

Electronic Supplementary Information

Dissolution, regeneration and characterisation of formic acid and Alcell lignin in ionic liquid-based systems

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Three phenylpropanoid monomers of lignin

Lignin is rich in benzene rings, and the lignin aromatic moieties can be classified into three types: syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) units.

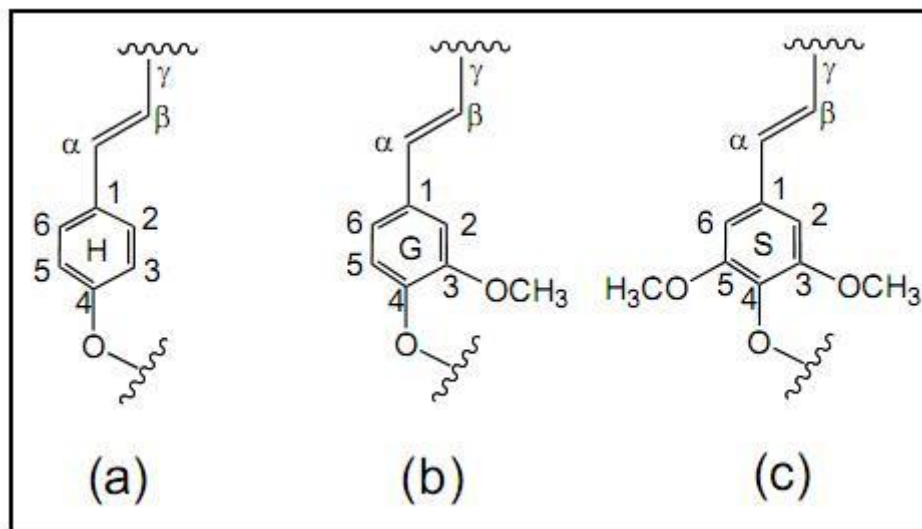


Fig. S1 Schematic of various lignin components (a) H-type lignin, (b) G-type lignin and (c) S-type lignin.

Ionic liquids (ILs)

ILs used in this study including 1-butyl-3-methylimidazolium chloride ([bmim]Cl), 1-ethyl-3-methylimidazolium acetate ([emim][OAc]), 1-butyl-3-methylimidazolium hydrogen sulfate ([bmim][HSO₄]), and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]).

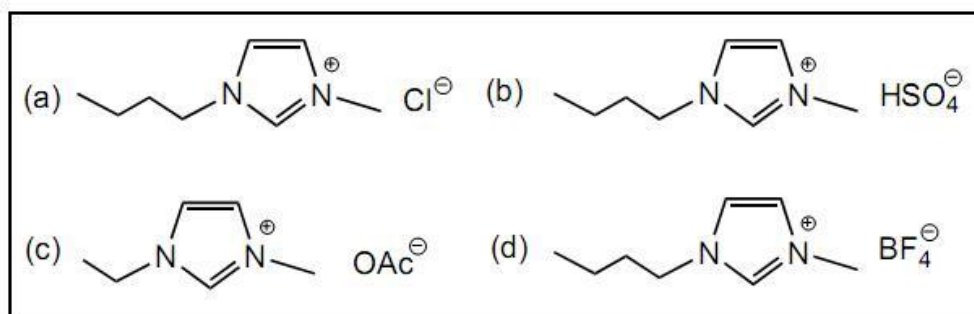


Fig. S2 Ionic liquids used in the experiments (a) [bmim]Cl; (b) [bmim][HSO₄]; (c) [emim][OAc]; and (d) [bmim][BF₄].

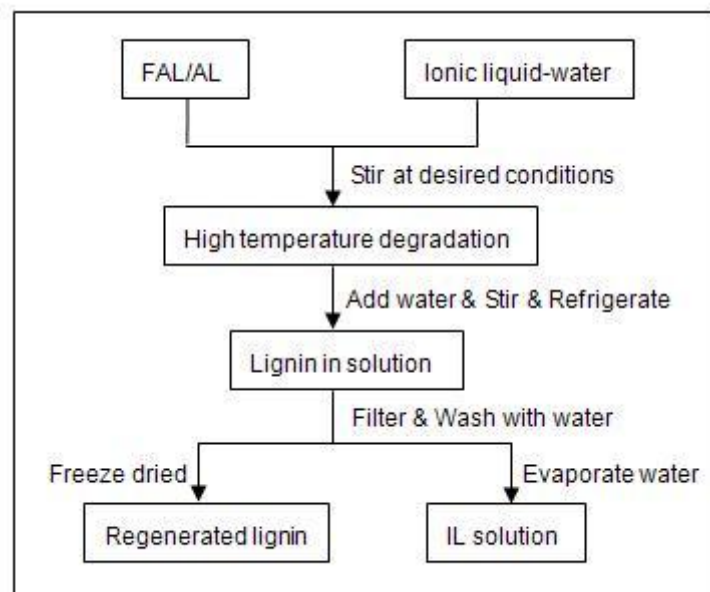


Fig. S3 The procedure for lignin dissolved in ILs-water systems with water as precipitating solvent.

Lignin was precipitated in two parts: first part, lignin regenerated with different proportions of ethanol-water mixtures; second part, lignin regenerated with water.

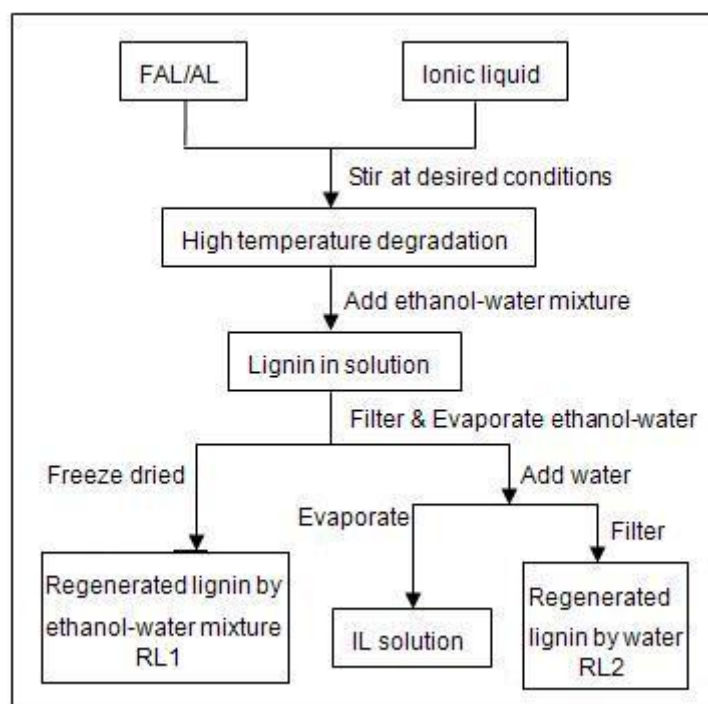


Fig. S4 The procedure for lignin successively regenerated in ethanol-water mixture (RL1) and water (RL2).

Molecular weight distribution of the FAL, AL and Re-lignin

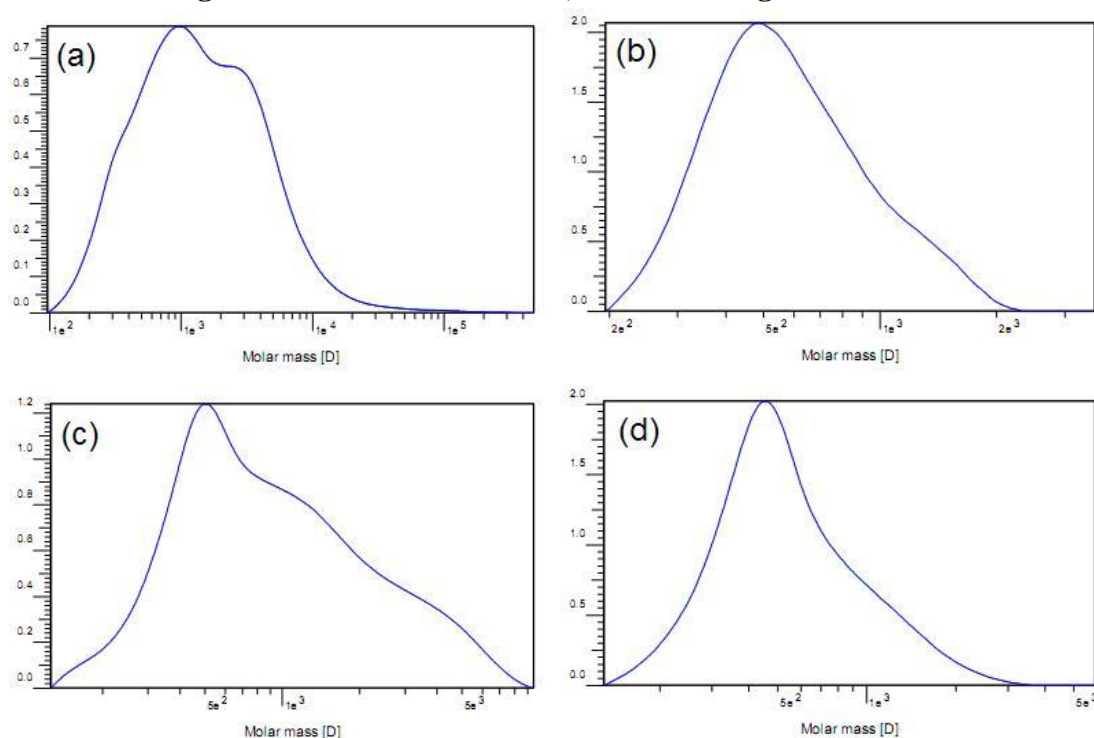


Fig. S5 Molecular weight distribution of lignin: (a) original bamboo lignin (FAL); (b) Re-lignin (entry 7, 180 °C); (c) original eucalyptus lignin (AL); and (d) Re-lignin (entry 20, 180 °C).

FT-IR analysis

Fig. S6 shows the FT-IR spectra of original lignin and regenerated lignin from bamboo and eucalyptus. A number of bands were used to monitor the chemical changes that occurred in lignin regeneration process. Generally, the main differences of the lignin existed at wave numbers lower than 1900 cm^{-1} . As shown in Fig. S6a, the raw bamboo lignin fraction (FAL, curve d) exhibited a wide and high absorption band at 1720 cm^{-1} , which is assigned to C=O stretching of unconjugated ketone, carbonyl, and ester groups. The reduced signals of this band in curves a, b, and c indicated that the lignin structure changed after ILs dissolving and regeneration process at $120\text{--}180\text{ °C}$. The C=O groups might disappear or might also react at the C2 position of the imidazolium in ILs.^{2,3} The water regenerated lignin (curves 4 and 7) showed shifted peaks (1731 and 1561 cm^{-1}) as compared to the FAL fraction (1720 and 1591 cm^{-1}). It is probably related to the influence of some groups formed in this process, which could affect the infrared absorption. The peaks at 1591 , 1507 , and 835 cm^{-1} are assigned to the characteristic stretching of structural benzene ring in lignin.⁴ The absorption bands at 1458 and 1421 cm^{-1} corresponds to the vibration of the asymmetric bending in C-H deformation of methyl and methylene groups and aromatic skeletal vibrations combined with C-H in-plane deformation; the S unit breathing with C=O stretching and G rings breathing with carbonyl stretching appears at 1323 and 1262 cm^{-1} , respectively. The spectrum of Re-lignin at 180 °C (curve b) shows a relatively high absorption band at 1262 cm^{-1} as compared with the other

spectra, indicating more condensed G unit existed in the regenerated lignin. The wide bands at 1217 and 1116 cm^{-1} are due to the C-C, C-O, and C=O stretching and aromatic C-H deformation in S ring, respectively. The presence of a small band at 1168 cm^{-1} in all spectra is typical of the *p*-hydroxyphenyl structures of bamboo lignin. In addition, the absorption bands at 1030 and 853 cm^{-1} are considered to be the aromatic C-H in-plane and out-of-plane deformation of aromatic rings, respectively. All these bands indicated that the Re-lignin displayed a similar infrared absorption bands as that of original lignin. It is believed that all the lignin fractions are GSH-type lignin, while the different characteristic absorptions probably occurred in the side chain of lignin.

The FT-IR spectra of AL fractions regenerated from ILs are shown in Fig. S6b. The characteristic absorbance for aromatic skeleton vibration observed was relatively weak in Re-lignin obtained at 180 °C (curve e), indicating that the lignin experienced a large content of decomposition during dissolving and regeneration process. The band at 1700 cm^{-1} corresponds to conjugated carbonyl groups, while this band seems almost disappeared in curves e and f. It can be concluded that high reaction temperature could decrease the content of conjugated carbonyl groups and increase the unconjugated carbonyl groups during the IL dissolving process. Different S : G ratios has been reported in hardwood and dicotyl crops. As illustrated in Fig. S6b, the intensive ratio of 1510 to 1459 cm^{-1} decreased from curves h to g, to f, and to e, indicating that less content of S-type lignin produced as the reaction temperature increased in the [emim][OAc] solution. In addition, the band corresponding to the vibration of aromatic C-H and C-O in aliphatic alcohols, at 1028 cm^{-1} , is more intensive in original lignin (curve h) than in lignin (curves g, f, and e) regenerated in [emim][OAc]. This may be owing to the higher amount of aromatic C-H in guaiacyl rings, with three free positions in the ring, than in syringyl rings, with only two free positions.

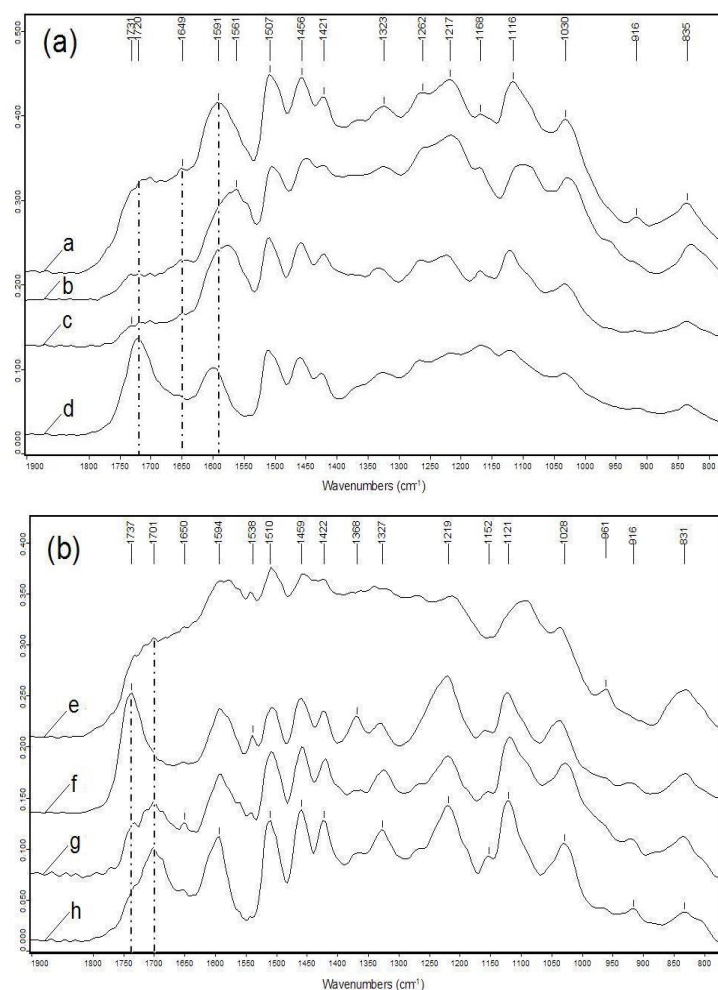


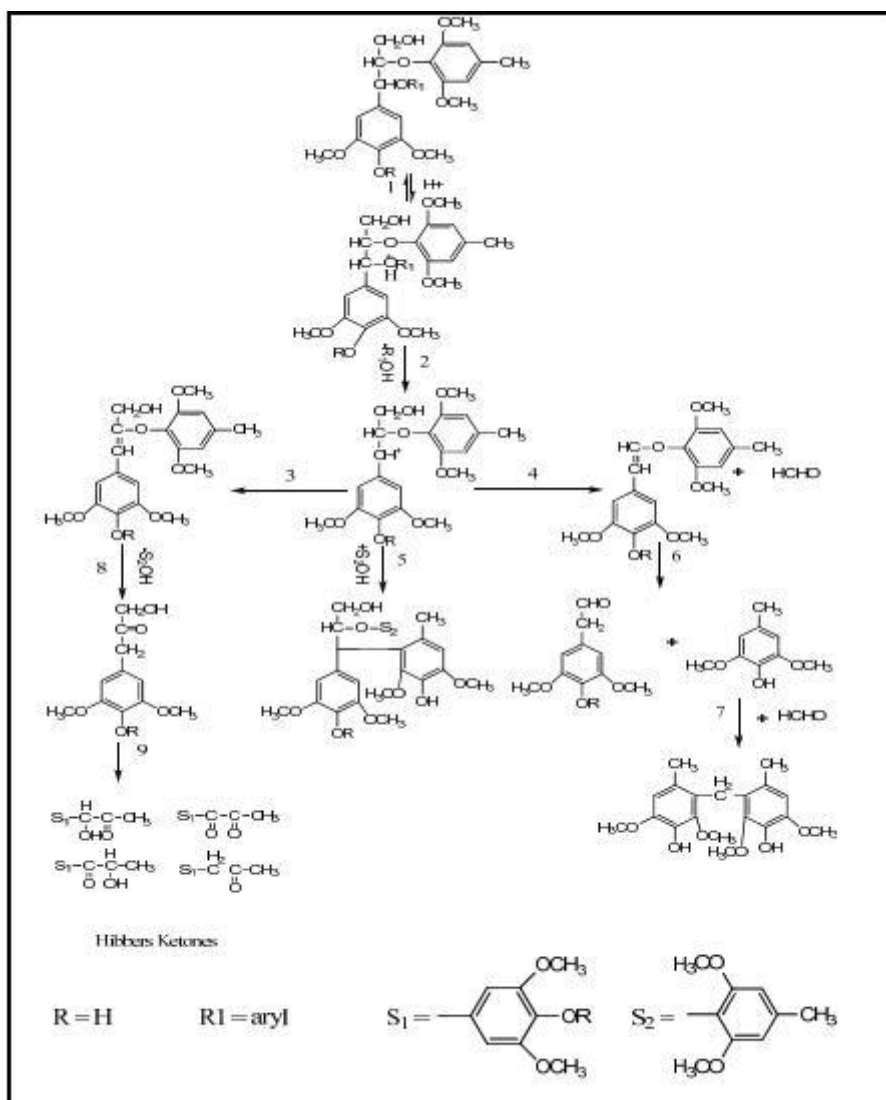
Fig. S6 FT-IR spectra of (a): curves of a, b, c, and d represent the lignin of entries 4, 7, 9, and original bamboo lignin (FAL), respectively. (b) curves of e, f, g, and h represent the lignin of entries 20, 19, 17, and original eucalyptus lignin (AL) respectively as shown in Table 1.

Table S1 The molecular weight of the THF-soluble compound and the regenerated lignin after treated with [emim][OAc]-water mixtures, corresponding to the lignin in Fig. 3.

Treatment condition	Lignin	Molecular weight					
		THF-soluble lignin in ILs ^b			Regenerated lignin		
		M_w	M_n	PI	M_w	M_n	PI
IL-water	FAL	560	490	1.14	880	660	1.33
5% [emim][OAc]:H ₂ O	FAL	570	490	1.16	860	650	1.32
15% [emim][OAc]:H ₂ O	FAL	600	510	1.17	670	550	1.22
35% [emim][OAc]:H ₂ O	FAL	580	500	1.16	630	510	1.24
50% [emim][OAc]:H ₂ O	FAL	790	580	1.37	680	540	1.26
65% [emim][OAc]:H ₂ O	FAL	650	530	1.23	860	530	1.62
85% [emim][OAc]:H ₂ O	FAL	580	520	1.12	970	680	1.43
100% [emim][OAc]	FAL						

Table S2 Assignment of main lignin ^1H - ^{13}C cross-signals in the HSQC spectra of the lignin fractions.

Labels	$\delta_{\text{H}}/\delta_{\text{C}}$ (ppm)	Assignment
D_{β}	2.85/	$\text{H}_{\beta}\text{-C}_{\beta}$ in β -1' (spirodienone) substructures (D)
B_{β}	3.06/53.4	$\text{H}_{\beta}\text{-C}_{\beta}$ in β - β' (resinol) substructures (B)
C_{β}	3.48/53.2	$\text{H}_{\beta}\text{-C}_{\beta}$ in β -5' (phenylcoumaran) substructures (C)
-OMe	3.73/55.6	H-C in methoxyls
A_{γ}	3.40/3.71/60.1	$\text{H}_{\gamma}\text{-C}_{\gamma}$ in β -O-4' substructures (A)
$(\text{A}', \text{A}'')_{\gamma}$	4.10/63.5	$\text{H}_{\gamma}\text{-C}_{\gamma}$ in γ -acetylated β -O-4' substructures (A' / A'')
B_{γ}	4.17/71.6 and 3.80/71.6	$\text{H}_{\gamma}\text{-C}_{\gamma}$ in β - β' (resinol) substructures (B)
A_{α}	4.87/71.8	$\text{H}_{\alpha}\text{-C}_{\alpha}$ in β -O-4' substructures linked to a S unit (A/A'/A'')
C_{γ}	3.42/63.0	$\text{H}_{\gamma}\text{-C}_{\gamma}$ in β -5' (phenylcoumaran) substructures (C)
I_{γ}	4.09/61.2	$\text{H}_{\gamma}\text{-C}_{\gamma}$ in <i>p</i> -hydroxycinnamyl alcohol end groups (I)
B_{α}	4.65/84.9	$\text{H}_{\alpha}\text{-C}_{\alpha}$ in β - β' (resinol) substructures (B)
$\text{A}_{\beta(\text{S})}$	4.12/85.7	$\text{H}_{\beta}\text{-C}_{\beta}$ in β -O-4' substructures linked to a S unit (A)
$\text{A}_{\beta(\text{G/H})}$	4.31/83.3	$\text{H}_{\beta}\text{-C}_{\beta}$ in β -O-4' substructures linked to a G and H units (A)
D_{α}	4.76/81.4	$\text{H}_{\alpha}\text{-C}_{\alpha}$ in β -1' (spirodienone) substructures (D)
C_{α}	5.48/86.7	$\text{H}_{\alpha}\text{-C}_{\alpha}$ in β -5' (phenylcoumaran) substructures (C)
PCE_8	6.26/113.6	$\text{H}_8\text{-C}_8$ in <i>p</i> -coumarate (PCE)
$\text{S}_{2,6}$	6.66/103.7 and 6.47/106.7	$\text{H}_{2,6}\text{-C}_{2,6}$ in syringyl units (S)
$\text{S}'_{2,6}$	7.31/106.2	$\text{H}_{2,6}\text{-C}_{2,6}$ in C_{α} -oxidized ($\text{C}_{\alpha}=\text{O}$) phenolic syringyl units (S')
G_2	6.93/110.3	$\text{H}_2\text{-C}_2$ in guaiacyl units (G)
G_5	6.68/114.9	$\text{H}_5\text{-C}_5$ in guaiacyl units (G)
G_6	6.78/118.4	$\text{H}_6\text{-C}_6$ in guaiacyl units (G)
$\text{H}_{2,6}$	6.98/130.2 and 6.92/128.1	$\text{H}_{2,6}\text{-C}_{2,6}$ in <i>p</i> -hydroxyphenyl units (H)
I_{α}	6.33/130.2	$\text{H}_{\alpha}\text{-C}_{\alpha}$ in <i>p</i> -hydroxycinnamyl alcohol end groups (I)
$\text{PCE}_{3,5}$	7.11/122.9	$\text{H}_{3,5}\text{-C}_{3,5}$ in <i>p</i> -coumarate (PCE)
$\text{PCE}_{2,6}$	7.49/129.9	$\text{H}_{2,6}\text{-C}_{2,6}$ in <i>p</i> -coumarate (PCE)



Scheme S1 Chemical degradation of β -O-4' linkage under acidic conditions.⁴

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