HSQC NMR spectra determination of flowthrough pretreatment derived the beetle-killed lodgepole pine wood technical lignin structure. (A, B) ball milled beetle-killed lodgepole pine wood lignin; (C, D) flowthrough pretreatment derived the beetle-killed lodgepole pine wood technical lignin.

It could be concluded from Fig. S1, technical lignin obtained from flowthrough pretreatment with addition of 0.05 wt% sulfuric acid at 240 °C showed similar chemical structure to ball milled native lignin. Fig. S1 also shows mainly three aliphatic linkages between aromatic centers in both kind of lignin, namely *β*-ether (*β*-O-4), resinol (*β*-*β*), and phenylcoumaran (*β*-5). Guaiacyl (G unit) was found to be the dominated units in both kinds of lignin. All these results showed that the technical lignin derived from dilute acid flowthrough pretreatment of pine wood kept the typical chemical structure of softwood lignin. Moreover, it can be seen in Fig. S1 (A) that some "not lignin derived" peaks exist in the 2D NMR spectra of ball-milled beetle-killed lodgepole pine wood lignin, but do not exist in that of technical lignin, indicating that technical lignin derived from flowthrough pretreatment of beetle-killed lodgepole pine wood lignin showed higher purity than ball milled lignin.

2.1 FTIR spectroscopy determination of lignin structure

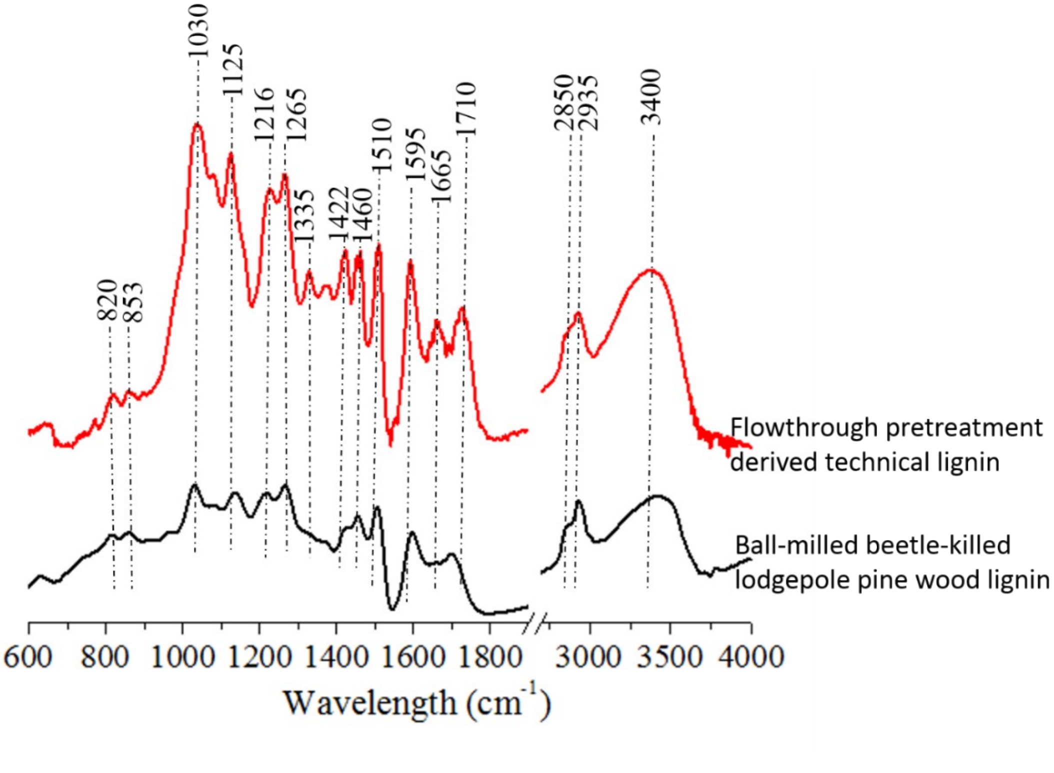


Figure S2. FTIR characterization of the ball-milled beetle-killed lodgepole pine wood lignin and flowthrough pretreatment derived technical lignin

For further investigation of the chemical structure of technical lignin, the obtained lignin samples were analyzed by ATR-IR spectroscopy, and compared with the ball-milled lignin that was representative of native lignin (Fig. S2). The absorption bands in the ATR-IR spectra can be readily assigned to both kinds of lignin, providing information on the chemical structure features of lignin. All assignments are based on previously published data.[5] Both of the two samples showed a strong and broad absorption band centered at 3400cm^{-1} that originated from the O-H stretching vibration in the phenolic and aliphatic hydroxyl groups. Another relatively strong band around 1270-1212 cm^{-1} was derived from C-O stretching vibration, indicating ether bonds widely existence in the beetle-killed lodgepole pine wood. The technical lignin presented clearer peaks with higher intensities, further demonstrating the higher purity of technical lignin compared to the ball-milled beetle-killed lodgepole pine wood lignin.

Table S1. Identification of FTIR bands for the beetle-killed lodgepole pine wood lignin

No.	IR wavelength (cm^{-1})	Characteristic groups
1	3500-3100	O-H stretching vibration
2	2935-2850	C-H stretching in methyl, methylene and methyne groups
3	1728-1691	C=O stretch in unconjugated ketone and carboxyl group
4	1664-1660	Stretching vibrations of the C=O bonds at α and β location
5	1593-1613	C=O stretching conjugated to the aromatic ring
6	1510-1505	Aromatic skeletal vibrations
7	1470-1460	C-H bending vibration in methyl groups
8	1423-1427	C-H deformation in lignin
9	1377	Aliphatic C-H stretch in CH_3
10	1331	Syringyl ring breathing with C-O stretching
11	1270-1212	C-O stretching vibration in guaiacol rings
13	1157-1126	aromatic C H in-plane deformation
14	1082-1039	Aromatic C-H in-plane deformation for guaiacyl type
15	1462-1425	CH_2 in Lignin
16	1137	Aromatic C-H in-plane deformationforsyringyl type
17	1031	C-O stretching of primary alcohol
18	860	Deformation vibrations of C-H bonds in associated to aromatic rings
19	821-817	C-H bending of syringyl units

2.3 Effects of reaction time on technical lignin liquidation in highly concentrated $ZnCl_2$ solution

The time profile of the technical lignin conversion in 63 wt% $ZnCl_2$ solution was studied (Fig.S3). Lignin liquefaction in the initial stage of reaction was very fast, indicating the high catalytic activity of the incompletely coordinated Zn^{2+} in C-O-C bonds cleavage. The highest liquid product yield was obtained after reacting for about 6 h. Further increasing the reaction time resulted in lower liquid product yield. This is mainly because the repolymerization of the degraded lignin intermediates is faster than the degradation of lignin polymers.

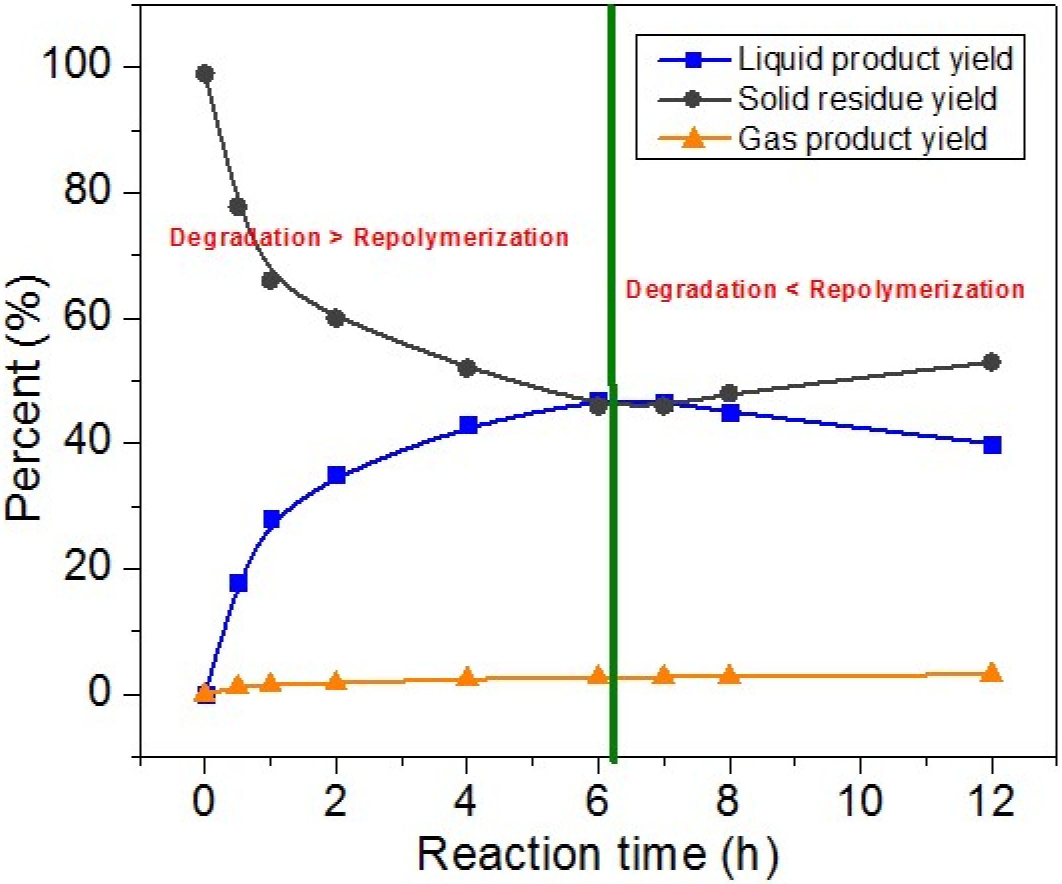


Figure S3. Effects of reaction time on technical lignin conversion in highly concentrated $ZnCl_2$ solution. Reaction conditions: lignin 200 mg, 63 wt. % $ZnCl_2$ solution 7 mL, PH_2 4 MPa, T=200 ^oC.

References

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