Supporting information for:

Cleavage of ethers and demethylation of lignin in acidic concentrated lithium bromide (ACLB) Solution

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Table S1 Effect of acid concentration, temperature, and time on demethylation of creosol in the ACLB system

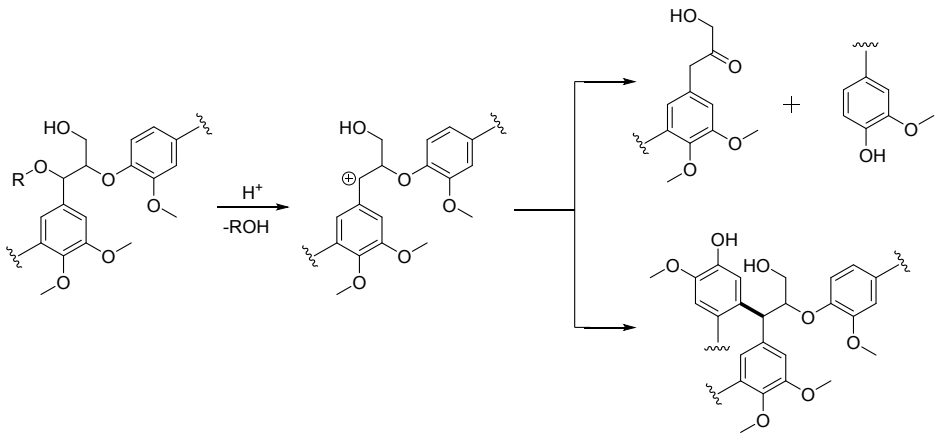
Entry	System	T (°C)	T (h)	Creosol conversion (%)	4-Methylcatechol Yield (%)
1	12 wt% HBr	r.t.	20	0	0
2	12 wt% HBr	r.t.	48	<5%	0
3	3 wt% HBr	80	3	<5%	0
4	4.8% wt% HBr	90	4	83	71
5	6 wt% HBr	100	2	98	81
6	6 wt% HBr	100	4	100	83

Reaction conditions: 0.1 g creosol, 6.1 g LiBr, and 3.9 g water.

Table S2 [1]H-NMR and GPC analysis of demethylated organosolv ethanol poplar lignin (EPL) [a]

Entry	Temperature (°C)	Time (h)	LiBr (wt%)	OMe (mmol/g)	ArOH (mmol/g)	AlkOH (mmol/g)	M_n	M_w	PDI
1	Original	Original	61	7.87	3.65	3.97	1080	2500	2.31
2	100	4	53	2.19	8.27	5.10	1620	2840	1.76
3[a]	100	4	0	1.27	5.09	5.82	1630	2960	1.82
4	50	4	53	7.32	4.07	5.14	1050	1450	1.38
5	75	4	53	5.06	6.35	5.37	1270	1930	1.52
6	120	4	53	1.63	8.54	6.20	1650	3140	1.90
7	100	8	53	1.12	8.11	6.84	1670	2920	1.75
8	100	24	53	0.542	6.55	4.88	1600	2750	1.72
9[b]	100	4	30	7.79	4.79	3.67	1330	2320	1.75
10[b]	100	4	40	6.45	5.42	4.77	1300	2210	1.70
11[b]	100	4	47	3.76	7.43	5.73	1600	2770	1.73
12[b]	100	4	61	1.38	8.38	6.52	1670	2830	1.70

All reactions and NMR tests are conducted in duplicates except for Entry 1 and 2 (triplicates) and 9-12 (single). Reaction conditions: 0.5 g EPL, 6.1 g LiBr, 3.9 mL water, and 1 mL 48% HBr. a: 7.75 mL (11.5 g) 48% HBr. b: 10 g aqueous LiBr with different concentrations, 1 mL 48% HBr.



Scheme S1 Competition between the depolymerization by cleaving β-O-4 structure and the repolymerization via the condensation between the α-carbocation and a reactive aromatic carbon [1].

Table S3 Effect of co-solvent on demethylation of ethanol poplar lignin in the ACLB system

Entry	Co-solvent	OMe (mmol/g)	ArOH (mmol/g)	AlkOH (mmol/g)	M_n	M_w	PDI
1	Original lignin	7.87	3.65	3.97	1080	2500	2.31
2	None	2.19	8.27	5.10	1620	2840	1.76
3	Acetic acid	1.43	7.61	6.11	1410	2860	2.03
4	Ethanol	6.58[a]	5.18	2.67	1280	2100	1.65
5	Acetone	1.90	7.25	4.36	1530	2780	1.83

Reaction conditions: 0.5 g EPL, 6.1 g LiBr, 3.9 g solvent (absolute water or 3.4 g water and 0.5 g co-solvent), 1 mL 48 wt% HBr, 100 °C, and 4 h. a: the signals of OMe and OEt are supposed to be overlapped from 4.1 to 3.1 ppm.

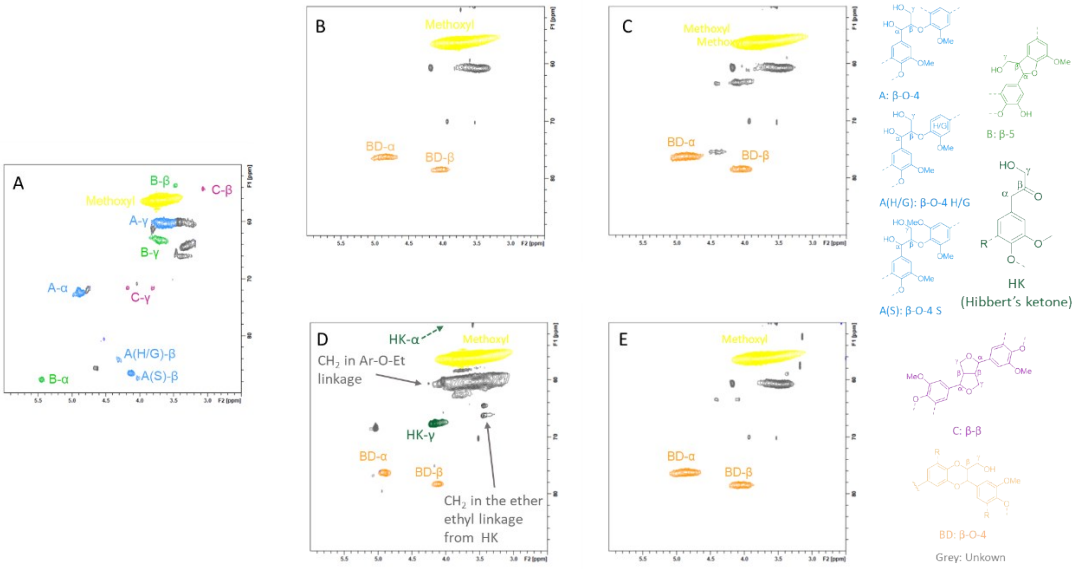


Figure S1 Aliphatic region of the HSQC spectra of original and demethylated EPL in DMSO-d6. A: original EPL; B: demethylated EPL in the ACLB without co-solvents; C: demethylated EPL in the ACLB with acetic acid; D: demethylated EPL in the ACLB with ethanol; E: demethylated EPL in the ACLB with acetone. Reaction conditions: 0.5 g lignin, 6.1 g LiBr, 3.9 g solvent (absolute water or water and 0.5 g co-solvent), 1 mL HBr, 100 °C, and 4 h.

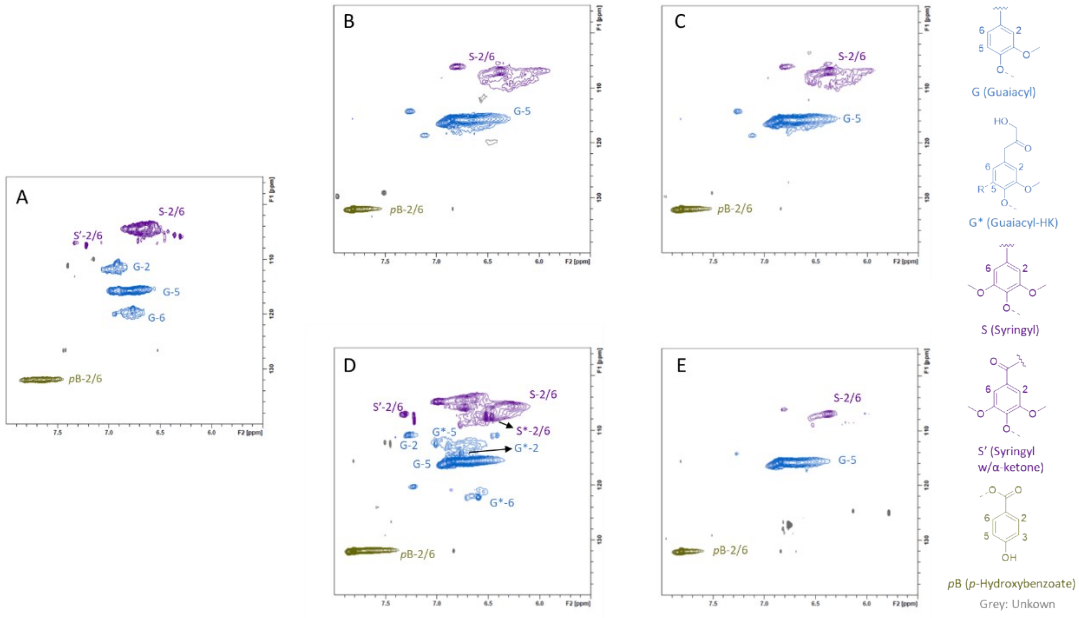


Figure S2 Aromatic region of the HSQC spectra of original and demethylated EPL in DMSO-d6. A: original EPL; B: demethylated EPL in the ACLB without co-solvents; C: demethylated EPL in the ACLB with acetic acid; D: demethylated EPL in the ACLB with ethanol; E: demethylated EPL in the ACLB with acetone. Reaction conditions: 0.5 g lignin, 6.1 g LiBr, 3.9 g solvent (absolute water or water and 0.5 g co-solvent), 1 mL HBr, 100 °C, and 4 h.

Table S4 Detailed ^{1}H NMR and GPC results of the four typical lignin samples[a]

Lignin	Status	OMe (mmol/g)	ArOH (mmol/g)	AlkOH (mmol/g)	M_n	M_w	PDI
HKL	Original	7.56 (0.698)	5.05 (0.463)	4.06 (0.259)	850	1150	1.35
	Demethylated	1.36 (0.279)	7.40 (1.74)	4.58 (1.23)	1330	2300	1.73
CSL	Original	4.50 (0.378)	2.85 (0.286)	2.53 (0.195)	630	1090	1.72
	Demethylated	1.39 (0.204)	4.13 (0.522)	2.58 (0.313)	1370	3080	2.25
ELPPL	Original	5.76 (0.401)	3.23 (0.148)	4.70 (0.130)	1170	3200	2.73
	Demethylated	1.01 (0.403)	4.00 (1.06)	3.33 (0.762)	1600	4810	3.00
EPL	Original	7.87 (0.670)	3.65 (0.354)	3.97 (0.397)	1080	2500	2.31
	Demethylated	2.19 (0.455)	8.27 (0.225)	5.10 (0.693)	1620	2840	1.76

a: All reactions and NMR tests were conducted in triplicate. The standard deviations are listed in the brackets. Reaction conditions: 0.5 g lignin, 6.1 g LiBr, 3.9 mL water, and 1 mL 48% HBr, 100 °C, and 4 h.

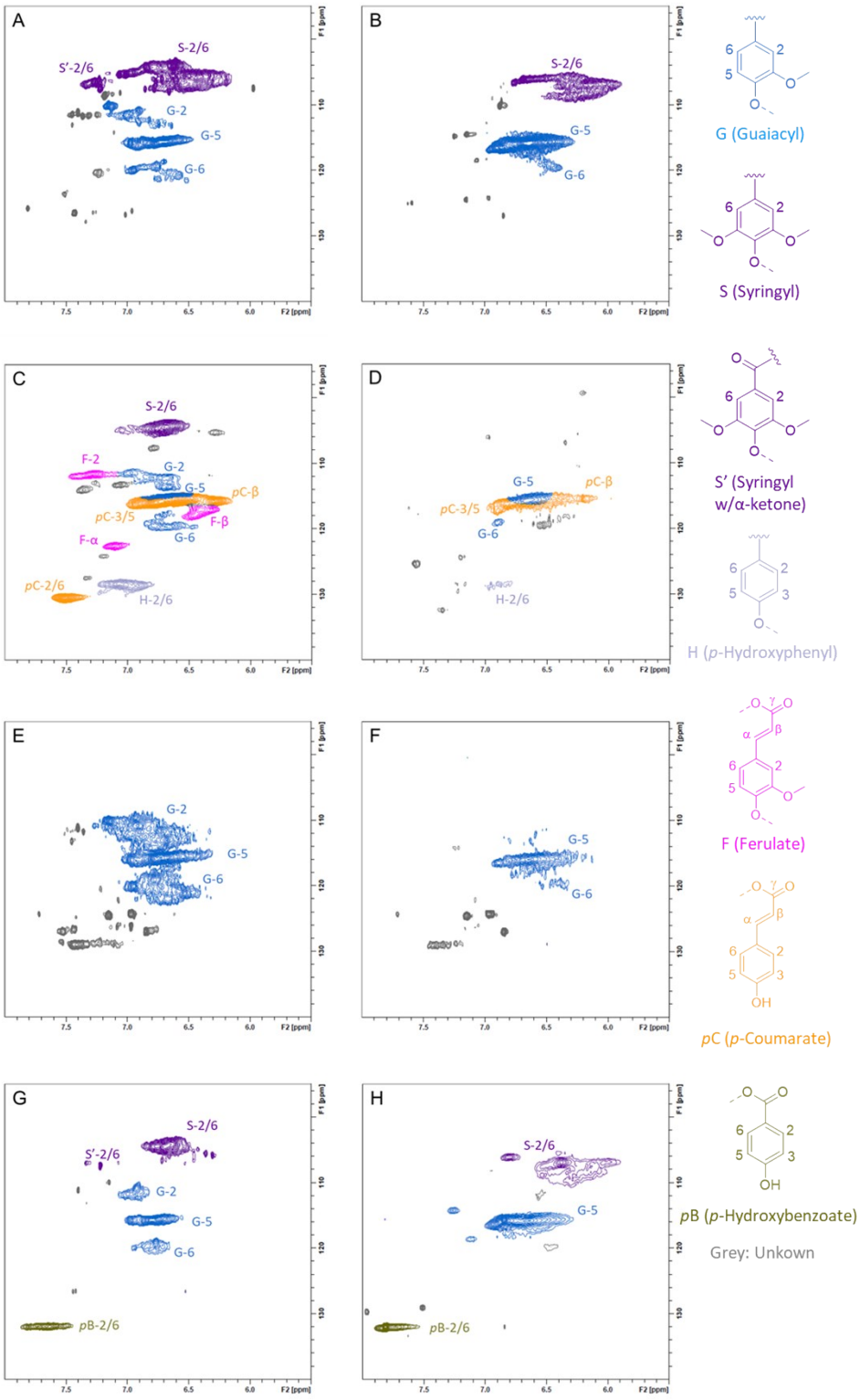


Figure S3 Aromatic region of the HSQC spectra of original and demethylated lignin samples in DMSO-d6. A: original HKL; B: demethylated HKL; C: original CSL; D: demethylated CSL; E: original ELPPL; F: demethylated ELPPL; G: original EPL; H: demethylated EPL. Reaction conditions: 0.5 g lignin, 6.1 g LiBr, 3.9 g water, 1 mL HBr, 100 °C, and 4 h.

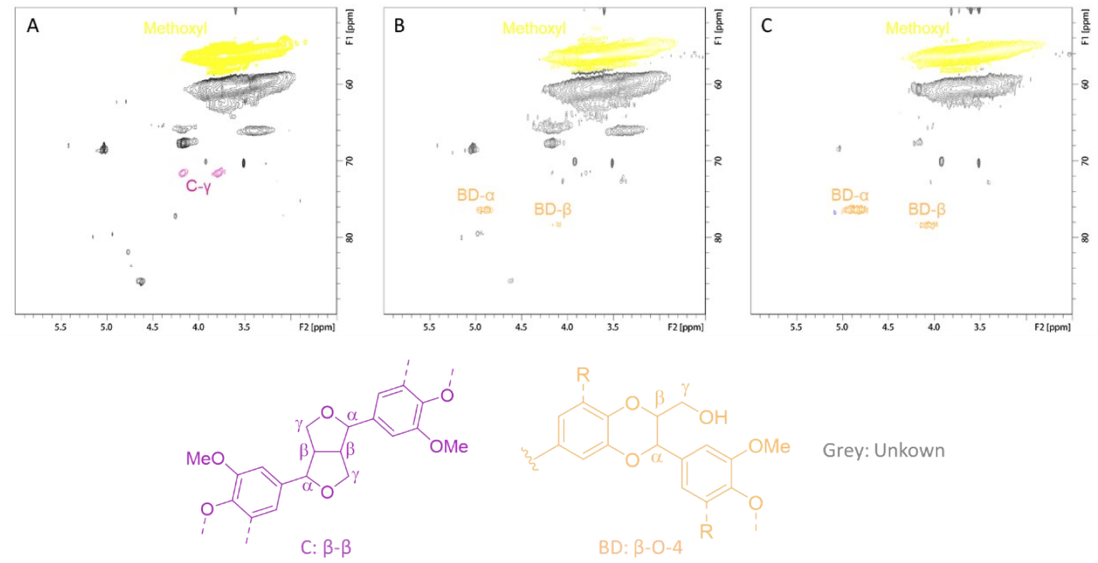


Figure S4 Aliphatic region of the HSQC spectra of the demethylated EPL in the ACLB with different concentrations of LiBr (A: 30% LiBr; B: 40% LiBr; C: 47% LiBr). The solvent was in DMSO-d6. Reaction conditions: 0.5 g lignin, 10 g aqueous LiBr with different concentrations, 1 mL HBr, 100 ℃, and 4 h.

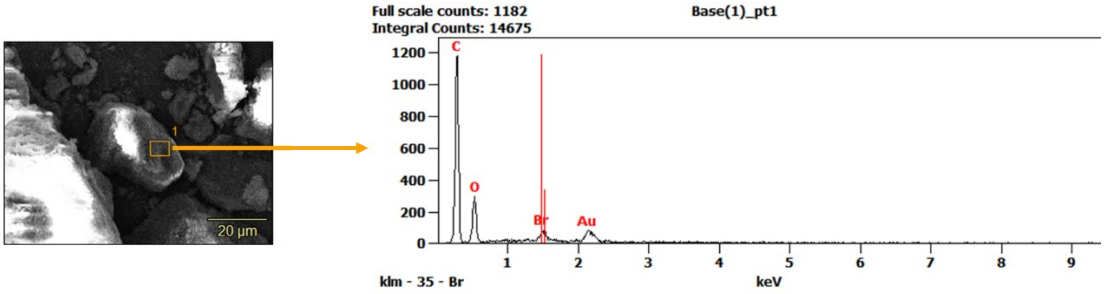


Figure S5 SEM-EDS spectrum of demethylated EPL.

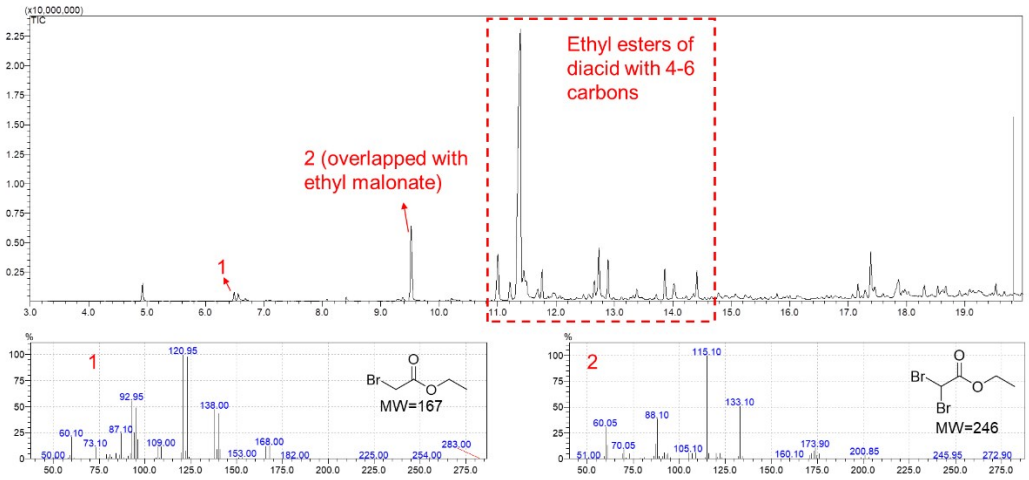


Figure S6 GC-MS spectrum of the esterified oxidation mixture of demethylated EPL. Reaction conditions: 0.4 g water-washed demethylated lignin, 5 mL H_2SO_4 (3 mol/L), 5 mL 30% H_2O_2, 100 °C, 4 h 40 min. The reaction mixture was diluted with 50 mL ethanol, dehydrated over 12.78 g Na_2SO_4, and then esterified at 60 °C overnight.

References

1. J. Li, G. Henriksson and G. Gellerstedt, *Bioresour Technol*, 2007, **98**, 3061-3068.