

Electronic Supplementary Information

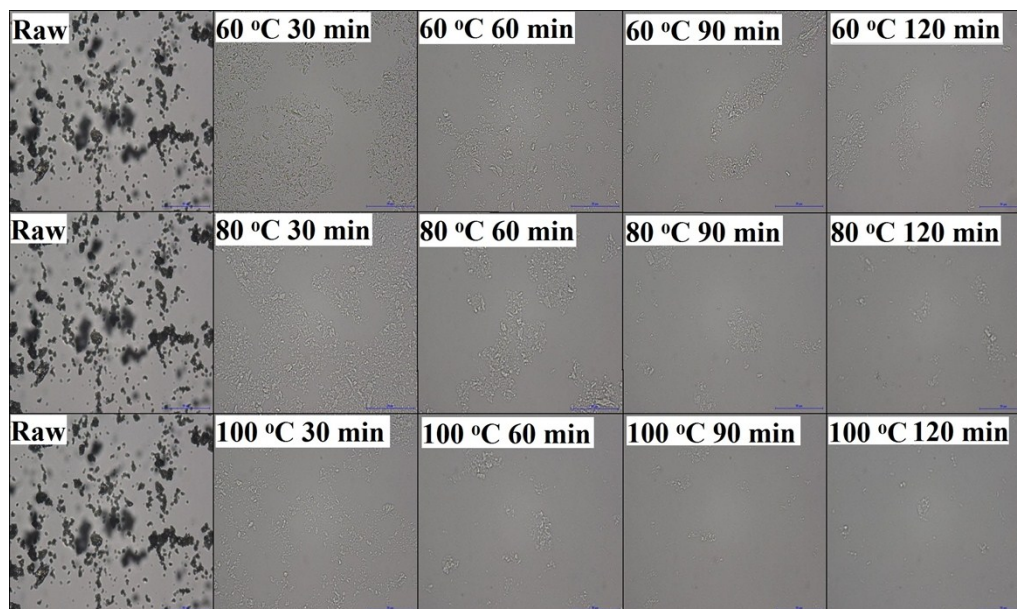


Fig. S1. Dissolution of ball-milled wood in DMSO/[Emin]OAc solvent system under different temperatures (Optical microscopy).

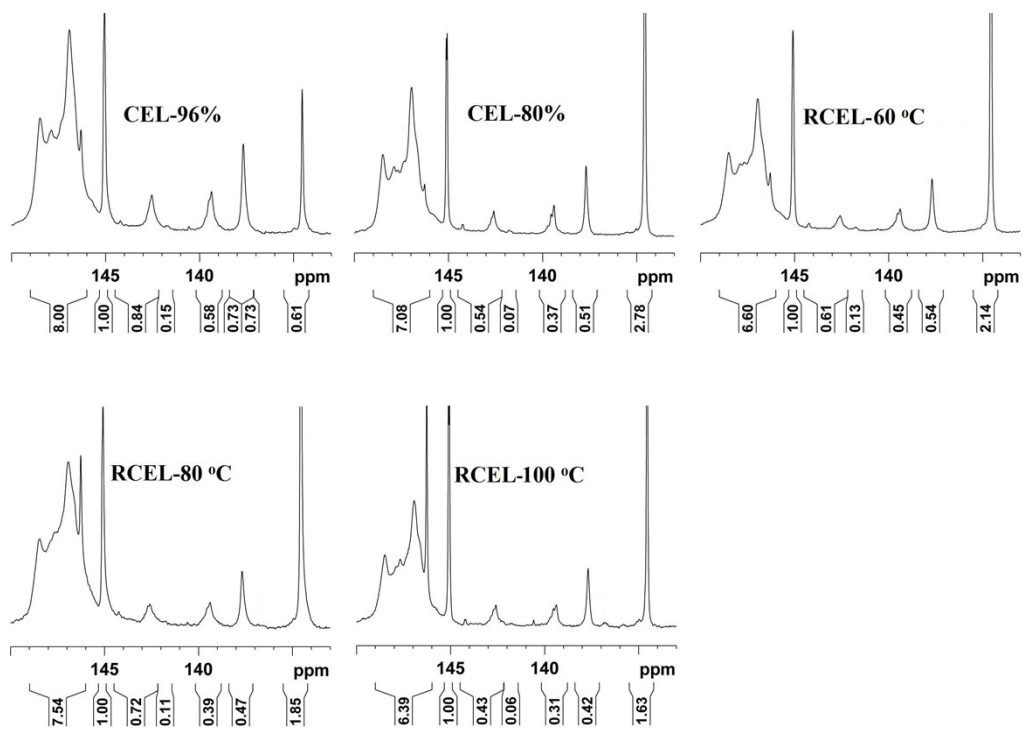


Fig. S2. ^{31}P -NMR spectra of the lignin fractions isolated from poplar wood

Table S1Quantification of the raw and regenerated poplar wood by CP/MAS ¹³C-NMR

Samples	Crystalline region	Amorphous region	CrI ^a (%)
Raw	1.00	4.08	19.68
R-raw-60 °C	1.00	3.15	24.10
R-raw-80 °C	1.00	2.81	26.26
R-raw-100 °C	1.00	3.68	21.36

^a Crystallinity index

$$\text{CrI (\%)} = I_{\text{Crystalline region}} / I_{\text{Crystalline region} + \text{Amorphous region}}$$

Table S2

Assignments of ^{13}C - ^1H correlation signals in the HSQC spectra of the lignin from poplar wood (according to the previous publications¹⁻⁴).

Labels	$\delta_{\text{C}}/\delta_{\text{H}}$ (ppm)	Assignment
C_{β}	52.9/3.45	C_{β} - H_{β} in phenylcomaran structures(C)
B_{β}	53.5/3.05	C_{β} - H_{β} in resinol substructures(B)
- OCH_3	55.6/3.72	C-H in methoxyls
A_{γ}	59.5/3.70 and 3.39	C_{γ} - H_{γ} in β - O -4' substructures(A)
D_{β}	59.7/2.73	C_{β} - H_{β} in spirodienone substructures(D)
I_{γ}	61.4/4.10	C_{γ} - H_{γ} in cinnamyl(sinapyl/coniferyl) alcohol end groups(I)
C_{γ}	62.3/3.73	C_{γ} - H_{γ} in phenylcomaran structures(C)
X_5	62.5/3.39	C_5 - H_5 β -D-xylopyranoside substructures(X)
A'_{γ}	63.1/4.29	C_{γ} - H_{γ} in γ -acylated β - O -4' substructures(A')
B_{γ}	71.1/3.81 and 4.17	C_{γ} - H_{γ} in resinol substructures(B)
A_{α}	71.9/4.86	C_{α} - H_{α} in β - O -4' substructures(A)
D'_{α}	79.4/4.10	C_{α} - H_{α} in spirodienone substructures(D')
BE	81.0/4.65	C_{α} - H_{α} in benzyl-ether (BE) linkage
D_{α}	81.1/5.09	C_{α} - H_{α} in spirodienone substructures(D)
A_{β} (G/H)	83.4/4.43	C_{β} - H_{β} in β - O -4' linked to a G/H unit(A)
B_{α}	84.8/4.65	C_{α} - H_{α} in resinol substructures(B)
A_{β} (S)	85.8/4.11	C_{β} - H_{β} in β - O -4' linked to a S unit(A)
C_{α}	86.79/5.46	C_{α} - H_{α} in phenylcomaran structures(C)
$\text{S}_{2,6}$	103.9/6.71	$\text{C}_{2,6}$ - $\text{H}_{2,6}$ in syringyl units(S)
$\text{S}'_{2,6}$	106.2/7.32	$\text{C}_{2,6}$ - $\text{H}_{2,6}$ in oxidized(C=O) phenolic syringyl units(S')
G_2	110.9/6.96	C_2 - H_2 in guaiacyl units(G)
G_5	114.9/6.76	C_5 - H_5 in guaiacyl units(G)
G_6	119.0/6.78	C_6 - H_6 in guaiacyl units(G)
$\text{H}_{2,6}$	127.8/7.22	$\text{C}_{2,6}$ - $\text{H}_{2,6}$ in <i>p</i> -hydroxyphenyl units(S)
$\text{PB}_{2,6}$	131.2/7.66	$\text{C}_{2,6}$ - $\text{H}_{2,6}$ in <i>p</i> -hydroxybenzoate units(S)

Reference

- 1 S. Ralph, J. Ralph, L. Landucci and L. Landucci. *US Forest Prod. Lab., Madison, WI* (<http://ars.usda.gov/Services/docs.htm>). 2004.
- 2 H. Kim and J. Ralph. *Org. Biomol. Chem.* 2010,**8**,576-591.
- 3 J. C. Del Río, J. Rencoret, P. Prinsen, A. n. T. Martínez, J. Ralph and A. Gutiérrez. *J. Agric. Food Chem.* 2012,**60**,5922-5935.
- 4 T.-Q. Yuan, S.-N. Sun, F. Xu and R.-C. Sun. *J. Agric. Food Chem.* 2011,**59**,6605-6615.

2. Methods

2.1. Structure elucidation of CELs and RCELs

Acetylation of Lignin Samples

About 50 mg of CEL and RECL were dissolved in a solution of dimethyl sulfoxide: 1-methylimidazole (2:1, v/v) 3mL and stirred without direct light at room temperature for 12 h. Acetic anhydride (1 mL) was added to the reaction mixture and continued reacting for 2 h. The reaction mixture was dropped slowly into 100 mL acid water (pH=2) to induce precipitation followed by centrifugation. The acetylated lignin was dissolved in tetrahydrofuran (THF) (2 mg/mL), and the solution was filtered through a 0.22 μm filter. The filtered solution (20 μL) was injected into the HPLC system and detected using an UV detector setting at 280 nm. THF was used as the mobile phase and the flow rate was 0.8 mL/min. Standard PL polystyrene samples were used for calibration. GPC analyses were run at least twice.

2D-HSQC NMR

About 50 mg of lignin was dissolved in 0.5 mL of DMSO- d_6 (99.8% D). For quantitative 2D-HSQC spectra, the Bruker standard pulse program hsqcetgpsi2 was used for HSQC experiments. The spectral widths were 5000 Hz and 20000 Hz for the ^1H - and ^{13}C -dimensions, respectively. The number of collected complex points was 1024 for ^1H -dimension with a recycle delay of 1.5 s. The number of transients was 64, and 256 time increments were always recorded in the ^{13}C -dimension. The $^1J_{\text{CH}}$ used was 145 Hz. Prior to Fourier transformation, the data matrixes were zero filled up to 1024 points in the ^{13}C -dimension. Data processing was performed using standard Bruker Topspin-NMR software.

A quantitative analysis of the intensities of the HSQC cross-signal was performed according to the following formula: ¹⁻²

$$I(\text{C}_9) \text{ units} = 0.5I(\text{S}_{2,6}) + I(\text{G}_2)$$

Where $I(\text{S}_{2,6})$ is the integration of $\text{S}_{2,6}$, including S and S', $I(\text{G}_2)$ is the integral value of G_2 . $I(\text{C}_9)$ represents the integral value of the aromatic ring. According to the internal standard ($I(\text{C}_9)$), the amount of $I(\text{X})\%$ could be obtained by the following formula:

$$I(\text{X})\% = I(\text{X})/I(\text{C}_9) \times 100\%$$

Where $I(\text{X})$ is the integral value of the α -position of A (β -O-4'), B (β - β), and C (β -5), the integration should be in the same contour level.

In the aromatic region, $\text{C}_{2,6}$ - $\text{H}_{2,6}$ correlations from S units and C_2 - H_2 correlation from G units were used to estimate the S/G ratio of lignin. The S/G ratio could be obtained by the following formula:

$$\text{S/G} = 0.5I(\text{S}_{2,6})/I(\text{G}_2)$$

Quantitative ³¹P NMR

20 mg lignin was dissolved in 500 μ L of anhydrous pyridine and deuterated chloroform (1.6:1, v/v) under stirring. This was followed by the addition 100 μ L of cyclohexanol (10.85 mg/mL in anhydrous pyridine and deuterated chloroform 1.6:1, v/v) as an internal standard and 100 μ L of Chromium (III) acetylacetonate solution (5 mg mL⁻¹ in anhydrous pyridine and deuterated chloroform 1.6:1, v/v) as relaxation reagent. The mixture was reacted with 100 μ L of phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, TMDP) for about 10 min and was transferred into a 5 mm NMR tube for subsequent NMR analysis.

Reference

- 1 M. Sette, R. Wechselberger and C. Crestini. *Chem-Eur.* 2011,**17**,9529-9535.
- 2 J.-L. Wen, S.-L. Sun, B.-L. Xue and R.-C. Sun. *Materials.* 2013,**6**,359-391.