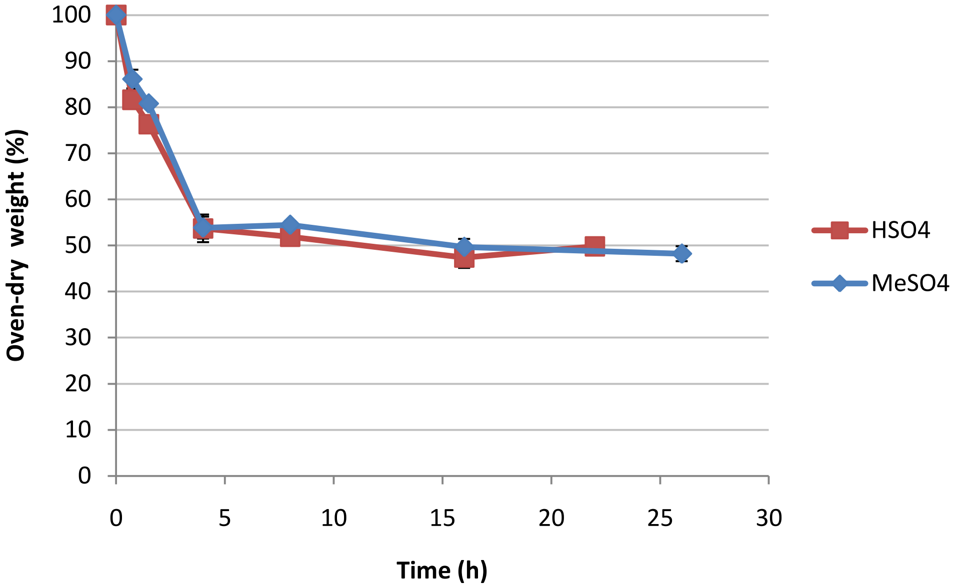
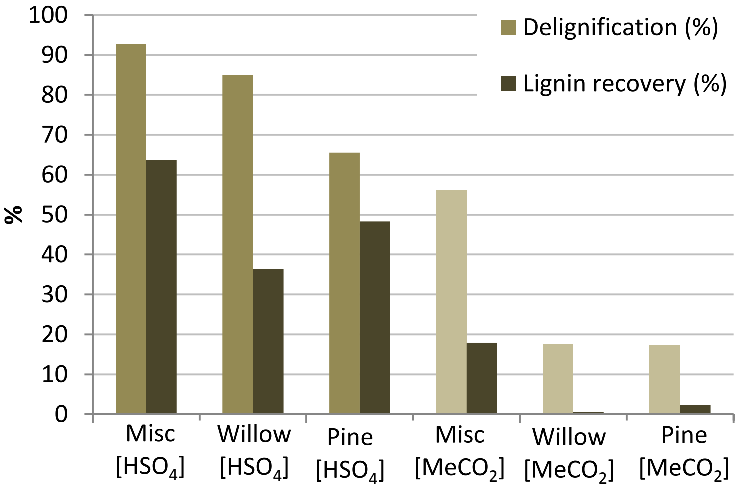
Electronic supplementary information

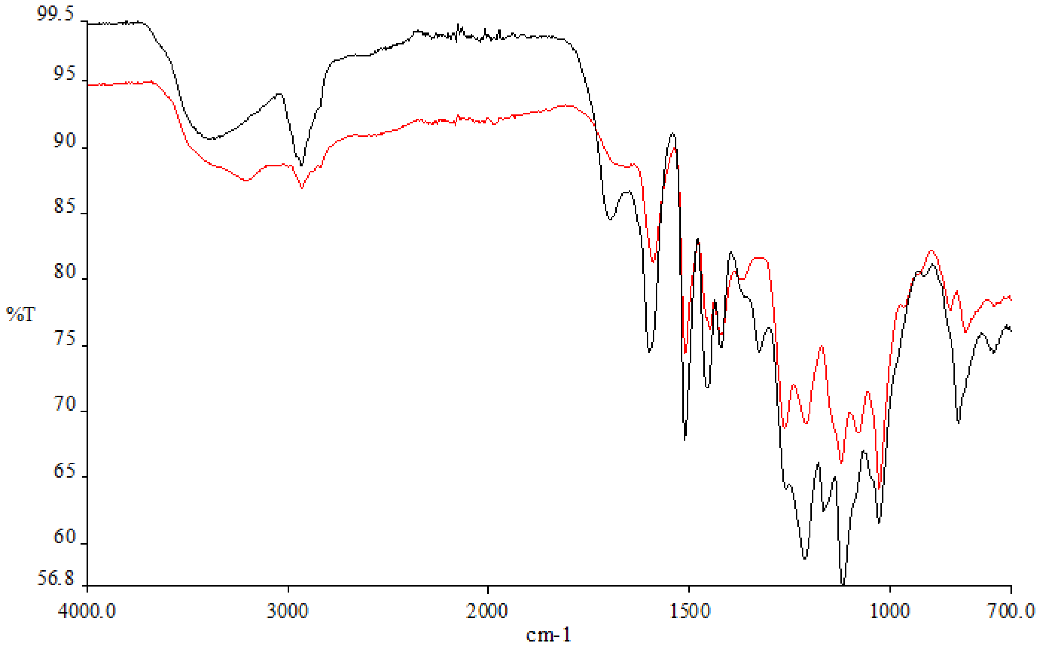
Figures



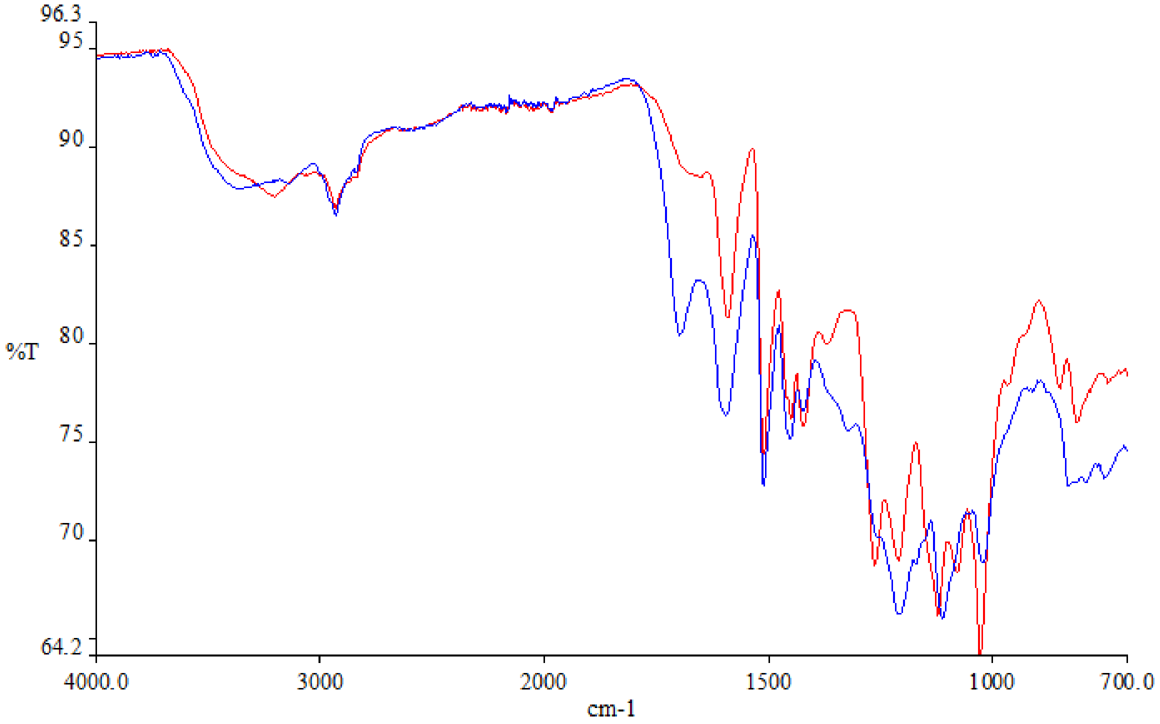
1: Biomass recovery after [C_4C_1im][$MeSO_4$]$_{80\%}$ and [C_4C_1im][HSO_4]$_{80\%}$ pretreatment at 120°C.



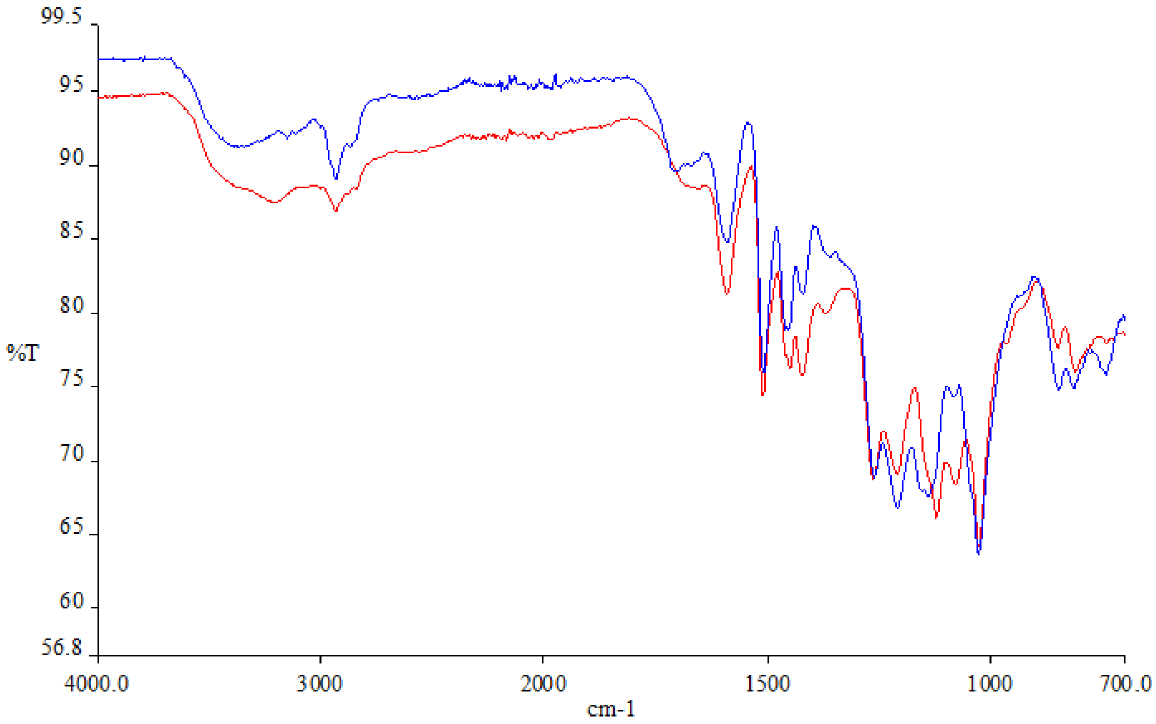
2: Delignification and precipitate yield obtained from ground Miscanthus, Willow an Pine after a 22 h treatment at 120°C with [C_4C_1im][HCO_4]$_{80\%}$ and [C_2C_1im][$MeCO_2$]$_{80\%}$. The slightly higher yield obtained from Miscanthus (compared to Figure 7 in main article) could be due to the larger batches (1.4 g instead of 0.5 g oven-dried biomass) used in this experiment, reducing the importance of losses during isolation.



3: IR spectra of lignin isolated from Miscanthus treated with $[C_4C_1im][HSO_4]_{80\%}$ for 22 h (black) and alkali lignin (Aldrich, red).



4: IR spectra of lignin isolated from Miscanthus treated with $[C_4Him][HSO_4]_{80\%}$ for 20 h (blue) and alkali lignin (Aldrich, red)



5: IR spectra of lignin isolated from pine treated with $[C_4C_1im][HSO_4]_{80\%}$ for 22 h (blue) and alkali lignin (Aldrich, red).

Elemental analysis

Table 1: Elemental composition of the lignin precipitate obtained after $[C_4C_1im][HSO_4]_{60\%}$ treatment of Miscanthus and of a reference lignin (alkali lignin, Aldrich)

	C (%)	H (%)	N (%)	S (%)
Precipitate	62.1	5.75	1.19	1.90
Alkali lignin	61.3	5.87	1.00	2.03

Ionic liquid synthesis

Methanesulfonic acid (≥99.5%), dimethyl carbonate (≥99%, anhydrous) and methanol (HPLC grade, anhydrous) were purchased from Sigma-Aldrich and used as received. 1-Butylimidazole was dried over KOH and distilled under reduced pressure. Ethyl acetate was dried over calcium hydride and distilled under a nitrogen atmosphere. Acetonitrile was dried over activated zeolithes. ^{1}H-NMR and proton-decoupled ^{13}C-NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm (relative to tetramethylsilane). LSIMS mass spectrometry was performed on a Micromass AutoSpec Premier. IR spectra were recorded on a Perkin Elmer spectrum 100 FTIR using the ATR inset with diamond crystal. Elemental analysis was carried out by the London Metropolitan University Service.

Synthesis of 1-butyl-3-methylimidazolium hydrogen sulfate, [C_4C_1im][HSO_4]

170.7 g (682 mmol) 1-butyl-3-methylimidazolium methyl sulfate (Basionic AC01, Sigma-Aldrich) was mixed with 25 ml distilled water in a round-bottomed flask with vertical Graham condenser and a horizontal Liebig condenser on top to capture the methanol. The mixture was heated to reflux for 24 h. The temperature of the cooling water in the Graham condenser was maintained at 65°C using a temperature-controlled circulator. The Liebig condenser was cooled with tap water. The ionic liquid was dried *in vacuo* at 45°C. The product was a very viscous yellowish liquid (147g, 98%).

δ_H (400 MHz; DMSO-d_6) 9.22 (1H, s, C*H*-2), 9.01 (1H, s, *H*SO_4) 7.82 (1H, s, C*H*-5), 7.74 (1H, s, C*H*-4), 4.18 (2H, t, N-C*H*$_2$-), 3.87 (3H, s, N-C*H*$_3$), 2.34 (3H, s, *H*$_3$C-SO_3), 1.73 (2H, m, N-CH_2-C*H*$_2$-), 1.20 (2H, m, N-$(CH_2)_2$-C*H*$_2$-) and 0.82 (3H, t, N-$(CH_2)_3$-C*H*$_3$). δ_C (100 MHz; DMSO-d_6) 137.18 (*C*-2), 123.98 (*C*-5), 122.74 (*C*-4), 48.84 (N-$CH_2(CH_2)_2CH_3$), 36.06 (N-CH_3), 31.88 (N-$CH_2CH_2CH_2CH_3$), 19.16 (N-$(CH_2)_2CH_2CH_3$) and 13.64 (N$(CH_2)_3CH_3$). ν(neat)/cm^{-1} 3149 3107 (aromatic C-H stretch, m), 2962 2936 2875 (aliph. C-H str., m), 1571 (arom. ring def., w), 1466 (aliph. C-H def., w), 1161 (asym. S=O str. and ring rocking, shs), 1043 (sym. O-C str., s), 1006 (sym. S=O str., s), 842 (m) and 753 (w). *m/z* (LSIMS$^+$) 139 (100%, [C_4C_1im]$^+$). *m/z* (LSIMS$^-$) 97 (100%, [$MeSO_3$]$^-$) and 333 (2, [(C_4C_1im)$(MeSO_3)_2$]$^-$). Found: C, 40.76; H 6.74, N, 11.72%. Calc. for $C_9H_{18}N_2O_3S$: C40.66; H, 6.38; N, 11.86%.

Synthesis of 1-butyl-3-methylimidazolium methanesulfonate, [C_4C_1im][$MeSO_3$]

50.0 ml (0.380 mol) 1-butylimidazole, 42 ml (0.495 mol) dimethyl carbonate and 100 ml methanol were charged into a 300 ml stainless steel pressure reactor with Teflon lining and stir bar (Parr). The mixture was heated to 140°C for 24 h, which yielded a yellowish solution. 33.7 g (351 mmol) methanesulfonic acid was added to a solution of methanol containing 351 mmol 1-butyl-3-methylimidazolium methyl carbonate. Vigorous gas formation was observed. The solvent was removed *in vacuo* until crystals appeared. The solid was recrystallised twice in acetonitrile, washed with ethyl acetate and dried under reduced pressure. The product was obtained as a white hygroscopic solid (58.5 g, 70%) with a melting point of 72°C.

δ_H (400 MHz; DMSO-d_6) 9.28 (1H, s, $C\mathit{H}$-2), 7.82 (1H, s, $C\mathit{H}$-5), 7.75 (1H, s, $C\mathit{H}$-4), 4.18 (2H, t, N-$C\mathit{H}_2$-), 3.87 (3H, s, N-$C\mathit{H}_3$), 2.34 (3H, s, H_3C-SO_3), 1.77 (2H, m, N-CH_2-$C\mathit{H}_2$-), 1.26 (2H, m, N-$(CH_2)_2$-$C\mathit{H}_2$-) and 0.90 (3H, t, N-$(CH_2)_3$-$C\mathit{H}_3$). δ_C (100 MHz; DMSO-d_6) 137.15 (*C*-2), 124.08 (*C*-5), 122.74 (*C*-4), 48.88 (N-$\mathit{C}H_2(CH_2)_2CH_3$), 40.25 ($H_3\mathit{C}$-$SO_3$) 36.14 (N-$\mathit{C}H_3$), 31.83 (N-$CH_2\mathit{C}H_2CH_2CH_3$), 19.22 (N-$(CH_2)_2\mathit{C}H_2CH_3$) and 13.72 (N$(CH_2)_3\mathit{C}H_3$). ν_{max}(neat)/cm^{-1} 3149 3103 (aromatic C-H stretch, m), 2962 2936 2876 (aliph. C-H str., m), 1573 (arom. ring def., m), 1466 (aliph. def. C-H, w), 1167 (sym. S-O str., s), 1039 (asym. S-O str., s) and 786 (S-C str., m). *m*/z (LSIMS$^+$) 139 (100%, $[C_4C_1im]^+$) and 373 (5, $[(C_4C_1im)_2MeSO_3]^+$); *m/z* (LSIMS$^-$) 95 (100%, $[MeSO_3]^-$), 329 (10, $[(C_4C_1im)(MeSO_3)_2]^-$) and 563 (4, $[(C_4C_1im)_2(MeSO_3)_3]^-$). Found: C, 45.96; H 7.92, N, 11.84%. Calc. for $C_9H_{18}N_2O_3S$: C, 46.13; H, 7.74; N, 11.96%.

Synthesis of 1-butylimidazolium hydrogen sulfate, $[C_4Him][HSO_4]$

A 250 ml aqueous solution of 95% H_2SO_4 (46 ml, 0.82 mol) was added dropwise to a 150 ml aqueous solution of butylimidazole (100 g, 0.81 mol). The mixture was stirred overnight to produce a slightly coloured liquid, which upon treating with charcoal, filtering through neutral silica and removal of water *in vacuo* yielded a colourless viscous liquid of $[C_4Him][HSO_4]$ (176 g, 99%).

δ_H (400 MHz; DMSO-d_6) 8.66 (1H, s, $N_2C\mathit{H}$), 7.60(1H, s, $NC\mathit{H}$), 7.43(1H, s, $N\mathit{H}$), 4.12 (2H, t, $NC\mathit{H}_2CH_2CH_2CH_3$), 1.75(2H, quintet, $NCH_2C\mathit{H}_2CH_2CH_3$), 1.25(2H, sextet, $NCH_2CH_2C\mathit{H}_2CH_3$) and 0.89 (3H, t, $NCH_2CH_2CH_2C\mathit{H}_3$). δ_C (100 MHz; DMSO-d_6) 136.33 (s, $N_2\mathit{C}H$), 123.05 (s, $N\mathit{C}H$), 121.58 (s, $N\mathit{C}H$), 47.86 (s, $N\mathit{C}H_2CH_2CH_2CH_3$), 32.26(s, $NCH_2\mathit{C}H_2CH_2CH_3$), 19.38 (s, $NCH_2CH_2\mathit{C}H_2CH_3$) and 13.76 (s, $NCH_2CH_2CH_2\mathit{C}H_3$). *m/z* (LSIMS$^+$) 69 (30%, $[HHim]^+$), 125 (100, $[C_4Him]^+$), 249 (5, $[(C_4Him)(C_4im)]^+$) and 347 (5, $[(C_4Him)_2(HSO_4)]^+$). *m/z* (LSIMS-) 97 ($[HSO_4]^-$, 15%), 147 (10), 195 (55, $[(HSO_4^-)(H_2SO_4)]^-$) and 280 (100). ν_{max}(neat)/cm^{-1} 3419 (N-H and O-H, b, w), 3120-3057 (aromatic C-H str., w), 2960-2581 (aliphatic C-H, w), 1950 (ring overtone, b, w), 1645 (w, C=C), 1579-1547(ring def., s), 1465(aliph. C-H def., s), 1408 (C=C, w), 1381 (CH_3, w), and 1164-1020 (S=O str. and aromatic C-H bend, s). Found: C, 37.96; H 6.45; N, 12.48%. Calc. for $C_7H_{14}N_2O_4S$: C, 37.83; H, 6.35; N, 12.60%.