

Table S1 Alkaline lignin oxidation products in MeOH and its DES system

No.Product	Structure	Content(%) in different system			
		MeOH	MeOH-ChCl 1:1	MeOH-ChCl 4:1	MeOH-ChCl 8:1
1 Methyl formate	-	2.44	-	-	18.59
2 Methyl acetate	-	6.68	13.74	-	-
3 4-Methyl-3-Heptanone	-	14.97	-	-	-
4 2-Methyl-3-Pentanone	-	1.46	-	-	-
5 Methyl 2-Methylbutyrate	-	1.98	-	-	-
10 Glycolic acid	-	3.49	-	-	-
11 Cyclopentanone	-	0.78	-	-	-
12 1,3,5-Trioxane	-	0.66	-	-	-
13 Dimethyl sulfone	-	0.63	-	-	-
14 3-Tetrahydrofuranmethanol	-	-	-	-	0.96
15 Dimethyl oxalate	-	-	-	0.66	1.53
16 Acetic acid	-	31.41	36.35	16.36	26.51
17 Formic acid	-	-	-	4.26	3.47
18 Dimethyl sulfoxide	-	-	14.07	58.01	32.35
19 1,2-ethanediol	-	-	3.95	3.06	1.16
20 Guaiacol	G	3.53	5.40	2.75	2.40
21 Dimethyl sulfone	-	-	-	1.32	-
22 3-(2-furyl)-3-Penten-2-one	-	0.52	-	-	-
23 1,5-Dihydroxynaphthalene	-	0.50	-	-	-
24 4-Vinyl-2-Methoxy-Phenol	G-CH=CH ₂	0.70	2.04	-	-
25 2,4-Di-Tert-Butylphenol	(CH ₃) ₃ C-H-C(CH ₃) ₃	0.52	-	-	-
26 2,3-Dihydrobenzofuran	-	0.44	-	-	-
27 Phenol	H	2.12	-	-	-
28 2-Coumaranone	-	5.96	-	-	-
29 Vanillin	G-CHO	12.12	13.88	6.24	8.74
30 Vanillic acid	G-COOH	-	2.23	-	-
31 Vanillic acid methyl ester	G-COOCH ₃	1.69	-	3.56	2.97
32 Acetovanillone	G-COCH ₃	1.65	2.08	1.27	1.33
4-Hydroxy-3-	G-CH ₂ COCH ₃	-	-	1.07	-
33 Methoxypropiophenone		0.42	-	-	-
34 6-Methoxycoumarin-7-Ol-3-One -		0.49	-	-	-
2,5-Dicyclopentenyl-	-	-	-	-	-
35 Cyclopentanone		0.65	-	-	-
36 P-Hydroxybenzaldehyde	H-CHO	0.65	-	-	-
4-Hydroxy-3-Methoxy-	G-CH ₂ CH ₂ CH ₂ OH	3.54	6.25	1.44	-
37 Phenylpropanol		-	-	-	-

G, guaiacyl; H, p-hydroxyphenyl

Table S2 Nuclear magnetic resonance assignment of different lignin

Label	$\delta_{\text{C}}/\delta_{\text{H}}$ (ppm) ^a	$\delta_{\text{C}}/\delta_{\text{H}}$ (ppm) ^b	$\delta_{\text{C}}/\delta_{\text{H}}$ (ppm) ^c	$\delta_{\text{C}}/\delta_{\text{H}}$ (ppm) ^d	$\delta_{\text{C}}/\delta_{\text{H}}$ (ppm) ^e	Assignment
IC _B	48.94/3.18	-	-	-	55.66/3.41	C _B -H _B in phenylcoumaran substructures (IC)
B _B	-	49.05/3.17	49.06/3.18	48.79/3.13	-	C _B -H _B in β-β (resinol) substructures (B)
B _B	-	53.63/3.1	53.66/3.11	53.54/3.16	53.58/3.13	C _B -H _B in β-β (resinol) substructures (B)
B _B	-	-	-	56.39/3.11	57.70/4.55	C _B -H _B in β-β (resinol) substructures (B)
OMe	-	55.96/3.83	-	55.58/3.83	-	C-H in methyl's (OMe)
OMe	-	-	-	55.62/3.46	-	C-H in methyl's (OMe)
A _γ	60.42/3.6	-	-	-	55.59/3.83	C _γ -H _γ in β-O-4 substructure (A)
A' _γ	-	-	67.87/4.15	67.35/3.84	-	C _γ -H _γ in γ-hydroxylated β-O-4 substructures (A')
IC _γ	-	63.23/3.39	66.81/3.57	67.34/3.47	64.01/3.73	C _γ -H _γ in phenylcoumaran substructures (IC)
B _γ	-	70.27/3.51	70.27/3.52	-	67.38/3.84	C _γ -H _γ in β-β (resinol) substructures (B)
B _γ	-	-	-	-	67.39/3.42	C _γ -H _γ in β-β (resinol) substructures (B)
B _α	84.59/4.27	-	-	-	-	C _α -H _α in β-β (resinol) substructures (B)
A _α	71.64/4.75	-	-	-	-	C _α -H _α in β-O-4 substructures linked to a G (A)
A _β (S)	85.6/4.62	-	-	89.69/4.49	-	C _β -H _β in β-O-4 substructures linked to a S (A)
)						
IC _a	87.24/5.46	-	-	-	-	C _a -H _a in phenylcoumaran substructures (IC)
G' ₂	111.19/7.4	-	-	-	-	C ₂ -H ₂ in guaiacyl units (G)
G ₅	-	-	-	-	116.1/6.83	C ₅ -H ₅ in guaiacyl units (G)
G ₆	119.5/6.76	-	-	-	-	C ₆ -H ₆ in guaiacyl units (G)
S' _{2,6}	-	-	-	-	104.84/7.33	C _{2,6} -H _{2,6} , C(α)=O in syringyl units (S')
H _{2,6}	126.6/7.42	-	-	-	-	C _{2,6} -H _{2,6} in p-hydroxyphenyl units (H)
pCA _{2,6}	-	-	129.38/7.72	-	130.87/7.56	C _{2,6} -H _{2,6} in p-coumarate (pCA)
F' _B	126.18/6.96	-	-	-	-	C _B -H _B in cinnamaldehyde end groups (F)

a: Alkaline lignin

b: Solid residuals after alkaline lignin oxidation

c: Regenerated solid derived from dissolved lignin

d: Liquid fraction of alkaline lignin oxidation

e: DES-lignin