Electronic Supplementary Material (ESI) for Green Chemistry.

Electrical Supporting information

One-pot integrated biofuel production using low-cost biocompatible protic ionic liquids

Jian Sun[1,2], N.V.S.N. Murthy Konda[1,3#], Ramakrishnan Parthasarathi[1,2#], Tanmoy Dutta[1,2], Marat Valiev[4], Feng Xu[1,2], Blake A. Simmons[1,3], and Seema Singh[1,2*]

[1] Deconstruction Division, Joint BioEnergy Institute, Emeryville, CA, USA.

[2] Biomass Science and Conversion Technology Department, Sandia National Laboratories, Livermore, CA, USA.

[3] Biological Systems and Engineering Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA.

[4] Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, USA.

*Corresponding author: E-mail: seesing@sandia.gov

[#] Equal contribution as the co-second author

Table S1. Compositional analysis of major components in the switchgrass before and after pretreated and solid recovered after pretreatment.[a]

Solvent	Solid recovery/%	Glucan/%	Xylan/%	Lignin/%
/	/	32.9±0.1	20.4±0.1	22.2±0.1
HOAC	79.5	37.9±0.1	15.5±0.2	25.5±0.5
EOA	59.0	53.1±0.1	22.4±0.2	5.7±0.3

[a] Method is described in the main text.

Computational details for IL Screening

The geometry optimizations of ethanolamine (EOA), diethanolamine (DEOA), triethanolamine (TEOA), and triethylamine (TEA), with acetic acid, lactic acid, sulfuric acid, formic acid and hydrochloric acid (Fig. 2), were performed using density functional theory (DFT) with the M06-2X hybrid exchange-correlation functional and the 6-311++G(d, p) basis set. Frequency calculations were carried out to verify that the computed structures corresponded to energy minima. In the present study, density functional theory (DFT) based global reactivity descriptors, such as chemical hardness, chemical potential, and electrophilicity were calculated. Quantum chemical reactivity descriptors predicted acidity, basicity and net basicity, and showed good correlation with experimentally observed values for $[C_2C_1Im][OAc]$. These results provide a basis to describe the observed experimental delignification trend for a set of ILs. These descriptors were used to derive the molecular basicity, acidity, and net basicity values for the novel ILs. According to the DFT, the chemical potential (μ), and chemical hardness (η) are defined as,

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \tag{1}$$

and

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(\vec{r})} \tag{2}$$

where E is the total energy of the system, N is the number of electrons in the system and $v(\vec{r})$ is the external potential. μ is identified as the negative of the electronegativity (χ). By applying finite difference approximation to Eqs. (2) and (3) we get the operational definition for η and μ as,

$$\mu = -\frac{(IP+EA)}{2} \tag{3}$$

$$\eta = \frac{IP-EA}{2} \tag{4}$$

Chemical potential and chemical hardness can be rewritten using Koopmans' theorem in terms of the vertical ionization potential (IP) and electron affinity (EA) as,

$$\eta = \frac{E_{LUMO}-E_{HOMO}}{2} \tag{5}$$

$$\mu = \frac{E_{LUMO}+E_{HOMO}}{2} \tag{6}$$

where E_{LUMO} is the lowest unoccupied molecular orbital's energy and E_{HOMO} is the highest occupied molecular orbital's energy.

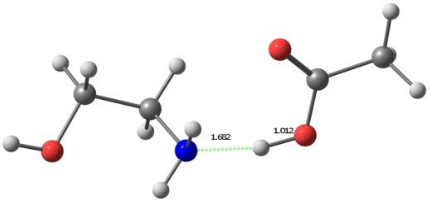
Upon formation of a hydrogen bond, electron density is transferred from the hydrogen bond acceptor towards the hydrogen bond donor. In the light of Hard Soft Acids Base (HSAB) concept the propensity of molecule to donate the electron density depends inversely on the electronegativity and hydrogen atom-attracting sites are formed through the interaction of intramolecular sites of different electronegativity. Hence, we define the hydrogen bonding basicity B^{IL} of an IL using simple working equation based on DFT based descriptors as follows

$$B^{IL} = \eta^2/\chi \tag{7}$$

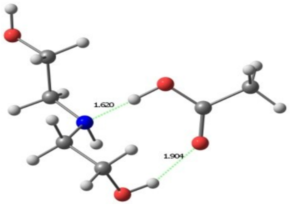
An increased electrostatic component and the high electronegativity of a molecule influence the hydrogen bonding ability. In the case of basicity, electronegativity is very important for hydrogen bonding. Therefore, molecular acidity dependence on the reduced orbital electronegativity of the molecule is considered. The formula for the acidity is written as follows

$$A^{IL} = \chi^2/2\eta \tag{8}$$

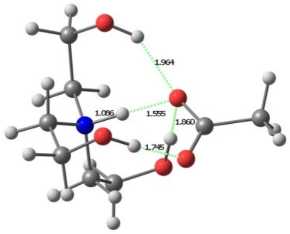
IL net basicity values were reported as a difference in B^{IL} - A^{IL}. All quantum chemical calculations were performed using the Gaussian 09 suite of programs.



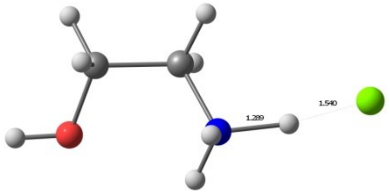
[EOA][OAc]



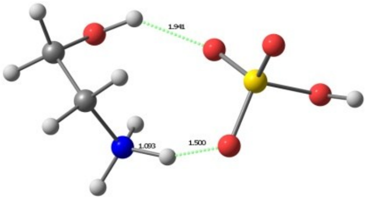
[DEOA][OAc]



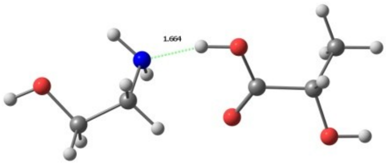
[TEOA][OAc]



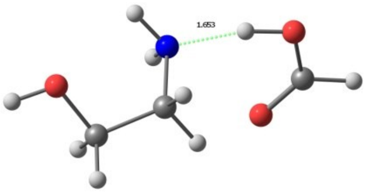
[EOA]Cl



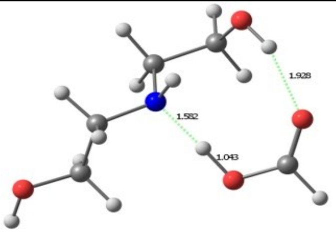
[EOA][HSO$_4$]



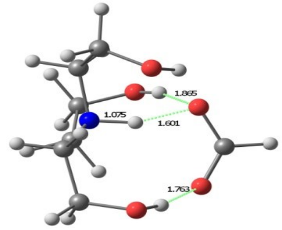
[EOA][La]



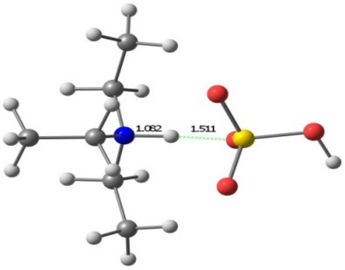
[EOA]F



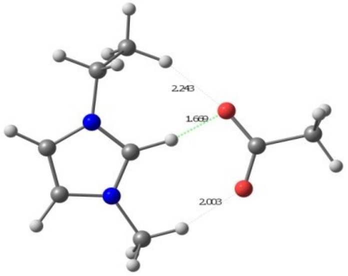
[DEOA]F



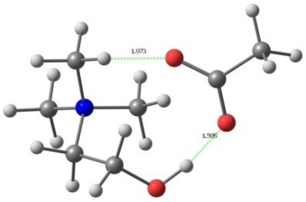
[TEOA]F



[TEA][HSO$_4$]



[C_2C_1Im][OAc]



[Ch][OAc]

Figure S1. Optimized geometries of ILs screened in this study.

NMR of ILs synthesized, ^{1}HNMR (up) and ^{13}CNMR (bottom)

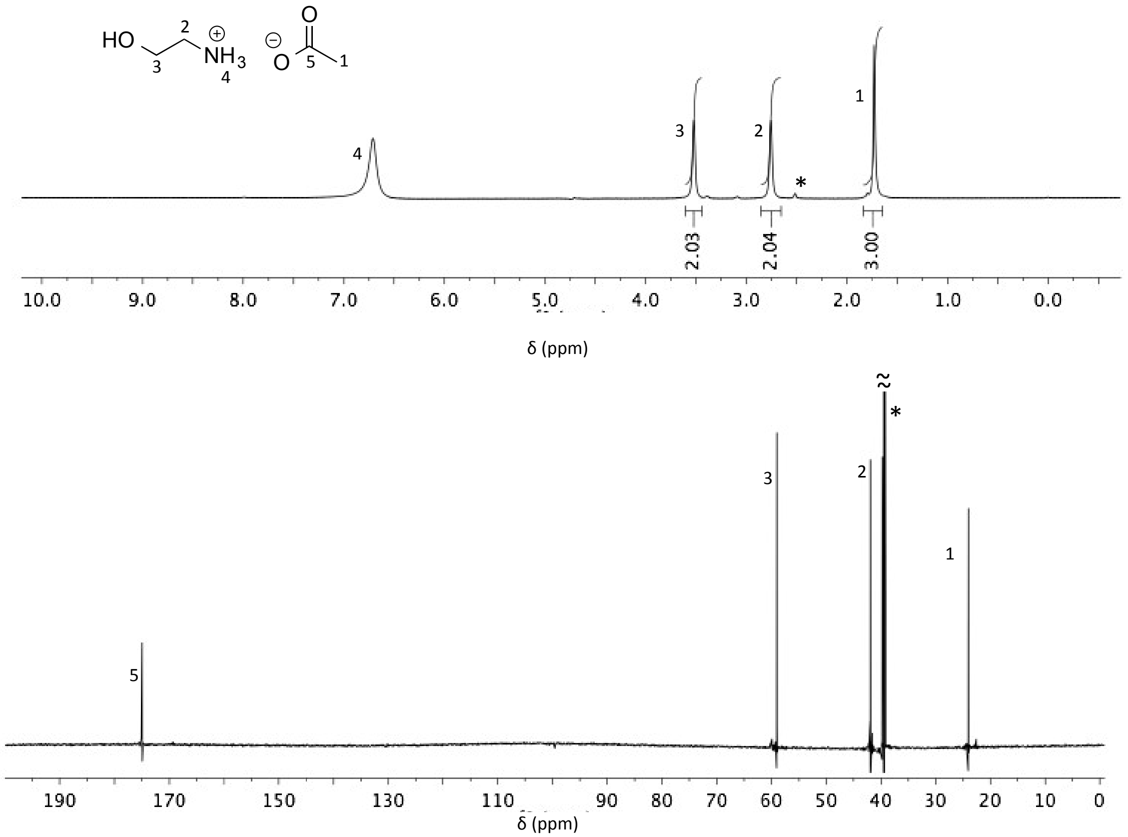


Figure S2. ^{1}HNMR and ^{13}CNMR spectrums of [EOA][OAc]

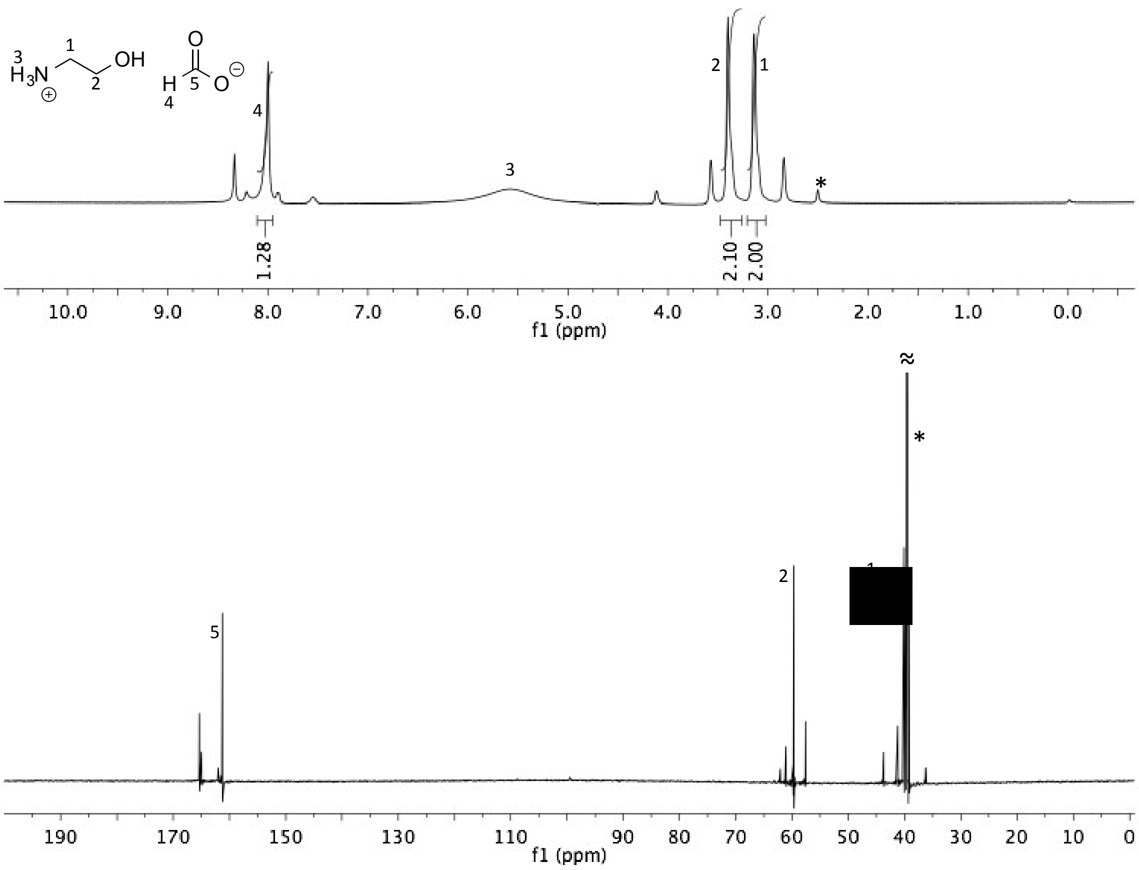


Figure S3. ^{1}HNMR and ^{13}CNMR spectrums of [EOA]F

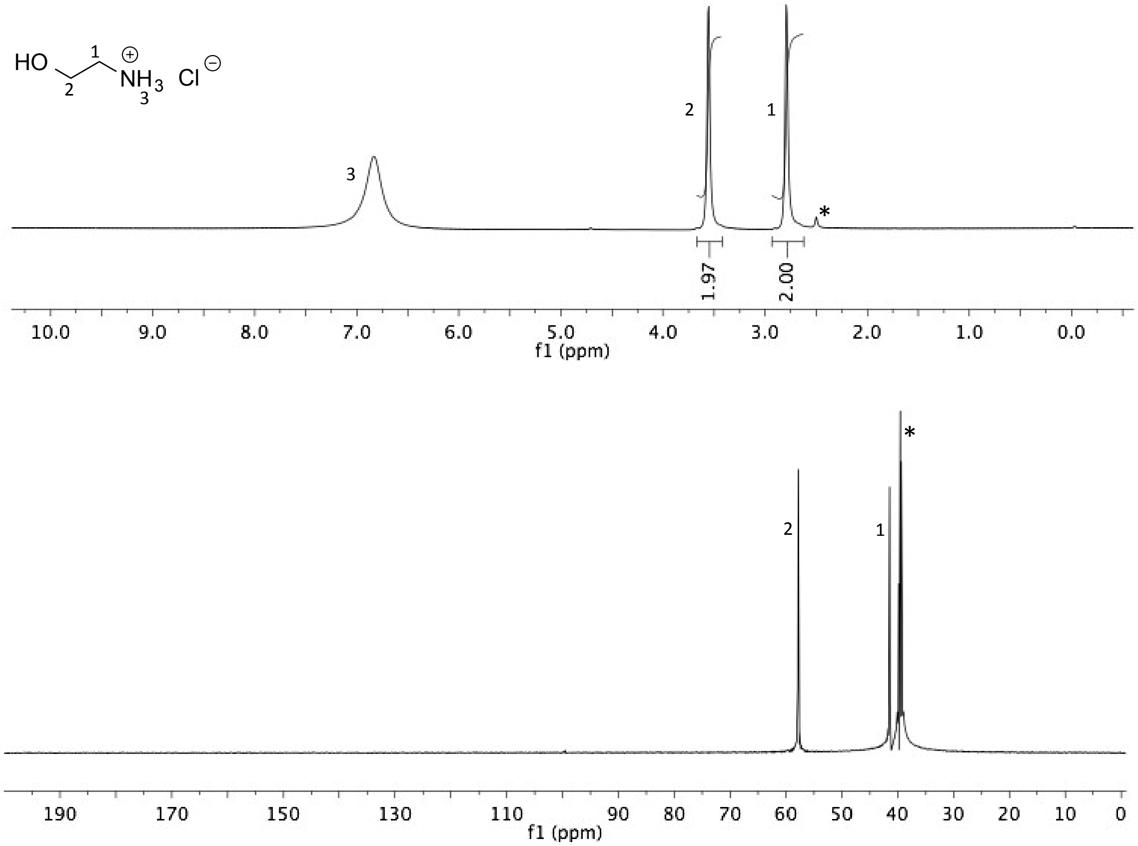


Figure S4. ^{1}HNMR and ^{13}CNMR spectrums of [EOA]Cl

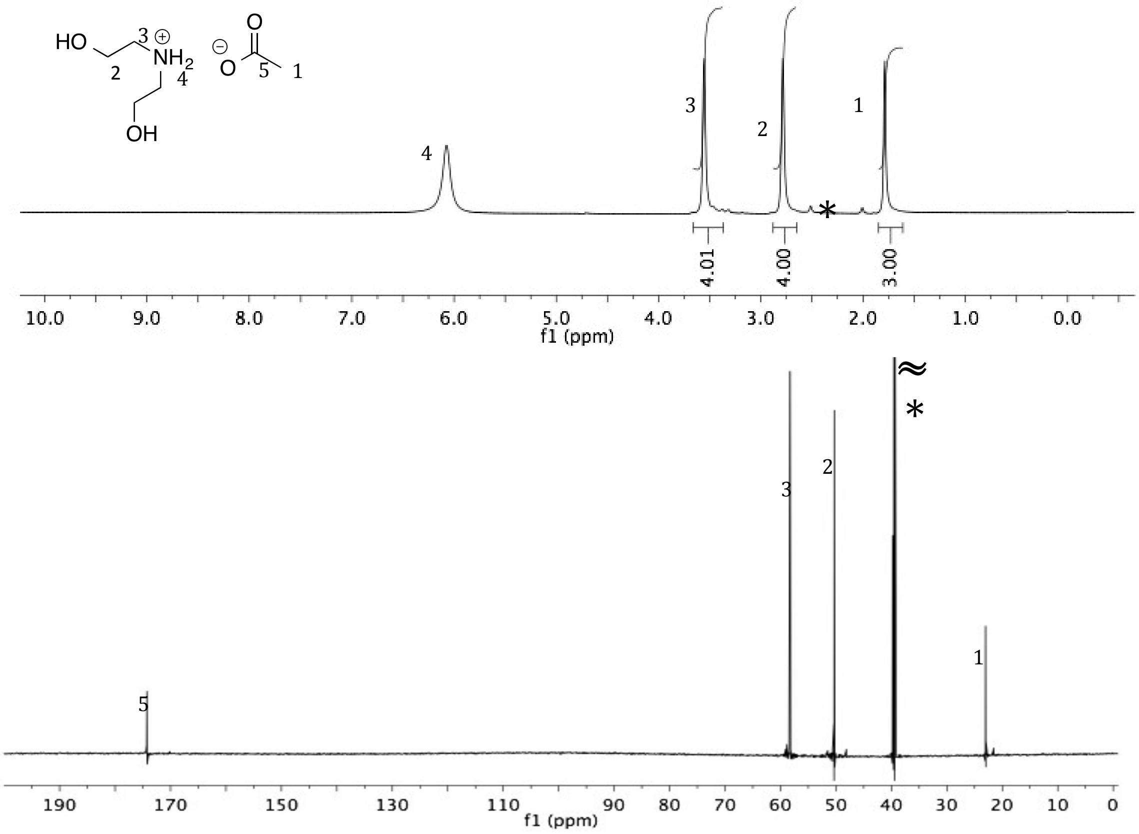


Figure S5. ^{1}HNMR and ^{13}CNMR spectrums of [DEOA][OAc]

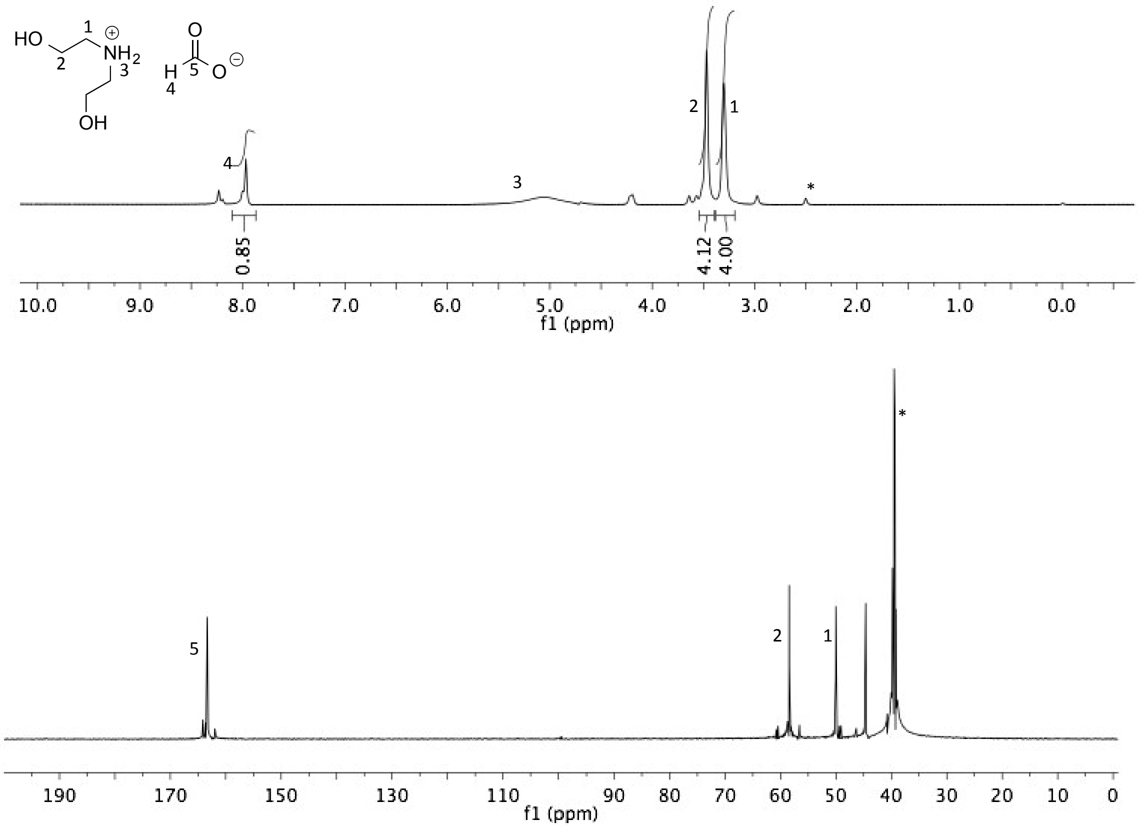


Figure S6. ^{1}HNMR and ^{13}CNMR spectrums of [DEOA]F

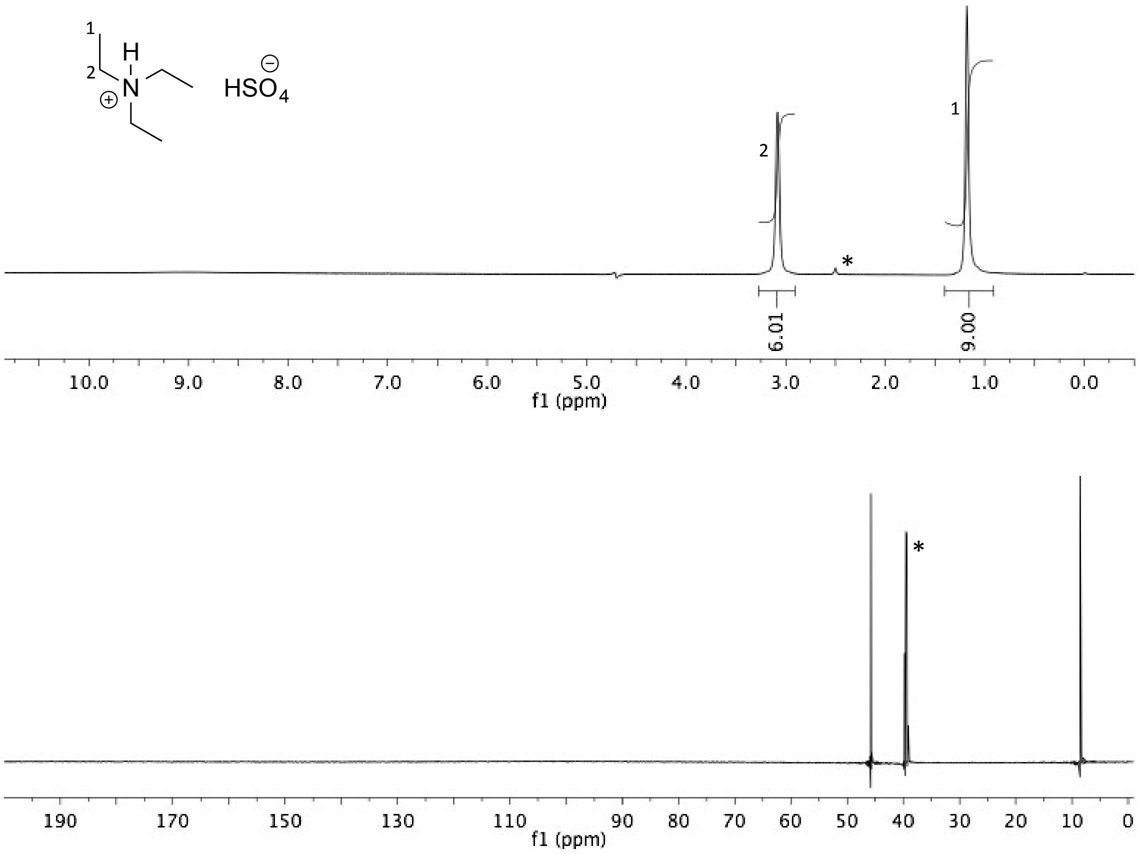


Figure S7. ^{1}HNMR and ^{13}CNMR spectrums of [TEA][HSO_4]

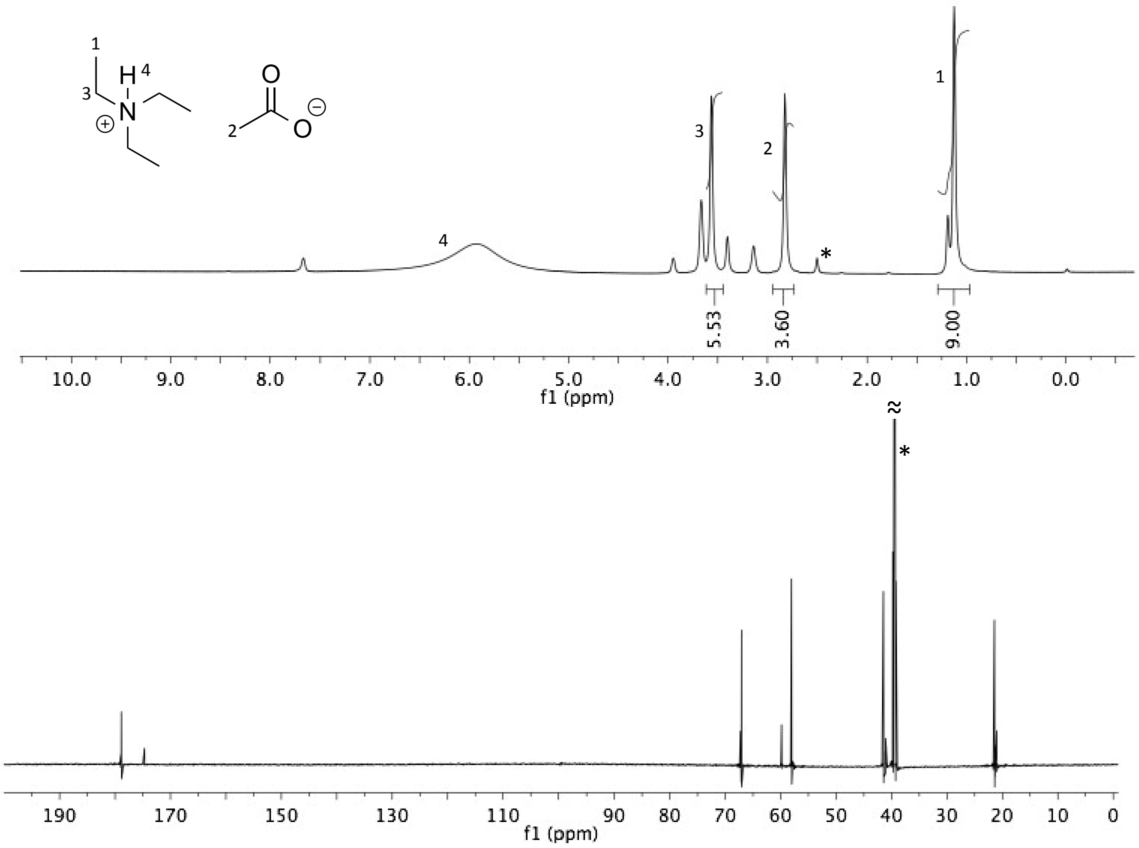


Figure S8. ^{1}HNMR and ^{13}CNMR spectrums of [TEA][OAc]

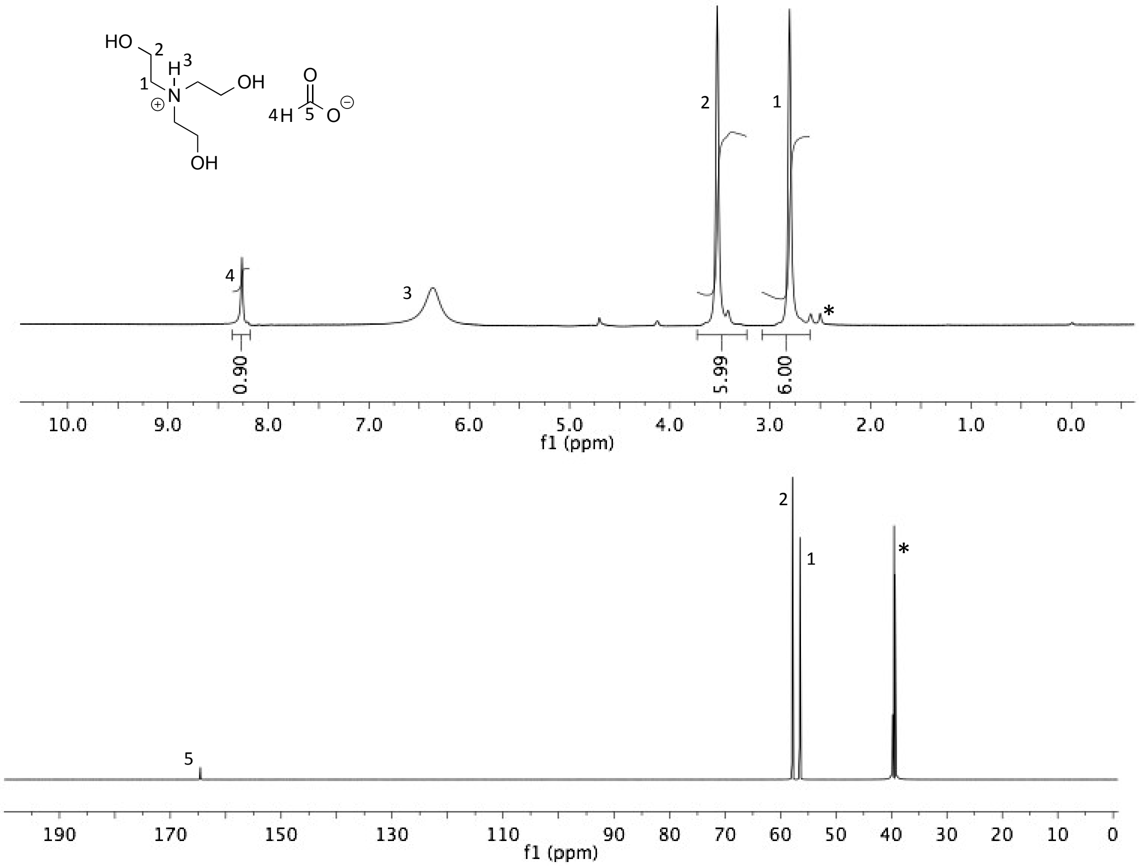


Figure S9. ^{1}HNMR and ^{13}CNMR spectrums of [TEOA]F

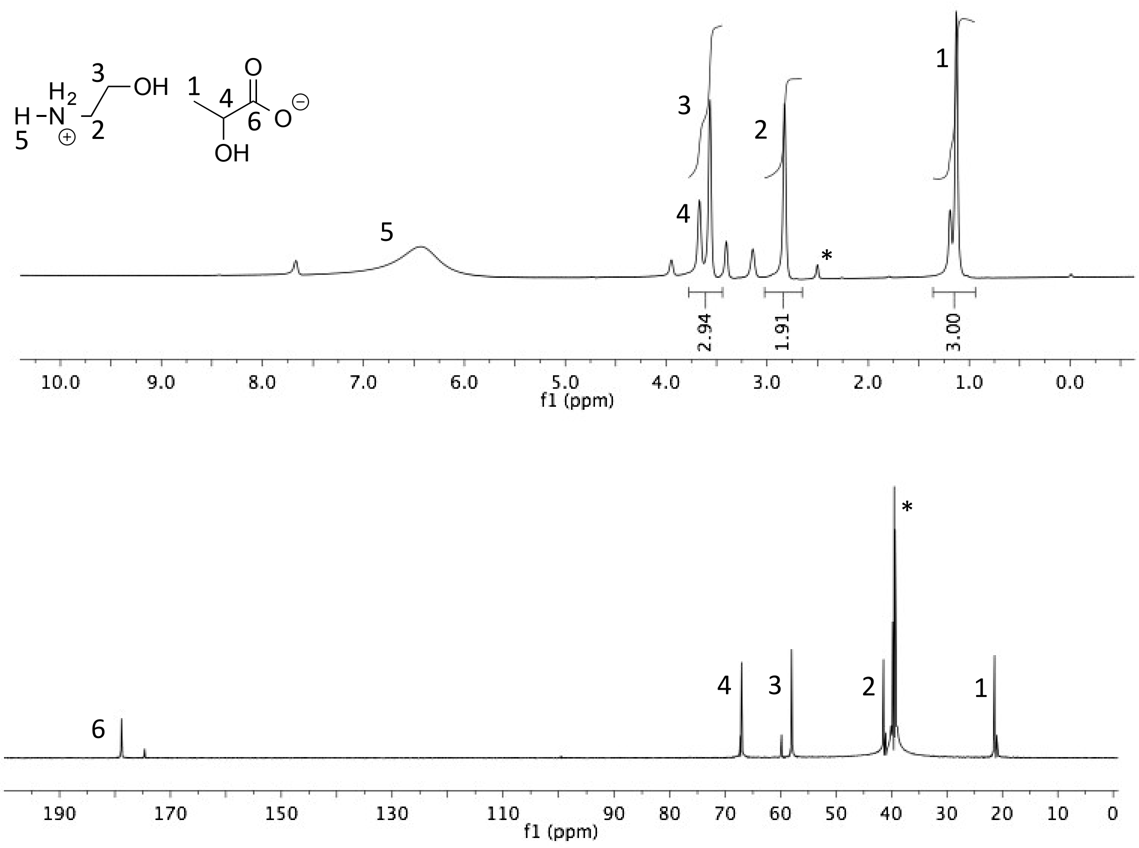


Figure S10. ^{1}HNMR and ^{13}CNMR spectrums of [EOA][La]

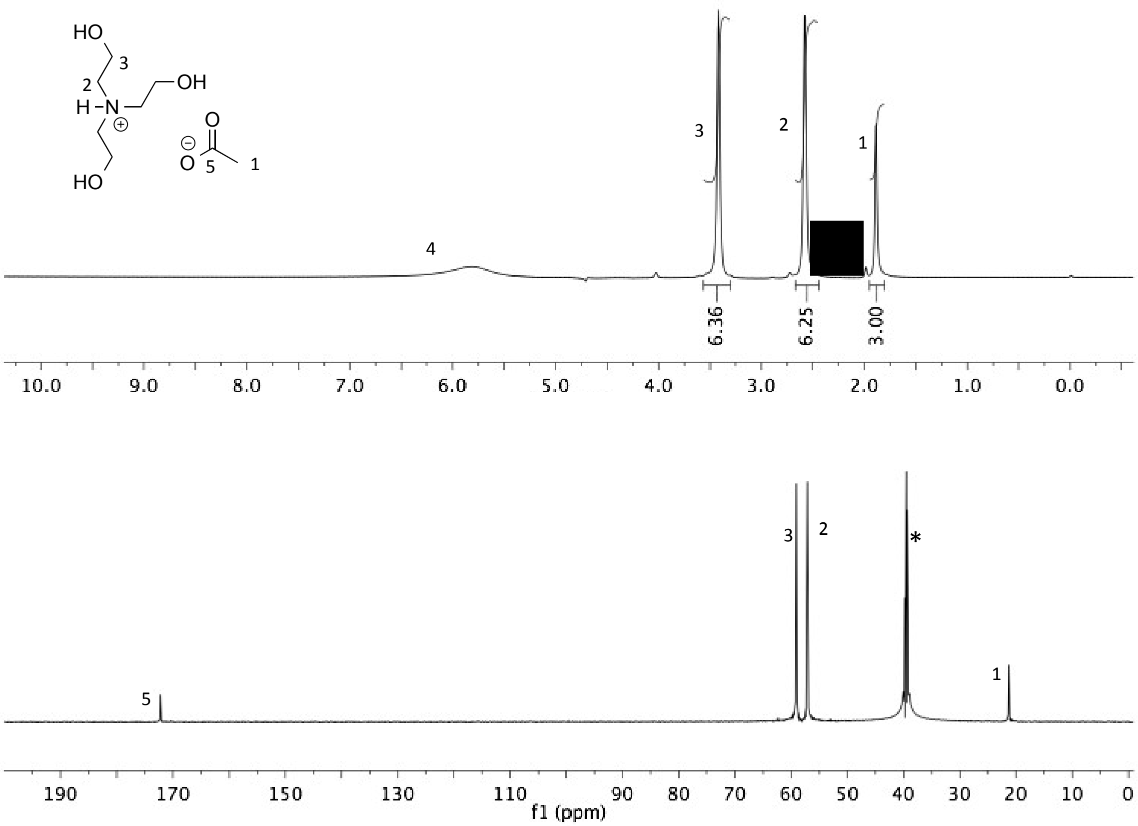


Figure S11. ^{1}HNMR and ^{13}CNMR spectrums of [TEOA][OAc]

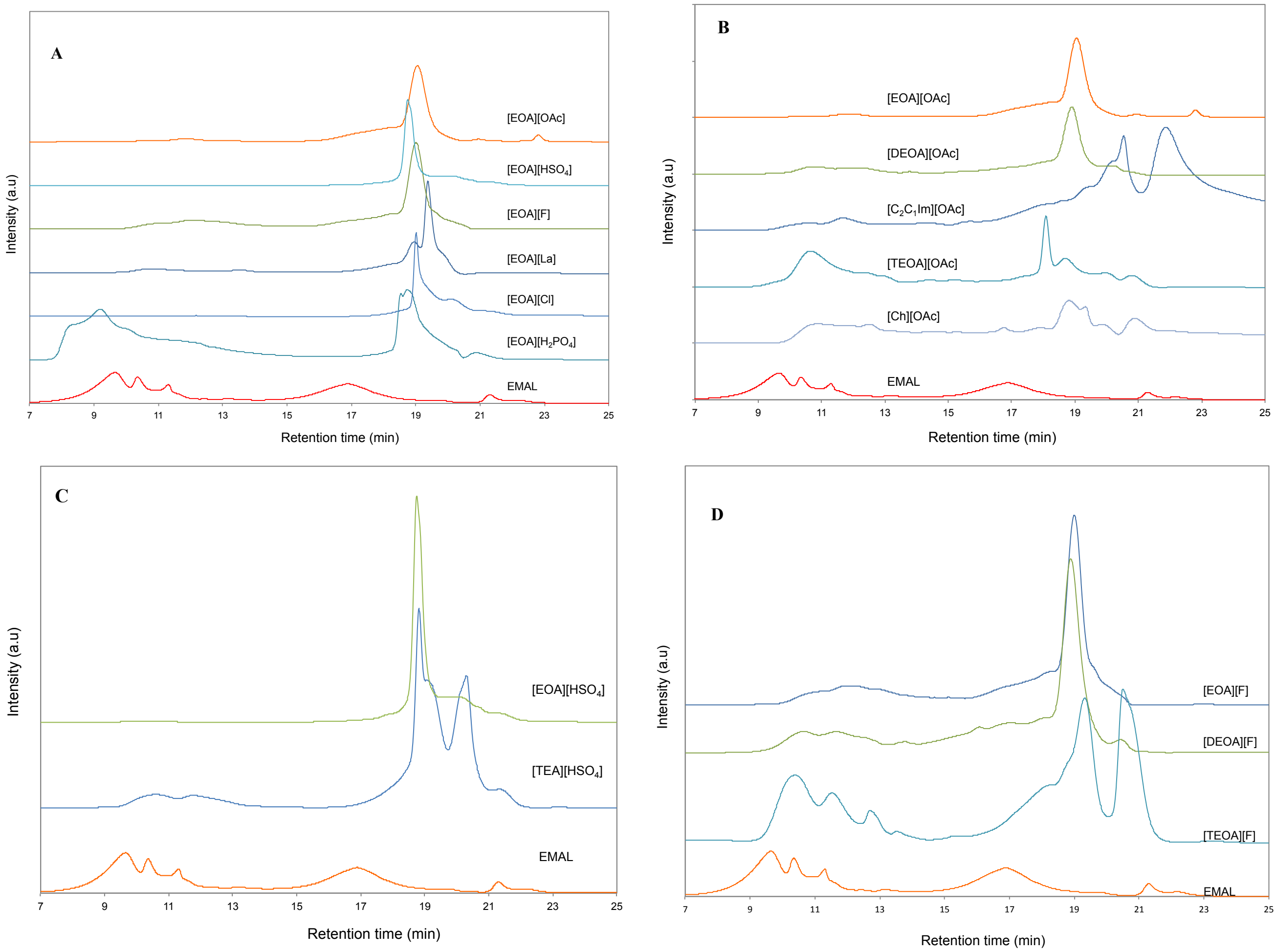


Figure S12. SEC chromatograms of extracted lignin streams from switchgrass pretreatment with (a) [EOA]-based; (b) [OAc]-based; (c) [HSO$_4$]-based; (d) [F]-based ILs along with EMAL lignin for comparison.

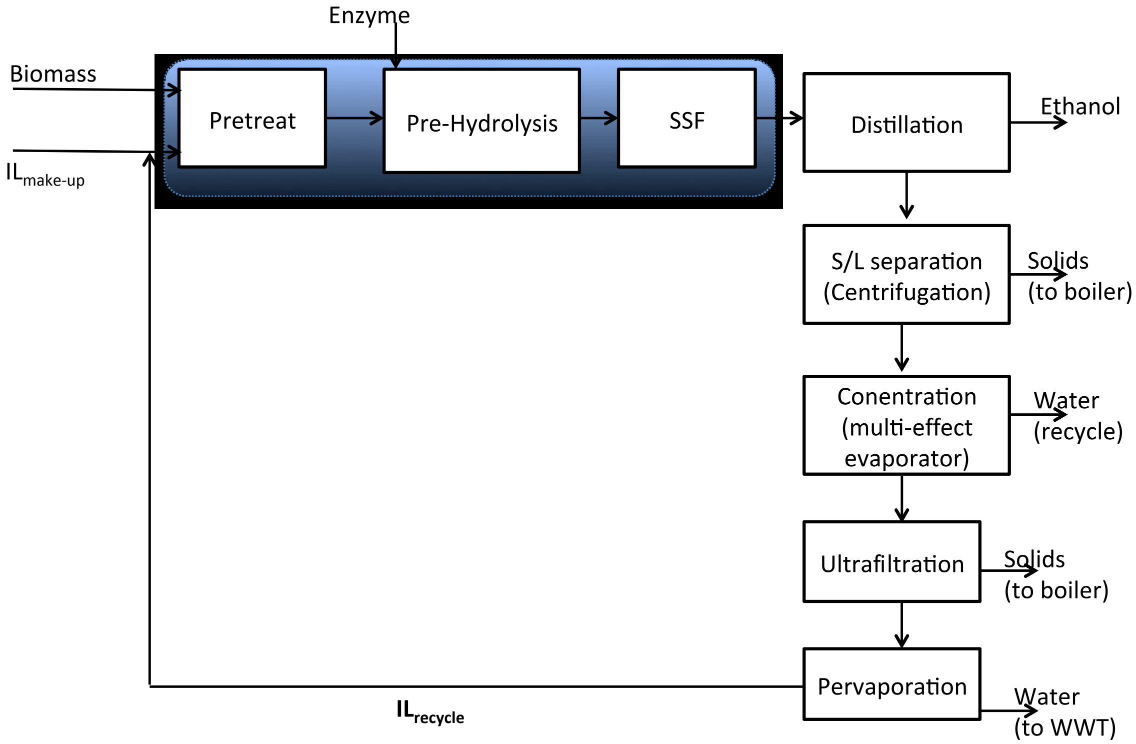


Figure S13. A simplified representation of the PIL based biorefinery process.

Table S2. Key process and cost parameters in the scenarios studied.

Scenario	S0	S1	S2	S3
Switchgrass processed (dry MT/day)	2000	2000	2000	2000
Feedstock price ($/dry ton, delivered at plant-gate)	80	80	80	80
Pretreatment				
Pure IL price ($/kg)*	2	2	2	2
IL purity (wt% in H_2O)	~100	~100	~25	~25
Biomass loading (wt%)	40	40	20	20
IL recovery (%)	99	99	99	99
SSF				
Enzyme loading (mg/g biomass)	20	20	20	7
Enzyme price ($/kg protein)**	5	5	5	5
IL concentration during SSF (wt%)	5	20	20	20
Pre-hydrolysis time (hr)	24	24	24	24
SSF time (hr)	72	72	72	72
Co-utilization of glucose and xylose	Yes	Yes	Yes	Yes
Overall ethanol yield (gal/dry ton switchgrass)	72	72	72	72

* Price of ILs is assumed to reflect on the fact that the hydroxyl ammonium based ILs such as [EOA][OAc] use cheaper raw materials and require simpler synthesis methods. For instance, according to the information available in the open literature (e.g., www.alibaba.com), ethanolamine and acetic acid (i.e., the primary raw materials used to synthesize [EOA][OAc]) can be purchased for about $800-$1500/MT and $300-$700/MT (depending on the supplier, quality and order quantity). Therefore, a price of $2/kg of [EOA][OAc] is a reasonable estimate in this preliminary TEA.

** The enzyme was estimated based on a design report from NREL (Humbird et al., 2011, see Ref. 46). The effective enzyme price obtained based on this report was ~ $4.3/kg which was reported in 2007$. Since our analysis is based on more recent year (2015), we estimated the enzyme price to be $5/kg with an average inflation rate of around 2%.