Supporting Information

Towards Understanding of Delignification of Grassy and Woody Biomass in Cholinium-based Ionic Liquids

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Table S1: Densities (ρ) of different Ionic liquids obtained from MD Simulations and compared with experimental density.

Ionic Liquid	IL molecules	Simulation box length (Å)			ρ_{exp} (g/cc)	ρ_{MD} (g/cc)	Error (%)
		X	Y	Z			
[Ch][For]	300	40.27	40.27	40.27	-	1.138	-
[Ch][Ace]	300	42.21	42.21	42.21	1.10	1.081	1.73
[Ch][But]	300	45.04	45.04	45.04	1.07	1.043	2.52
[Ch][Hex]	300	47.85	47.85	47.85	1.02	0.997	2.25
[Ch][Oct]	300	50.27	50.27	50.27	-	0.970	-
[Ch][Lys]	300	48.90	48.90	48.90	1.09	1.062	2.57

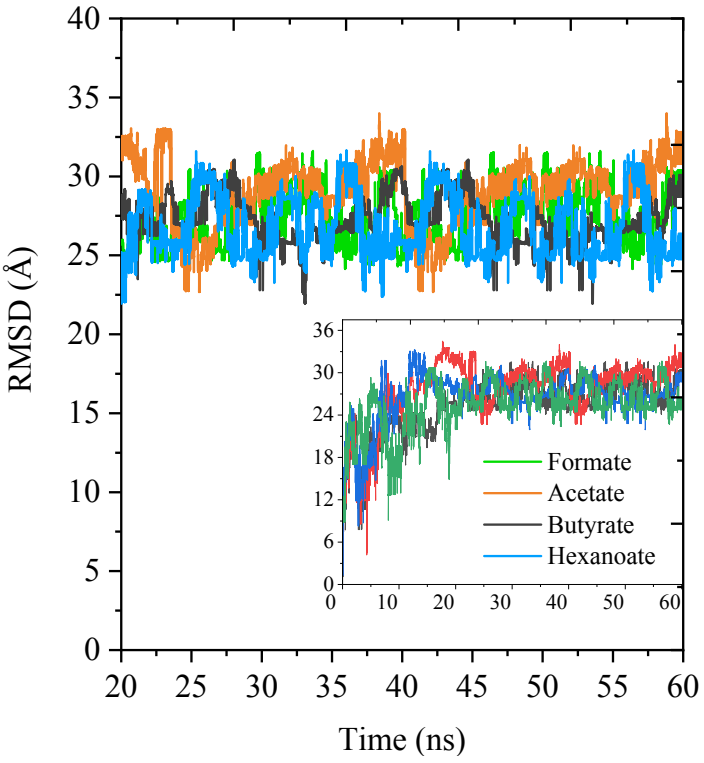


Figure S1: Root mean square deviation (RMSD) of Lignin as a function of MD simulation time step (in ns) for different Lignin-IL systems at 363.15 K

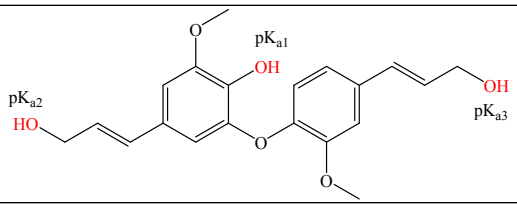
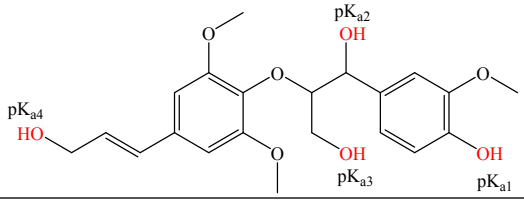
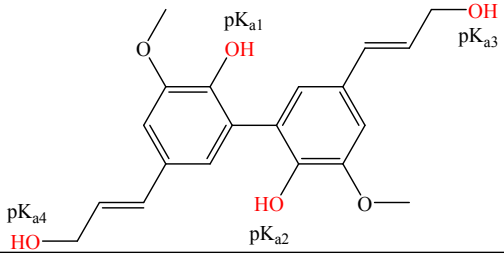
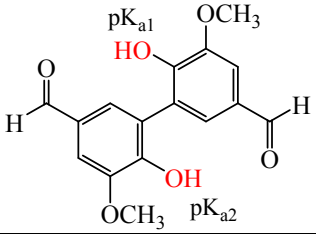
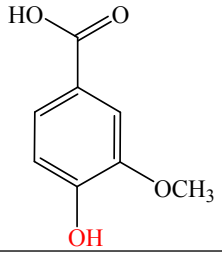
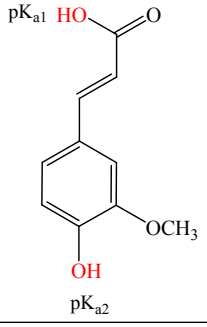
Table S2: Outline of investigated systems (different lignin linkage in [Ch][Lys]) in This Study.

Lignin	[Ch][Lys] molecules	Lignin molecules	Simulation box length (Å)			Density (g/cc)
			X	Y	Z	
4–O–5	300	30	50.96	50.96	50.96	1.0733
β–O–4	300	30	51.16	51.16	51.16	1.0788
5–5	300	30	51.02	51.02	51.02	1.0696

Table S3: MD predicted interaction energies between anion and cation in lignin 4–O–5/IL systems obtained from MD simulations.

IL-lignin system	Anion – Cation Interactions (kcal/mol)		
	E_{elec}	E_{vdW}	E_{total}
[Ch][For]	-408.69	3.10	-405.59
[Ch][Ace]	-367.05	1.14	-365.90
[Ch][But]	-323.14	-1.13	-324.27
[Ch][Hex]	-299.33	-1.95	-301.27
[Ch][Oct]	-285.77	-2.46	-288.23
[Ch][Lys]	-282.68	-2.34	-285.02

Table S4: Dissociation constant (pK_a) and experimental solubility of lignin in cholinium-based ILs.

Lignin/IL	Structure	pK_a	Lignin solubility
Lignin 4–O–5		pK_{a1} – 9.06 pK_{a2} – 15.32 pK_{a3} – 15.92	
Lignin β–O–4		pK_{a1} – 9.91 pK_{a2} – 13.44 pK_{a3} – 14.65 pK_{a4} – 15.67	
Lignin 5–5		pK_{a1} = 9.21 pK_{a2} = 13.75 pK_{a3} = 15.33 pK_{a4} = 15.93	
Bivanillin 5–5 linkage		pKa_1: 7.04 pKa_2: 11.59	
Vanillic acid		pKa_1: 4.16 pKa_2: 10.14	
Ferulic acid		pKa_1: 3.58 pKa_2: 9.98	

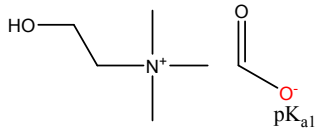
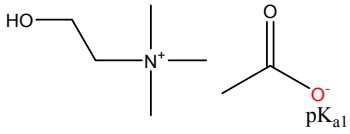
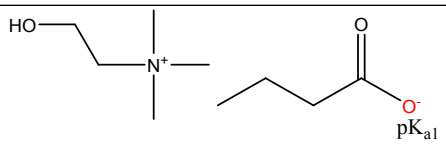
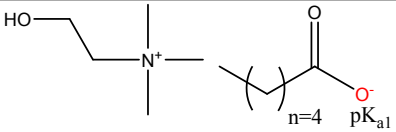
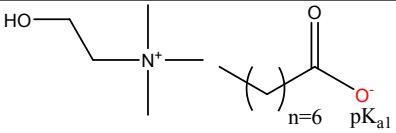
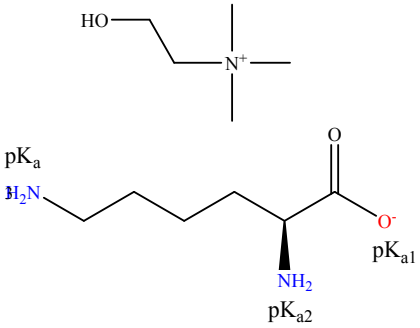
[Ch][For]		pK_{a1} = 4.27	28.3 g/mol; 45%
[Ch][Ace]		pK_{a1} = 4.76	31.0 g/mol
[Ch][But]		pK_{a1} = 4.91	32.5 g/mol
[Ch][Hex]		pK_{a1} = 5.09	37.2 g/mol
[Ch][Oct]		pK_{a1} = 5.19	39.5 g/mol; 52%
[Ch][Lys]		pK_{a1} = 2.74 pK_{a2} = 9.44 pK_{a3} = 10.29	77%

Table S5. Lignin dissolution in lysinate-based ionic liquids[a]

IL Type	IL	I.E.[b] (kcal mol^{-1})	Lignin removal (%)
Basic	[Ch][Lys]	-132.72	69.3[c], 85.1[d]
Basic	[C_2mim][Lys]	-123.25	80.3[c], 86.6[d]
Acidic	[Ch][Ace]	-139.73	17[c], 50.2[d]
Acidic	[C_2mim][Ace]	-134.28	16.5[c], 48.9[d]

[a] Data taken from Sun et al. (2014)[1]; [b] QC-based Interaction energies of dilignol-IL complexes; [c] at 90 °C/5 h; and [d] at 140 °C/1 h.

Table S6. Properties influencing lignin dissolution in ionic liquids

Ionic liquids		pK_a	Density[a]	Viscosity[b]
Name	Abbreviations			
Cholinium lysinate	[Ch][Lys]	2.74, 9.44, 10.29	1.062	187[c]
Cholinium formate	[Ch][For]	4.27	1.138	-[d]
Cholinium acetate	[Ch][Ace]	4.76	1.081	-[d]
Cholinium butyrate	[Ch][But]	4.91	1.043	-[d]
Cholinium hexanoate	[Ch][Hex]	5.09	0.997	-[d]
Cholinium octanoate	[Ch][Oct]	5.19	0.970	-[d]

[a] Calculated density (g/cc) using MD simulations. [b] Viscosity (Pa·s) data at 25 °C. [c] Santis et al. (2015)[2]. [d] Solid at 25 °C (Petkovic et al. (2010)[3]).

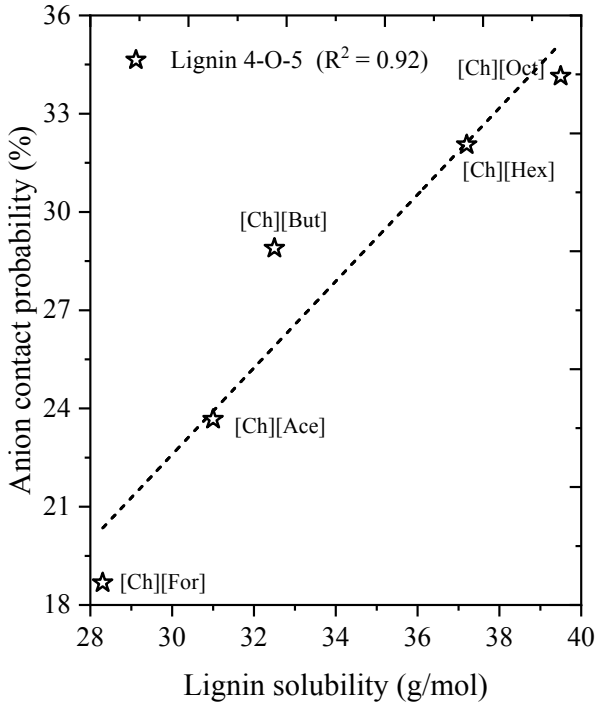


Figure S2: COSMO-RS predicted contact probability of lignin in choline-carboxylate anions and compared with the experimental lignin solubility data.

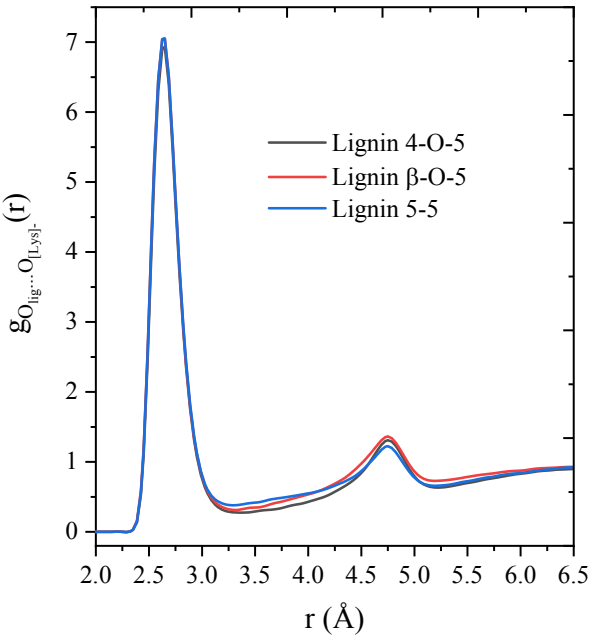


Figure S3: RDF plot between the O atom of Lignin with O atom of Lysinate for Lignin/[Ch][Lys] systems at 363.15

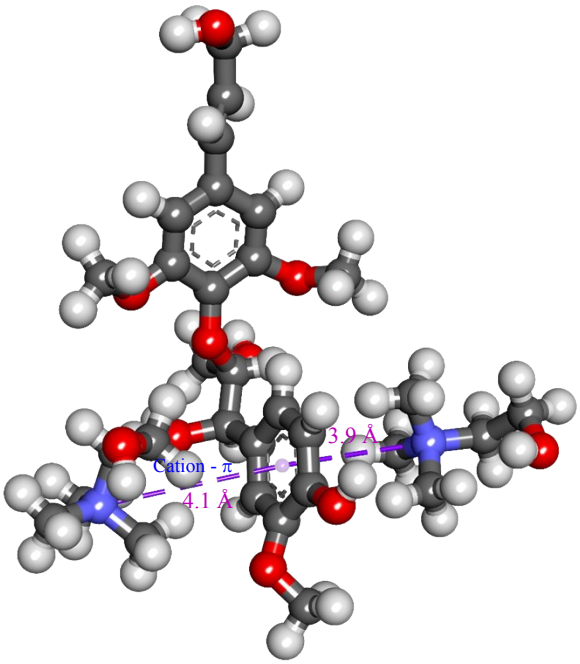
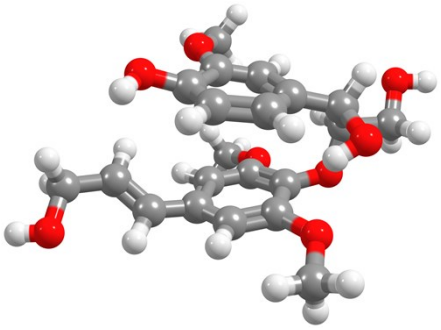
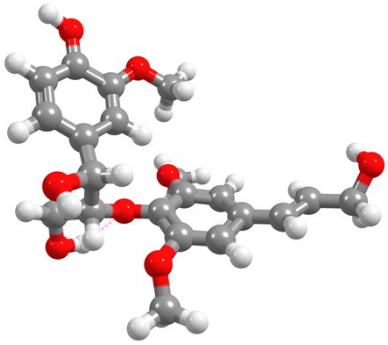


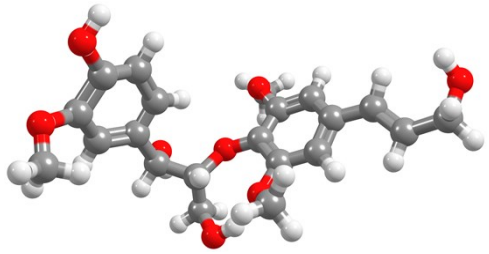
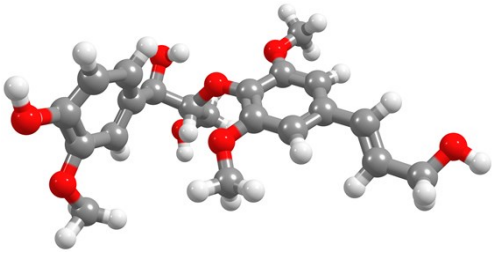
Figure S4: Graphical representation of cation-π interactions between Lignin β–O–4 and Choline for Lignin β–O–4/[Ch][Lys] system. The color scheme used for different atoms is C (ash), O (red), N (blue), and H (white), respectively.

Structural Confirmation of Lignin in [Ch][Lys]

Further, the structural conformation of lignin *β*–O–4 linkage is evaluated as a function of interaction energies between lignin-anion and lignin-cation (Table S7). Herein, we considered 4 unique conformer of the lignin *β*–O–4 dimer. It is worthy to mention that the probability of conformers 1 and 2 is unlikely owing to the geometric and steric limitations of bond rotation in real polymeric lignin. For lignin-IL interactions, parallel stacking-type of lignin *β*–O–4 structure exhibits lower interactions with [Ch][Lys], while an antiparallel stacking structure of lignin shows stronger interactions. The presence of lignin parallel stacking-type structure could lead to the poor solubility of lignin due to the strong intramolecular hydrogen bonding and π-π stacking in lignin. However, from the MD simulations, the convergence of lignin into the antiparallel staking is higher thus exhibited stronger interactions with [Ch][Lys] and leads to higher the solubility of lignin.

Table S7: β–O–4 lignin conformer structures and their interaction energies with [Ch][Lys]. The color scheme used for different atoms is C (ash), O (red), and H (white), respectively.

Conformer	Lignin - Lysinate		Lignin - Cholinium	
	E_{elec}	E_{vdW}	E_{elec}	E_{vdW}
 Conformer 1	-29.99	-15.71	-7.60	-8.57
 Conformer 2	-39.23	-13.40	-2.87	-8.35

 Conformer 3	-45.58	-24.04	-10.95	-18.10
 Conformer 4	-60.04	-19.03	-6.55	-19.48

References

1. N. Sun, R. Parthasarathi, A. M. Socha, J. Shi, S. Zhang, V. Stavila, K. L. Sale, B. A. Simmons and S. Singh, *Green Chem.*, 2014, **16**, 2546-2557.
2. S. De Santis, G. Masci, F. Casciotta, R. Caminiti, E. Scarpellini, M. Campetella and L. Gontrani, *Phy. Chem. Chem. Phy.*, 2015, **17**, 20687-20698.
3. M. Petkovic, J. L. Ferguson, H. N. Gunaratne, R. Ferreira, M. C. Leitao, K. R. Seddon, L. P. N. Rebelo and C. S. Pereira, *Green Chem.*, 2010, **12**, 643-649.