*Electronic Supplementary Information*

# Aprotic *vs* protic ionic liquids for lignocellulosic biomass pre-treatment: Anion effects, enzymatic hydrolysis, solid state NMR, distillation and recycle

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**Contains 15 pages (from S1 to S15), 4 Tables and 10 Figures**

**TABLES**

**Table S1:** List of physical properties for five different ILs used in this study.

| **Ionic liquid** | **Melting point (˚C)** | **pH at 100 g $l^{-1}$** | **Density (g $cm^{-3}$ )** | **Viscosity at 25 ºC (mPa s)** | **$T_{d\ (max)}$ (ºC)** |
|---|---|---|---|---|---|
| [Emim][OAc] | < 25 | 6.5 | 1.027[a,b] | 162[4] | 245 |
| [Emim]Cl | 82 ± 5 | 5.0 | 1.112[a,c] | - | 307 |
| [Eim][OAc] | < 25 | 7.0 | 1.026[b] | 4.2 | 193 |
| [Eim][HCOO] | < 25 | 5.1 | 1.092[b] | 6.9 | 190 |
| [Eim]Cl | 69 ± 5 | 5.5 | 1.128[c] | - | 276 |

[a] data from Sigma-Aldrich, [b] at 25 °C, [c] at 80 °C, $T_{d\ (max)}$ is the temperatures at maximum rate of thermal decomposition

**Table S2:** Maximum solubility of wood flour and percentage of recovered solid from different ILs.

| Ionic liquid | Maximum dissolution (wt%) | Recovered solid (wt%) |
|---|---|---|
| [Emim][OAc] | 5.5 (± 0.5) | 80 |
| [Emim]Cl | 2.5 (± 0.5) | 48 |
| [Eim]Cl | 3.5 (± 0.5) | 58 |
| [Eim][OAc] | No dissolution (only extract lignin) | 95 |
| [Eim][HCOO] | No dissolution (only extract lignin) | 92 |

Where, [Emim] = 1-ethyl-3-methylimidazolium, [Eim] = 1-ethylimidazolium, [OAc] = acetate and [HCOO] = formate.

**Table S3:** Maximum conversion efficiency from different ILs-treated wood after 96 h enzymatic hydrolysis.

| **Ionic liquid** | **Maximum enzymatic conversion (%)** |
|---|---|
| Untreated wood | 15.7 (± 0.6) |
| [Emim][OAc] | 86.7 (± 9.8) |
| [Emim]Cl | 56.2 (± 0.6) |
| [Eim]Cl | 74.6 (± 2.3) |
| [Eim][OAc] | 12.7 (± 1.5) |

Where, [Emim] = 1-ethyl-3-methylimidazolium, [Eim] = 1-ethylimidazolium and [OAc] = acetate.

**Table S4:** $^{13}C$ sNMR chemical shift assigned for various moieties of pine wood. All values and assignments are adapted from reference [1].

| Moiety / Functional group | Chemical shift region (ppm) |
|---|---|
| -COO/ $CH_3COO$ | 180-165 |
| Aromatic C-O (C3, 4 of lignin) | 160-141 |
| Aromatic C-C (C1 of lignin) | 141-125.8 |
| Aromatic C-H (C2, 5, 6 of lignin) | 125.8-108.5 |
| C1 of cellulose | 108.5-93.5 |
| C4 of cellulose (crystalline) | 93.5-86.6 |
| C4 of cellulose (amorphous) | 86.6-79.5 |
| C2, 3, 5 of cellulose | 79.5-68.0 |
| C6 of cellulose | 68.0-58.9 |
| $OCH_3$ of lignin | 58.9-50.8 |
| $CH_3$ of hemicellulose | 24.1-18.6 |

## FIGURES

**Figure S1:** Structure of five imidazolium-based protic ([Eim][OAc], [Eim][HCOO], [Eim]Cl) and aprotic ([Emim][OAc], [Emim]Cl) ionic liquids used for wood processing in this study.

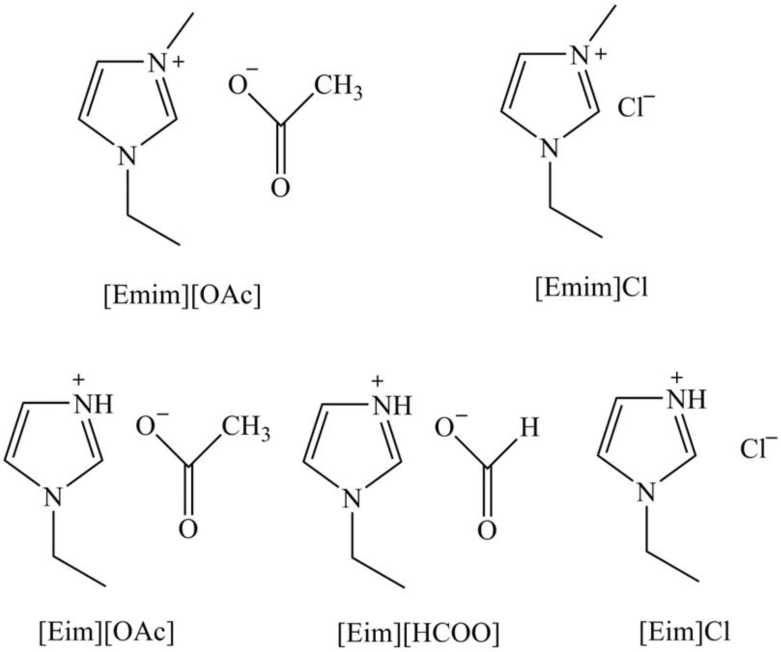


**Figure S2:** $^1$H NMR spectra for various [Eim]Cl in presence of excess 1-ethylimidazole (Eim) and HCl acid where the ratio of Eim and HCl was maintained as 1:0 (a), 1:0.5 (b), 1:1 (c), 1:1.5 (d) and 1:2 (e)

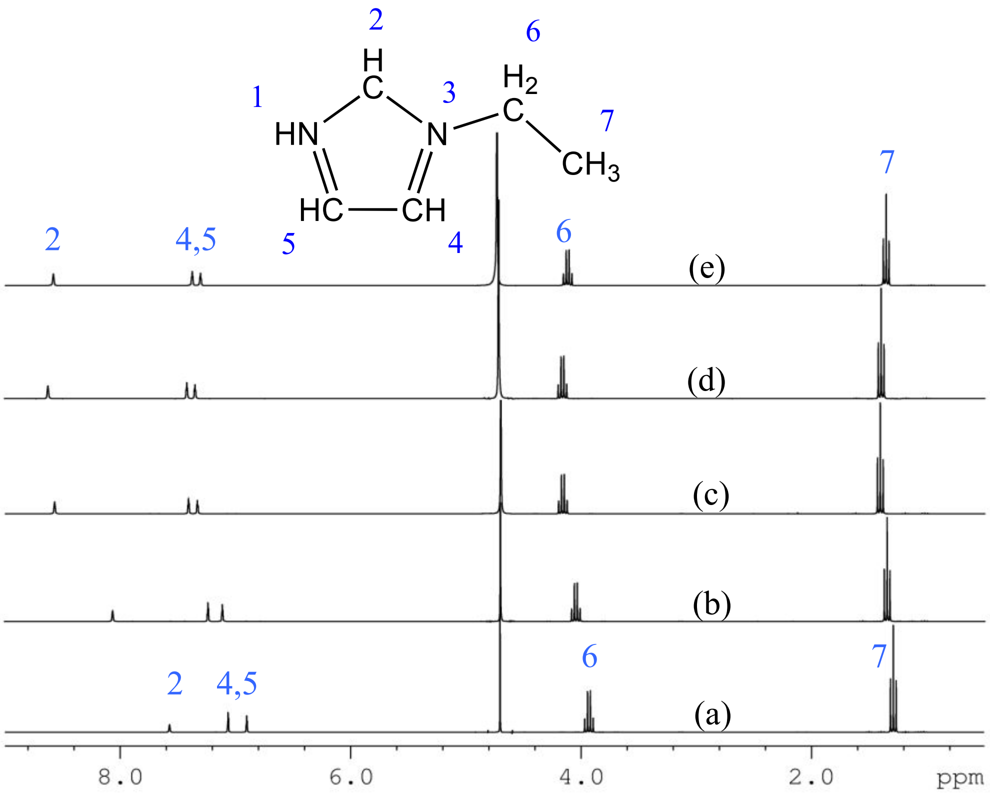


**Figure S3:** DSC curves for imidazolium-based protic ILs, [Eim][OAc], [Eim][HCOO], [Eim]Cl; their precursor 1-ethylimidazole and aprotic [Emim][OAc], [Emim]Cl ionic liquids.

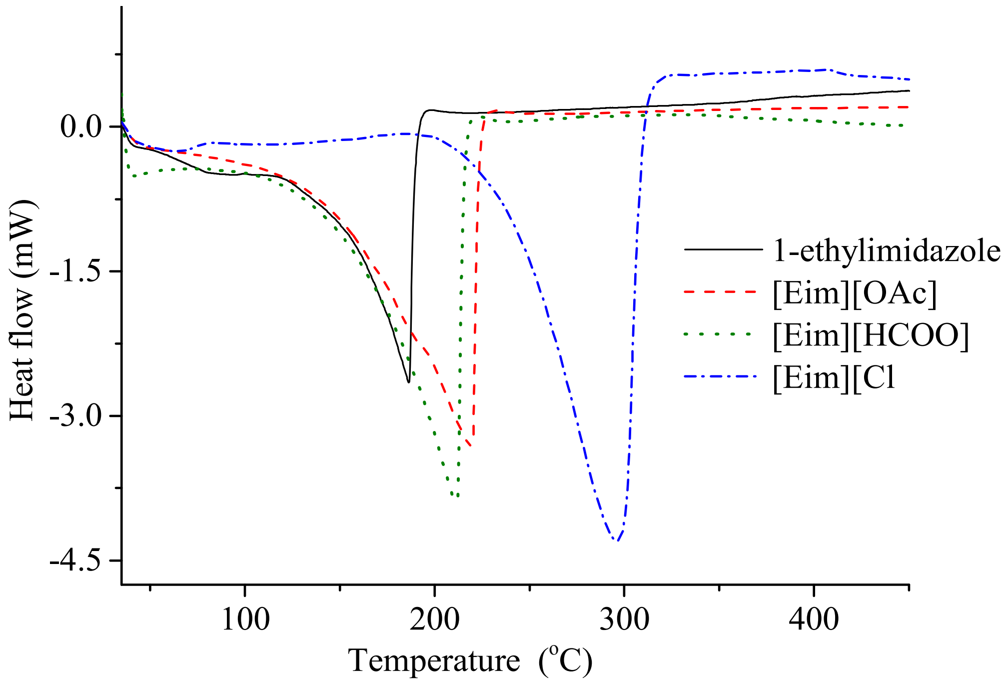
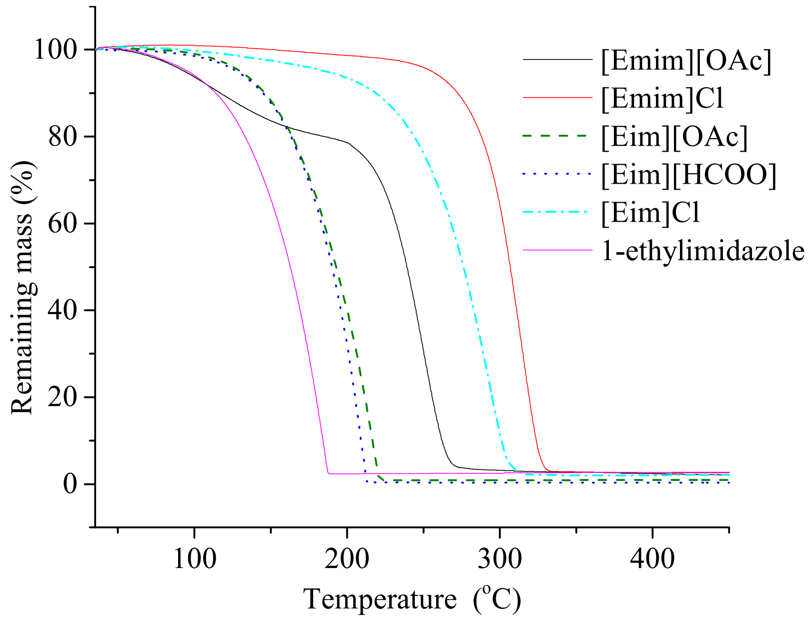


**Figure S4:** TGA curves for imidazolium-based protic ILs, [Eim][OAc], [Eim][HCOO], [Eim]Cl and their precursor, 1-ethylimidazole.




Please note [Eim][OAc], [Eim][HCOO] and [Eim]Cl were measured as synthesised, with water content <1wt%; the deliquescent, commercial [Emim]Cl was stored in a glovebox, and thus also had a water content of <1wt%; the commercial [Emim][OAc] was taken from the bottle directly (also <1wt% water content), but the significant mass loss before 200 °C is associated with water loss, whereby the water must have been uptaken by the sample from the atmosphere prior to measurement.

**Figure S5:** (a) UV-Vis spectra (b) plot of absorbance *vs* wood load for different amount of wood loading in [Eim][OAc] where 1 g of IL and different amount of wood flour were taken in round bottom flask at 115 °C for 18 h stirring at 700 rpm with reflux set-up.

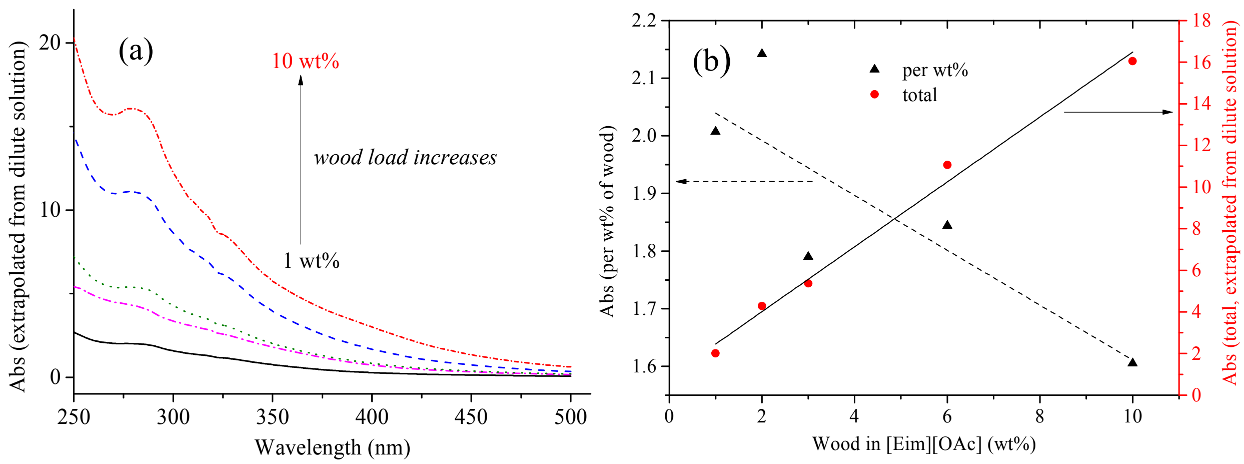


**Figure S6:** UV-Vis spectra for 1 wt% wood loading in [Eim][HCOO].

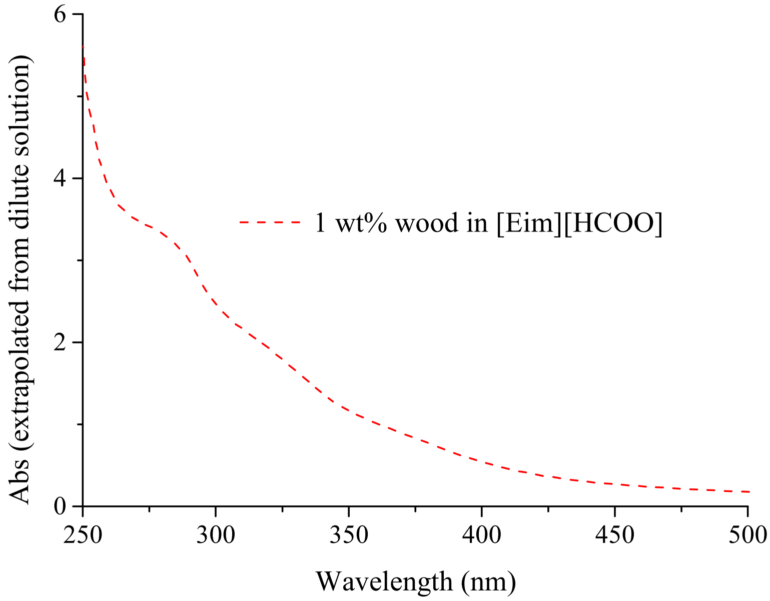


**Figure S7:** Calibration of commercial glucose sensor (Accuchek Active, used in this study) over its detection range (0.6 to 33.1 mM).

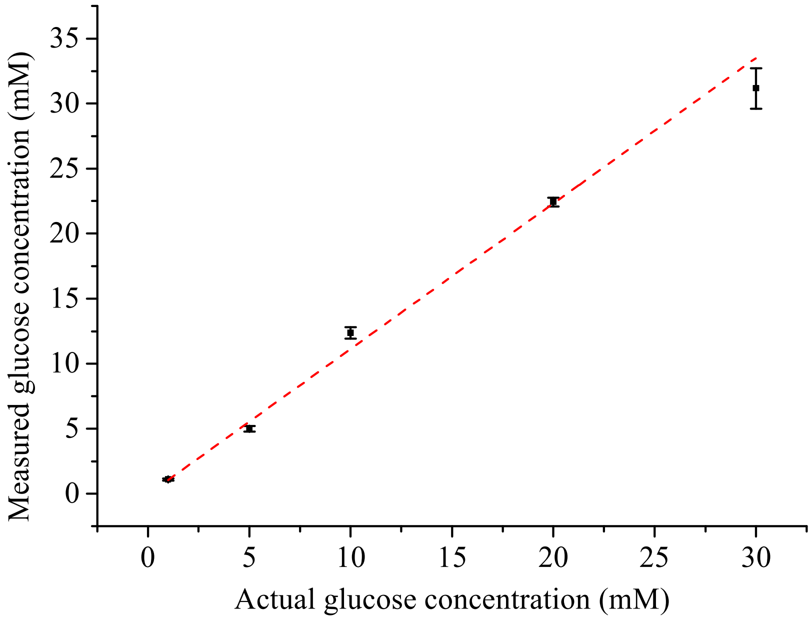


**Figure S8:** Thermogravimetric analysis of untreated wood and regenerated solid from different ionic liquids; [Emim][OAc], [Emim]Cl, [Eim][OAc], and [Eim]Cl.

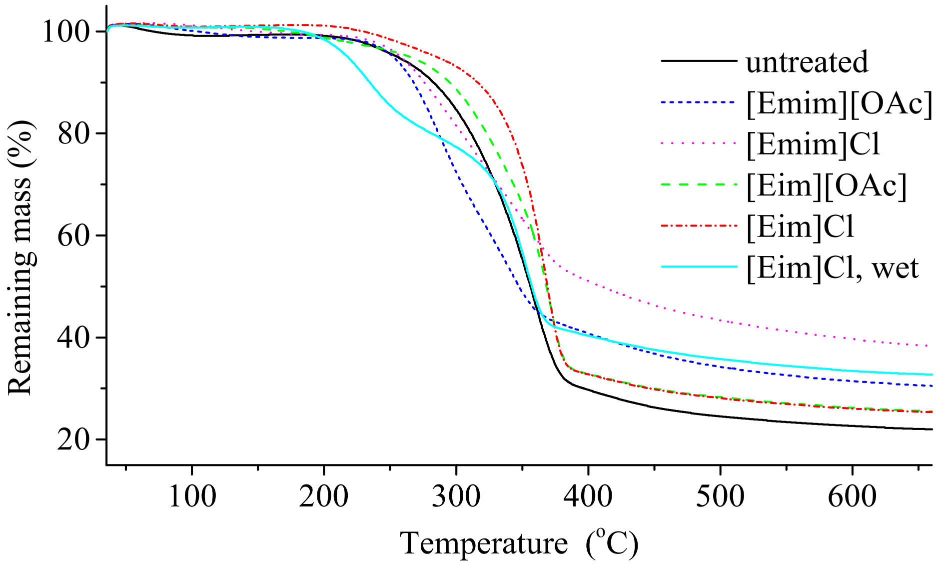


**Figure S9:** Photograph of contaminated [Eim]Cl distillation in Kugelrohr apparatus after 1st (a) and 2nd (b) distillation at 200 °C.

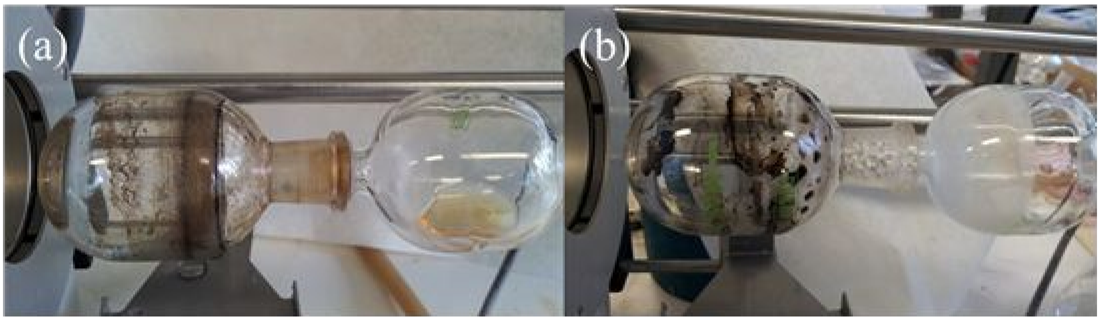
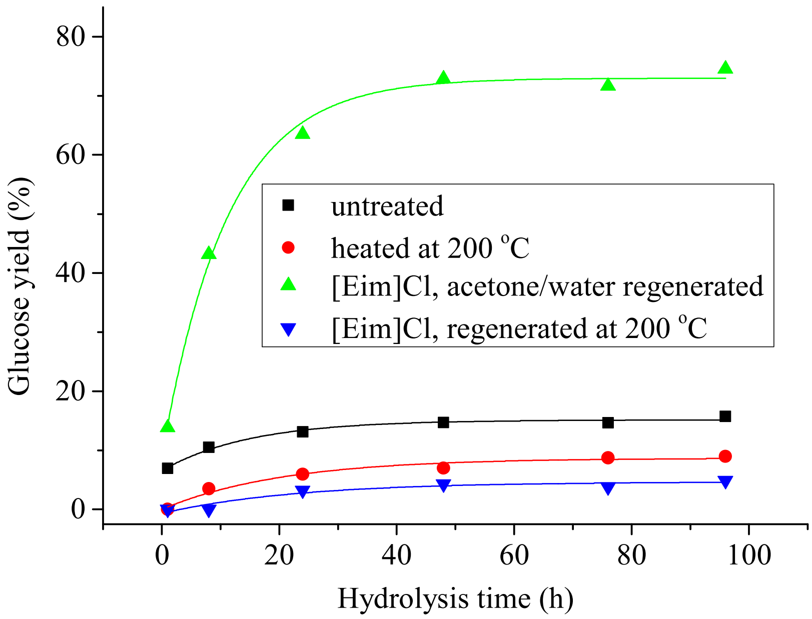


**Figure S10:** Enzymatic conversion of untreated wood, wood heated at 200 °C, regenerated solid from [Eim]Cl using acetone-water mixture, and regenerated solid from [Eim]Cl obtained after distillation in Kugelrohr apparatus.




**REFERENCES**


[1] Holtman, K. M.; Chen, N.; Chappell, M. A.; Kadla, J. F.; Xu, L.; Mao, J. *J. Agric. Food Chem.* **2010**, *58*, 9882.