# Supplementary Information

# The effect of the ionic liquid anion in the pretreatment of pine wood chips

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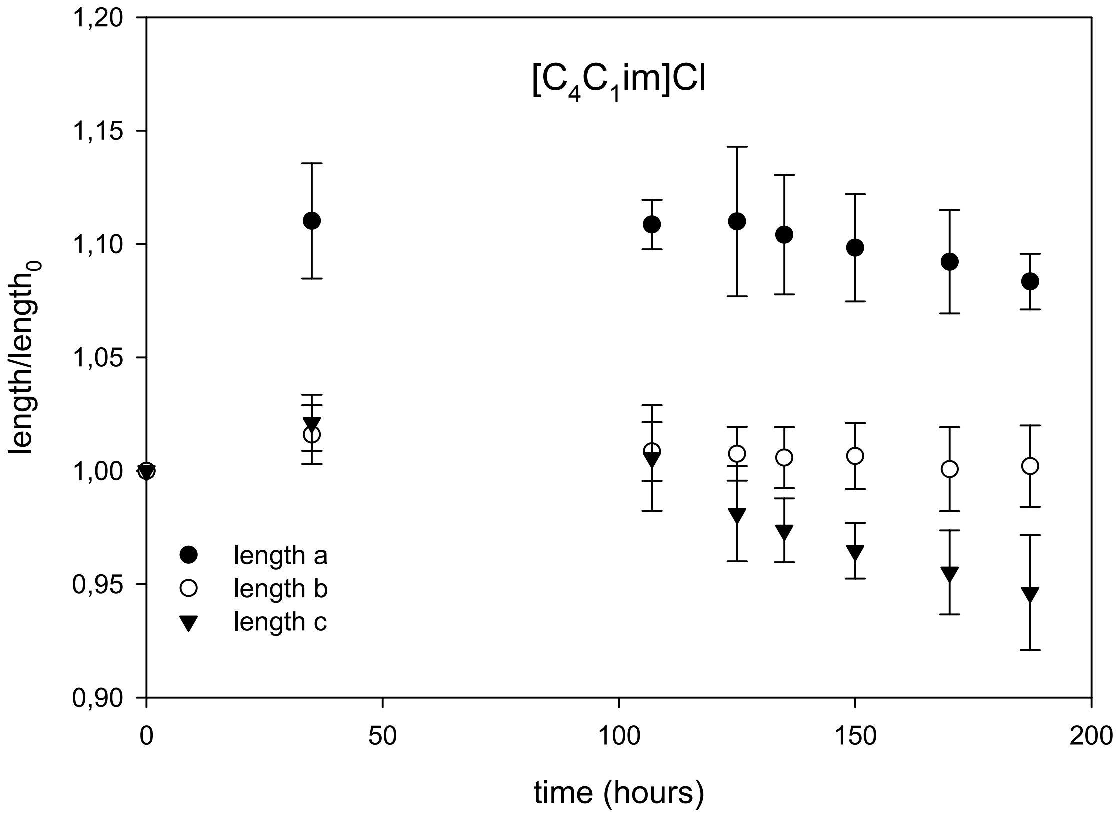

Fig. S1: Swelling and dissolution of air-dried pine wood chips in [$C_4C_1$im]Cl at 120°C. Swelling and slow dissolution of the wood chips was observed, analogous to pine chips being treated with [$C_4C_1$im][$MeCO_2$] and [$C_4C_1$im][$Me_2PO_4$].

## Synthesis of Ionic Liquids

### 1-Butyl-3-methylimidazolium chloride, [$C_4C_1$im]Cl

A solution of distilled 1-methylimidazole and dry ethyl acetate were mixed together in a round-bottomed flask. 1-Chlorobutane was added drop-wise and the mixture was stirred under a nitrogen atmosphere at 45°C for 14 days. The two-phase mixture was cooled to -20°C to allow crystallisation of the [$C_4C_1$im]Cl phase. The liquid was removed and the crystals washed five times with ethyl acetate and recrystallised in acetonitrile. The white crystals were dried and stored in the glove box for further use.

$^{1}$H-NMR (400 MHz, DMSO-d6) δ: 9.28 (1H, s, C*H*-2), 7.81 (H, s, C*H*-4), 7.74 (H, s, C*H*-5), 4.17 (2H, t, N-C$H_2$-), 3.85 (3H, s, N-C$H_3$), 1.76 (2H, m, N-$CH_2$-C$H_2$-), 1.24 (2H, m, N-$CH_2$-$CH_2$-C$H_2$-), 0.89 (3H, t, N-$CH_2$-$CH_2$-$CH_2$-C$H_3$) ppm.

1-Butyl-3-methylimidazolium bromide, [$C_4C_1$im]Br

100 ml (1.27 mol) of dry 1-methylimidazole was transferred into a dry 1L two-neck round-bottomed flask with stirring bar. 100 ml dry ethyl acetate was added and the mixture stirred. 143 ml (1.33 mol) of dry 1-bromobutane was added dropwise. The mixture was stirred at room temperature overnight. The temperature was raised to 35°C and the emulsion stirred for 4 days. The flask was cooled to -20°C in order to crystallise the [$C_4C_1$im]Br. The product was recrystallised in acetonitrile. The white crystals were dried and stored under a nitrogen atmosphere.

$^{1}$H-NMR (400 MHz, DMSO-$d_6$) δ: 9.23 (1H, s, C*H*-2), 7.80 (H, s, C*H*-4), 7.73 (H, s, C*H*-5), 4.17 (2H, t, N-C$H_2$-), 3.86 (3H, s, N-C$H_3$), 1.76 (2H, m, N-$CH_2$-C$H_2$-), 1.25 (2H, m, N-$CH_2$-$CH_2$-C$H_2$-), 0.90 (3H, t, N-$CH_2$-$CH_2$-$CH_2$-C$H_3$) ppm.

$^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ: 136.51 (s, *C*-2), 123.55 (s, *C*-4), 122.25 (s, *C*-5), 48.41 (s, N-$CH_2(CH_2)_2CH_3$), 35.76 (s, N-$CH_3$), 31.33 (s, N-$CH_2CH_2CH_2CH_3$), 18.74 (s, N-$(CH_2)_2CH_2CH_3$), 13.27 (s, N$(CH_2)_3CH_3$) ppm.

1-Butyl-3-methylimidazolium acetate, [$C_4C_1$im][$MeCO_2$]

130.2 g (0.594 mol) of [$C_4C_1$im]Br and 99.7 g (0.597 mol) of dry silver acetate were transferred into a 500 ml conical flask. The flask was covered with aluminium foil to prevent photodegradation of silver salts. 250 ml of distilled water were added and the suspension stirred overnight. The yellowish precipitate was filtered off and the filtrate tested for the presence of silver and bromide: one or two drops of the solution were diluted with 0.5 ml distilled water in a sample vial and one or two drops of test solution were added. The test solutions were dilute HCl for silver ions and 1M $AgNO_3$ for bromide. Aqueous $[C_4C_1im]Br$ was added dropwise. A sample was taken after each drop and the checked for AgCl formation with 1M silver nitrate. The addition of was stopped when the test for bromide and silver ions was negative. The solution was placed in the continuous extractor and extracted with ethyl acetate for 16 hours. The water was removed with the rotary evaporator. The ionic liquid was dried to completion using high vacuum at 60°C.

$^1$H-NMR (400 MHz, DMSO-$d_6$) $\delta$: 10.71 (1H, s, C*H*-2), 7.91 (H, s, C*H*-4), 7.83 (H, s, C*H*-5), 4.20 (2H, t, N-C$H_2$-), 3.88 (3H, s, N-C$H_3$), 1.75 (2H, m, N-$CH_2$-C$H_2$-), 1.58 (3H, m, $^-O_2C$-C$H_3$), 1.22 (2H, m, N-$CH_2$-$CH_2$-C$H_2$-), 0.87 (3H, t, N-$CH_2$-$CH_2$-$CH_2$-C$H_3$) ppm.

$^{13}$C-NMR (100 MHz, DMSO-$d_6$) $\delta$: 173.59 (s, *C*OO$^-$),137.04 (s, *C*-2), 124.02 (s, *C*-4), 122.27 (s, *C*-5), 48.41 (s, N-$CH_2(CH_2)_2CH_3$), 35.76 (s, N-$CH_3$), 31.33 (s, N-$CH_2CH_2CH_2CH_3$), 18.74 (s, N-$(CH_2)_2CH_2CH_3$), 13.27 (s, N$(CH_2)_3CH_3$) ppm.

m/z (Fab+): 139 (100%) $[C_4C_1im]^+$, 337 (14%) $[(C_4C_1im)_2CH_3CO_2]^+$. m/z (Fab-): 59 (100%) $[CH_3CO_2]^-$, 119 (61%) $[(CH_3CO_2)_2H]^-$, 257 (68%) $[(CH_3CO_2)_2(C_4C_1im)]^-$, 455 (28%) $[(C_4C_1im)_2(CH_3CO_2)_3]^-$.

1-butyl-3-methyl imidazolium dicyanamide, $[C_4C_1im][N(CN)_2]$

71.3 g (0.42 mol) of silver nitrate was dissolved in 150 ml of distilled water at 40°C. 39.2 g (0.44 mol) of sodium dicyanamide was dissolved in 150 ml of distilled water at 40°C. The silver nitrate solution was added slowly. The suspension was stirred for one hour. The precipitate was filtered and washed with 100 ml distilled water. The solid was dried at 80°C.

76.4 g (0.349 mol) of $[C_4C_1im]Br$ were dissolved in 50 ml of distilled water. 63.9 g (0.367 mol) dry silver dicyanamide was transferred into a 1L conical flask with stirring bar and 100 ml of distilled water were added. The $[C_4C_1im]Br$ solution was added dropwise. The colour of the solid changed gradually from white to yellow. The suspension was stirred overnight in a flask covered with aluminium foil. The precipitate was removed by filtration. Testing for silver ions (with dilute HCl) indicated that the amount of silver ions was below the detection limit. Bromide content could not be checked, because the dicyanamide anion forms a sparingly soluble precipitate with silver nitrate. The crude product was purified by continuous extraction with dichloromethane for 3 days. The dichloromethane phase was isolated and the solvent removed with the rotary evaporator. The ionic liquid dried to completion under high vacuum at 40°C. A second extraction of the water phase for 5 days yielded more $[C_4C_1im][N(CN)_2]$. The product was a clear, slightly greenish liquid. The combined yield was 51.3 g (0.250 mol; 71.6%).

$^1$H-NMR (400 MHz, DMSO-$d_6$) δ: 9.10 (1H, s, C*H*-2), 7.75 (H, s, C*H*-4), 7.68 (H, s, C*H*-5), 4.17 (2H, t, N-$CH_2$-), 3.85 (3H, s, N-$CH_3$), 1.77 (2H, m, N-$CH_2$-$CH_2$-), 1.26 (2H, m, N-$CH_2$-$CH_2$-$CH_2$-), 0.89 (3H, t, N-$CH_2$-$CH_2$-$CH_2$-$CH_3$) ppm.

$^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ: 136.96 (s, *C*-2), 124.02 (s, *C*-4), 122.68 (s, *C*-5), 199.55 (s, N*C*N*C*N) 49.00 (s, N-$CH_2(CH_2)_2CH_3$), 36.17 (s, N-$CH_3$), 31.80 (s, N-$CH_2CH_2CH_2CH_3$), 19.32 (s, N-$(CH_2)_2CH_2CH_3$), 13.65 (s, N$(CH_2)_3CH_3$) ppm.

m/z (Fab+): 139 (100%) $[C_4C_1im]^+$, 344 (8%) $[(C_4C_1im)_2(N(CN)_2)]^+$. m/z (Fab-): 66 (100%) $[N(CN)_2]^-$.

1-butyl-3-methyl imidazolium dimethylphosphate, $[C_4C_1im][Me_2PO_4]$

112.5 g (905.0 mmol) of distilled 1-butylimidazole was mixed with 100 ml ethyl acetate. 126.8 g (905.3 mmol) of dry trimethyl phosphate was added dropwise. The mixture was stirred under nitrogen atmosphere at 80°C for 20 hours. 50 ml of distilled water were added. The solution was placed in the continuous extractor and extracted with toluene for 16 hours in order to remove excess reactants. The aqueous phase was isolated and the water was removed and the ionic liquid dried to completion at 120°C. The product was a clear, colourless, oily liquid. The yield was 183 g (0.692 mol, 76.5%).

$^1$H-NMR (400 MHz, DMSO-$d_6$) δ: 9.92 (1H, s, C$H$-2), 8.05 (H, s, C$H$-4), 7.94 (H, s, C$H$-5), 4.22 (2H, t, N-C$H_2$-), 3.91 (3H, s, N-C$H_3$), 3.32 (6H, d, $H_3$C-O-P), 1.75 (2H, m, N-$\mathrm{CH_2}$-C$H_2$-), 1.21 (2H, m, N-$\mathrm{CH_2}$-$\mathrm{CH_2}$-C$H_2$-), 0.84 (3H, t, N-$\mathrm{CH_2}$-$\mathrm{CH_2}$-$\mathrm{CH_2}$-C$H_3$) ppm.

$^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ: 137.73 (s, $C$-2), 124.07 (s, $C$-4), 122.78 (s, $C$-5), 51.70 (d, $\mathrm{H_3}C$-O-P) 48.81 (s, N-$C\mathrm{H_2(CH_2)_2CH_3}$), 36.00 (s, N-$C\mathrm{H_3}$), 31.90 (s, N-$\mathrm{CH_2}C\mathrm{H_2CH_2CH_3}$), 19.22 (s, N-$\mathrm{(CH_2)_2}C\mathrm{H_2CH_3}$), 13.69 (s, $\mathrm{N(CH_2)_3}C\mathrm{H_3}$) ppm.

m/z (Fab+): 139 (100%) $[\mathrm{C_4C_1im}]^+$, 403 $[(\mathrm{C_4C_1im})_2\mathrm{Me_2PO_4}]^+$; m/z (Fab-): 125 (100%) $[\mathrm{Me_2PO_4}]^-$.

### 1-butyl-3-methyl imidazolium methylsulfate, $[\mathrm{C_4C_1im}][\mathrm{MeSO_4}]$

135 g (1.09 mol, 143 ml) dry n-butylimidazole was transferred into a 1L two-neck round bottomed flask with large stirring bar. 200 ml of dry toluene were added. The flask was placed in an ice bath. 103 ml (1.09 mol) of dry dimethylsulfate was added dropwise. The stirring was continued for 1 hour at room temperature. The top phase was decanted and the lower phase was washed three times with 50 ml of toluene. The ionic liquid was dried under vacuum. The product was a colourless, viscous liquid. The yield was 193 g (70.8%).

$^1$H-NMR (400 MHz, DMSO-$d_6$) δ: 9.12 (1H, s, C$H$-2), 7.79 (H, s, C$H$-4), 7.71 (H, s, C$H$-5), 4.17 (2H, t, N-C$H_2$-), 3.86 (3H, s, N-C$H_3$), 3.41 (3H, s, $H_3$C-O-S), 1.76 (2H, m, N-$\mathrm{CH_2}$-C$H_2$-), 1.24 (2H, m, N-$\mathrm{CH_2}$-$\mathrm{CH_2}$-C$H_2$-), 0.87 (3H, t, N-$\mathrm{CH_2}$-$\mathrm{CH_2}$-$\mathrm{CH_2}$-C$H_3$) ppm.

$^{13}$C-NMR (100 MHz, DMSO-$d_6$) δ: 137.04 (s, *C*-2), 124.02 (s, *C*-4), 122.72 (s, *C*-5), 53.41 (s, $H_3$*C*-O-S) 48.92 (s, N-*C*$H_2(CH_2)_2CH_3$), 36.09 (s, N-*C*$H_3$), 31.84 (s, N-$CH_2$*C*$H_2CH_2CH_3$), 19.20 (s, N-$(CH_2)_2$*C*$H_2CH_3$), 13.66 (s, N$(CH_2)_3$*C*$H_3$) ppm.

m/z (Fab+): 139 (100%) $[C_4C_1im]^+$, 389 (4%) $[(C_4C_1im)_2MeSO_4]^+$. m/z (Fab-): 111 (100%) $[MeSO_4]^-$, 361 (3%) $[(C_4C_1im)(MeSO_4)_2]^-$.