

# Supplementary Materials: Direct Catalytic Conversion of Cellulose to 5-Hydroxymethylfurfural Using Ionic Liquids

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## S1. The Synthesis of 5-Hydroxymethylfurfural (HMF) from Cellulose under Dry Conditions

The following two experiments were performed in duplicates in order to compare  $^1\text{H-NMR}$  spectroscopy and HPLC for the quantitative analysis of HMF synthesised in this system. Rigorously dry environments were employed to ensure that both techniques were analysing under the same conditions. All reagents were purchased from Sigma-Aldrich whereas  $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$  was synthesised and purified as described previously [52]. 1-butyl-3-methylimidazolium chloride ( $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$ ), cellulose (Sigmacell, 20  $\mu\text{m}$ ) and chromium(III) chloride hexahydrate ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ) are hygroscopic; therefore their handling and storage was carried out in a glovebox ( $\text{N}_2$  atmosphere). The glovebox water content was controlled in the presence of molecular sieves and the moisture and oxygen content was kept below 5 ppm. All handling was performed under air-free conditions, using standard Schlenk line techniques. The neat ionic liquid was dried under vacuum before use (24 h, 35  $^\circ\text{C}$ , 1.6 mbar).

According to the conditions in Table S1, cellulose was mixed with chromium(III) chloride hexahydrate in a 25 mL two-necked round bottom flask containing dry  $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$ . The reaction mixture was stirred at the indicated temperature for the set amount of time and samples were taken and analysed by both  $^1\text{H-NMR}$  spectroscopy (in  $d_6\text{-DMSO}$ ) and HPLC in order to calculate the yield of 5-hydroxymethylfurfural (HMF).

**Table S1.** Summary of reaction conditions of the direct HMF synthesis from cellulose.

Conditions	Experiment 1	Experiment 2
Cellulose	100 mg (0.62 mmol)	25 mg (0.15 mmol)
$[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$	700 mg (4.03 mmol)	700 mg (4.03 mmol)
$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	10.4 mg (6.3 mol %)	2.6 mg (6.3 mol %)
Temperature	120 $^\circ\text{C}$	150 $^\circ\text{C}$
Time	3 h	1 h

The reactions were performed in duplicate.

## S2. Quantitative Analysis of HMF Yield by HPLC

A sample was taken from the crude reaction mixture (13–17 mg) and mixed with 40 mg of water in a 1.5 mL centrifuge tube. The mixtures were vortex-mixed until a homogenous sample was obtained and centrifuged at maximum speed for 5 min. The supernatant was transferred to an HPLC vial with a 200  $\mu\text{L}$  insert and HPLC analysis was performed on a Shimadzu Prominence instrument (Shimadzu, Kyoto, Japan) with refractive index (RI) and ultraviolet (UV) detector. The HPLC column used was an Aminex HPX-87H column (Bio-Rad Laboratories, Hemel Hempstead, UK) with aqueous 10 mM sulfuric acid as the eluent. The column temperature was set at 55  $^\circ\text{C}$ , the flow rate and the injection volume were 0.6 mL/min and 10  $\mu\text{L}$  respectively with a run time of 45 min. Three standard mixtures, each containing a different amount of glucose (0.1, 1, 2, 4 mg/mL), fructose (0.1, 0.2, 0.4, 1 mg/mL) and HMF (0.1, 1, 2, 4 mg/mL) were prepared. Sugars were identified and quantified using the refractive index detector (RID) signal and HMF using the 210 nm photodiode array (PDA) signal of the UV/Vis trace. The retention times were 8.59 min (RID), 28.59 min (PDA) and 9.28 min (RID) for glucose, HMF and fructose respectively. The concentration in the HPLC samples was determined using the regression equations of the resulting calibration curves (Figure S1).

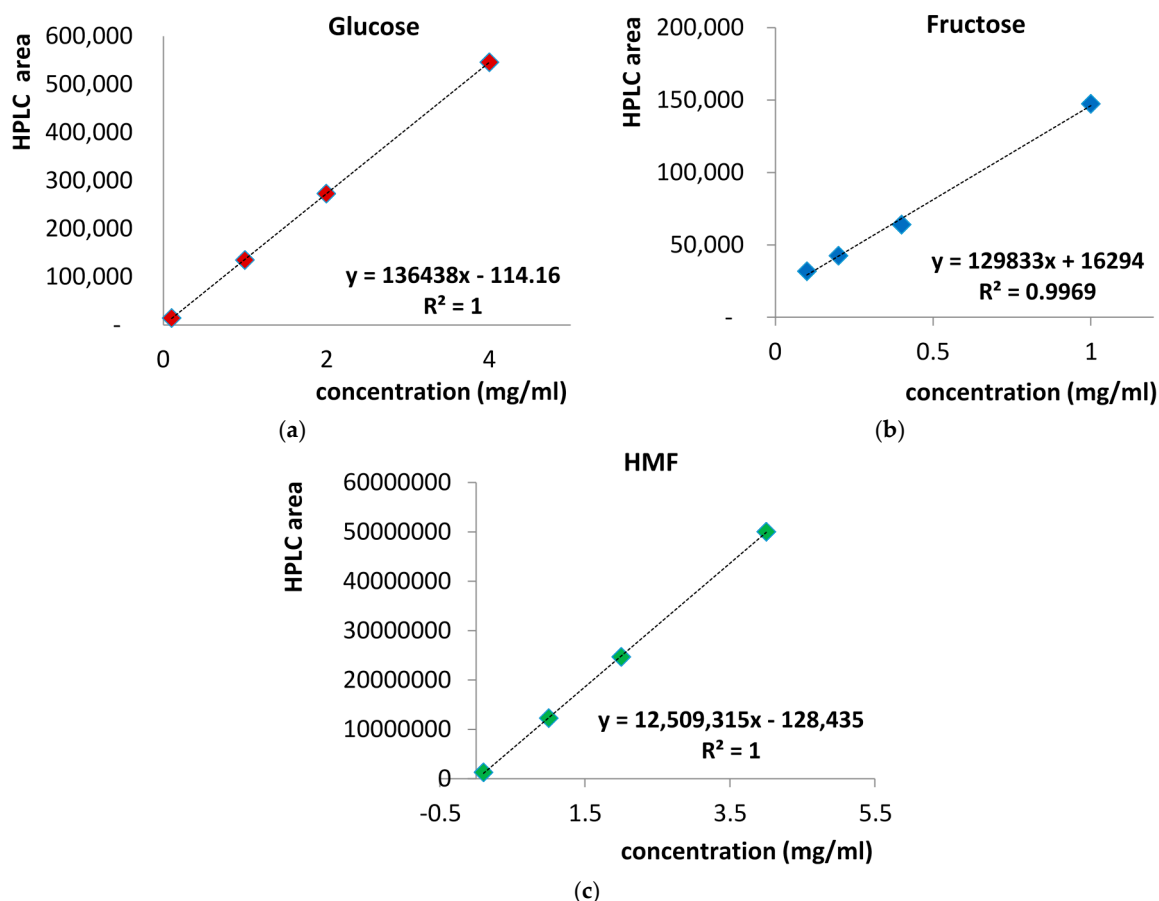


Figure S1. HPLC calibration curves; (a) glucose; (b) fructose & (c) HMF.

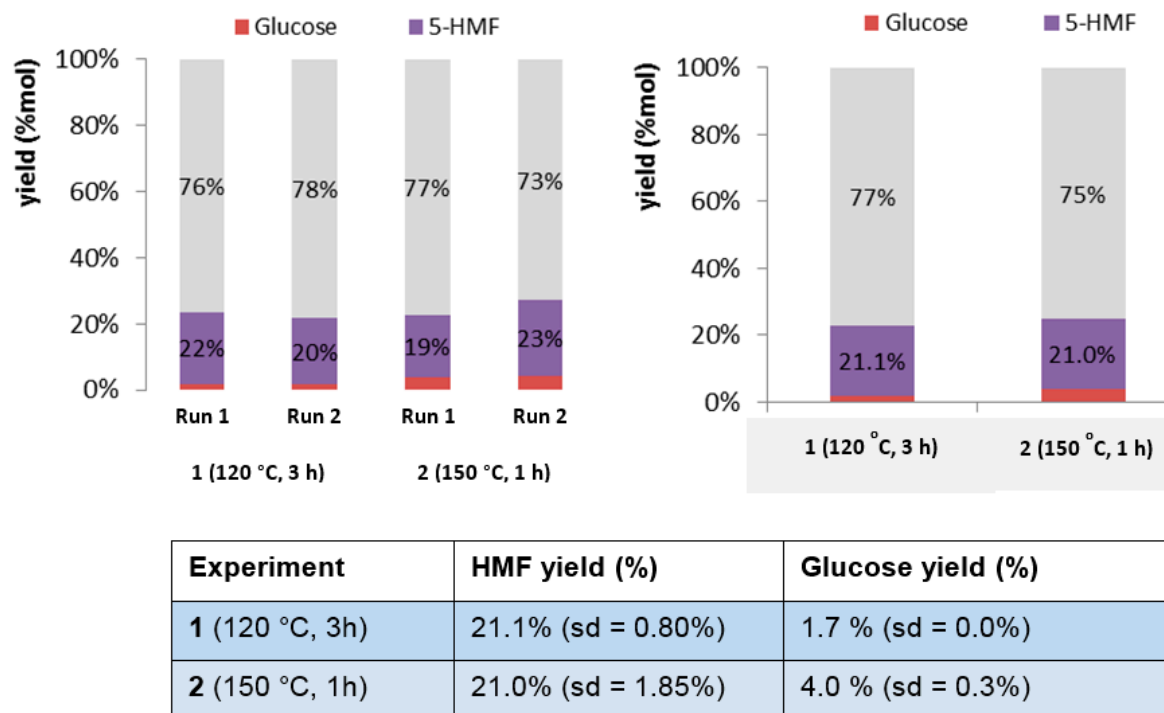
The concentration of glucose, fructose and HMF in the HPLC samples was converted into the concentration in the ionic liquid, followed by the calculation of the product yield (mol %) based on the initial cellulose concentration and the dilution factors applied to the HPLC samples (Table S2). More specifically, the HMF yield (mol %) was calculated by the applying the following equations:

$$(\text{HMF mmol}) = \frac{\left[ \left( \frac{C_{\text{HMF/HPLC}}}{\text{DF}} \right) * V([C_4\text{C}_{1\text{im}}]\text{Cl}) \right]}{M_w(\text{HMF})}$$

$$(\text{HMF } \%) = \frac{n_{\text{HMF}}(\text{mmol})}{\left( \frac{m_{\text{cellulose}}}{M_w(\text{G})} \right)}$$

Assumptions: (i) IL density:  $d_{[C_4C_{1im}]Cl} = 1.081 \text{ g/mL}$ ; (ii)  $V([C_4C_{1im}]Cl)$ : IL volume (mL); (iii)  $C_{\text{HMF/HPLC}}$  (mg/mL): HMF concentration in the HPLC samples; (iv) DF: dilution factor; (v)  $M_w(\text{G}) = M_w(\text{glucose units}) - M_w(\text{H}_2\text{O}) = 162.16 \text{ g/mol}$ .

Fructose was detected at negligible concentrations whereas only small amounts of glucose (1.8–4.3 mol %) were found in the crude reaction mixture at both experimental conditions (150 °C for 1 h and 120 °C for 3 h). Both experimental conditions gave similar HMF yields (21%) as illustrated in Figure S2 with the remainder being glucose (red) and other species (mainly unreacted cellulose plus some byproducts) shown in grey, accounting for more than 70%.



**Figure S2.** Average yields of HMF, glucose and combined other species (unreacted cellulose, byproducts), shown in grey, under different experimental conditions.

### S3. Quantitative Analysis of HMF Yield by $^1\text{H}$ -NMR Spectroscopy

The yields for Experiment 1 and 2 were determined by both  $^1\text{H}$ -NMR spectroscopy and HPLC chromatography in order to compare the two methods for their efficiency in quantitative analysis. The peak corresponding to the  $\text{C}^2$ -proton of the imidazolium ring ( $[\text{C}_4\text{C}_{1\text{im}}]^+$ ) was chosen as a reference peak for the solvent, given that it does not interfere with any product peaks. The amount of  $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$  in the flask is considered to be stable during the reaction. The HMF yield was calculated based on the known molar amount of the ionic liquid relative to the amount of cellulose added and thus the reaction yield was obtained.

Initially, to test the NMR integration itself, a known amount of commercial HMF was added to a known amount of  $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$  and both were mixed with  $\text{d}^6$ -DMSO in the absence of a catalyst. The sample was prepared under dry conditions (glove box) at room temperature, while another sample was prepared after mixing at 150 °C for 1 h in order to monitor any effect of heating on the stability of HMF.

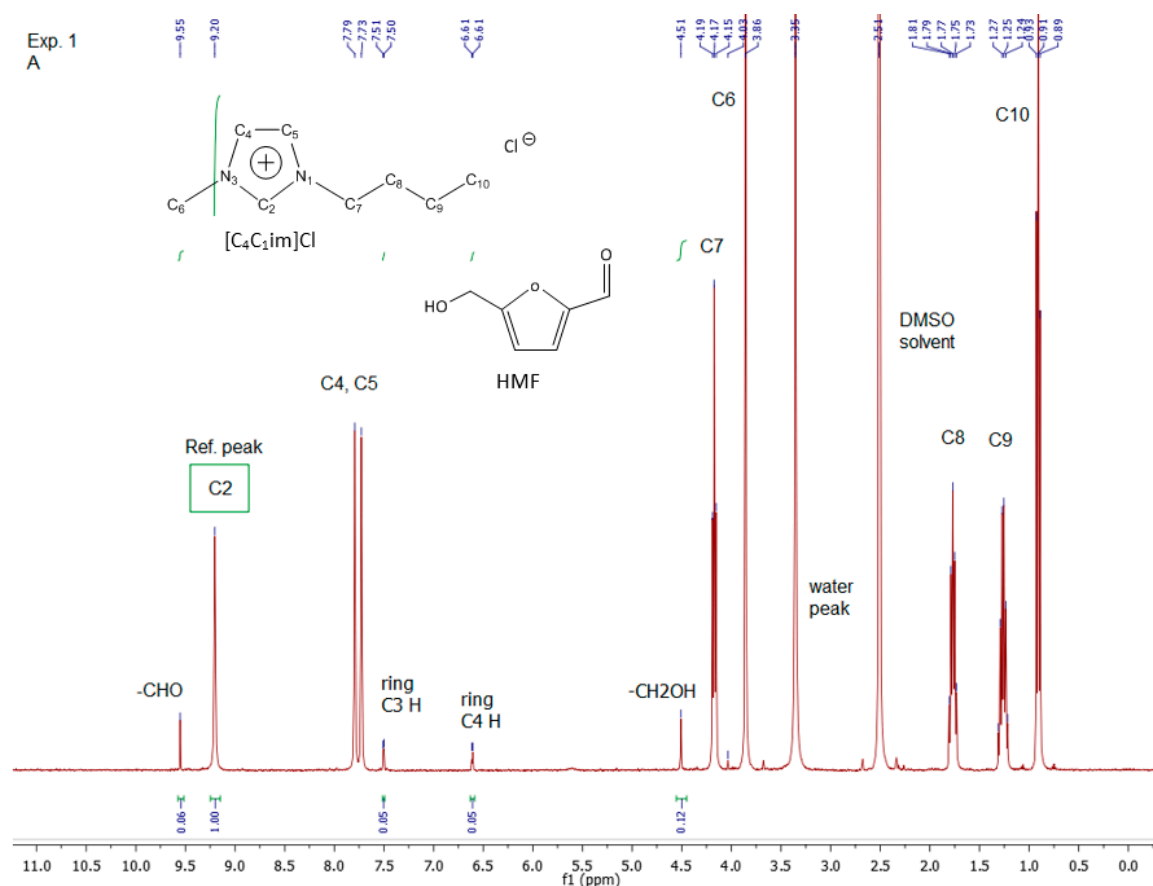
While the resonance chosen for determining the yield in the results presented in the main text was that at 9.55 ppm, here a number of HMF peaks were integrated (Table S2). This revealed that the  $^1\text{H}$ -NMR spectroscopic technique shows some variation dependent on which HMF peak is chosen for integration against the ionic liquid resonance. This may be explained in part by the difficulty in determining the area of the peak to be integrated (human error plus baseline noise), which results in under- or overestimation of the product yield depending on the peak chosen. Table S2 further reveals that the integration of the standard solution results in an underestimation of the yield at room temperature. Moreover, the results summarised in Table S2 indicate that HMF appears to show some instability on heating at 150 °C in the presence of  $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$ , as reflected in the reduced molar concentrations of HMF in the 150 °C standard sample.

**Table S2.** Integration of HMF  $^1\text{H}$ -NMR resonances against those of  $[\text{C}_4\text{Cim}]\text{Cl}$  and comparison of resulting yields with those determined by prior weighing.

$\delta$ (ppm)	HMF Integral <sup>b</sup>	HMF (mmol)	% HMF vs. Theoretical	HMF Integral <sup>b</sup>	HMF (mmol)	% HMF vs. Theoretical
Mixed at Room Temperature			Mixed at 150 °C for 1 h <sup>a</sup>			
9.55 ( $\text{CHO}$ )	0.28	0.372	76.3%	0.14	0.193	60.9%
7.50 (ring $\text{C}^3\text{H}$ )	0.35	0.465	95.3%	0.16	0.221	69.6%
6.60 ( $\text{C}^4\text{H}$ )	0.34	0.452	92.6%	0.15	0.207	65.2%
5.56 ( $-\text{OH}$ )	0.38	0.505	103.5%	0.19	0.262	82.6%
4.50 ( $\text{CH}_2\text{OH}$ )	0.78	0.518	106.2%	0.39	0.269	84.8%

<sup>a</sup> Mixing of  $[\text{C}_4\text{Cim}]\text{Cl}$  with HMF prior to dissolution in  $\text{d}^6$ -DMSO; <sup>b</sup> Reference peak:  $\text{C}^2$ -proton peak of  $[\text{C}_4\text{Cim}]\text{Cl}$ .

Next, the reaction Mixtures 1 and 2 (obtained from Reactions 1 and 2 described in Section S1) were also analysed by  $^1\text{H}$ -NMR spectroscopy in order to compare the NMR spectroscopically-determined yields with those from the HPLC analysis. A typical  $^1\text{H}$ -NMR spectrum of the reaction mixture and the applied integration method are shown below in Figure S3.

**Figure S3.**  $^1\text{H}$ -NMR spectrum of the reaction mixture (obtained as described in Section S1) on heating the reagents at 120 °C for 3 h.

As described above, some deviation was observed between the HMF yield calculated using different HMF peaks in the  $^1\text{H}$ -NMR spectrum. Since the quantitative  $^1\text{H}$ -NMR spectroscopy technique is therefore sensitive to which HMF peak is chosen, an average yield is reported (Tables S3 and S4). The use of smaller amounts of cellulose in Experiment 2 (Table S4) and thus the reduced HMF concentration in the melt is likely to increase the uncertainty of the percentage yield calculations, due to the larger excess of the ionic liquid.

Analysing the  $^1\text{H}$ -NMR spectra for both sets of samples, it can be concluded that similar average HMF yields were obtained at both higher (150 °C, 1 h, 34% yield) and lower temperature (120 °C, 3 h, 36% yield) conditions in the presence of the same catalyst loading (6.3 mol %). This is the same conclusion drawn from the HPLC analysis (Figure S2).

**Table S3.** Experiment 1: Yield of HMF (120 °C for 3 h) in  $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$  with  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (6.3 mol %) as determined by  $^1\text{H}$ -NMR spectroscopy.

$\delta$ (ppm)	HMF Integral <sup>a</sup>	HMF (mmol)	HMF Yield (%)	HMF Integral <sup>a</sup>	HMF (mmol)	HMF Yield (%)
		Run 1			Run 2	
9.55 ( $\text{CH}_\text{O}$ )	0.06	0.240	39.0%	0.05	0.200	32.5%
7.50 (ring $\text{C}^3\text{H}$ )	0.05	0.200	32.5%	0.05	0.200	32.5%
6.60 ( $\text{C}^4\text{H}$ )	0.05	0.200	32.5%	0.05	0.200	32.5%
4.50 ( $\text{CH}_2\text{OH}$ )	0.12	0.240	39.0%	0.12	0.240	39.0%
Average			35.7%			34.1%

<sup>a</sup> Reference peak:  $\text{C}^2$ -proton peak of  $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$ .

**Table S4.** Experiment 2: Yield of HMF (150 °C for 1 h) in  $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$  with  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (6.3 mol %) as determined by  $^1\text{H}$ -NMR spectroscopy.

$\delta$ (ppm)	HMF Integral <sup>a</sup>	HMF (mmol)	HMF Yield (%)
9.55 ( $\text{CH}_\text{O}$ )	0.01	0.200	26.0%
7.50 (ring $\text{C}^3\text{H}$ )	0.02	0.200	52.0%
6.60 ( $\text{C}^4\text{H}$ )	0.01	0.200	26.0%
4.50 ( $\text{CH}_2\text{OH}$ )	0.03	0.240	39.0%
Average			35.7%

<sup>a</sup> Reference peak:  $\text{C}^2$ -proton peak of  $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$ .

Comparing the yields determined by HPLC analysis and  $^1\text{H}$ -NMR spectroscopy, it appears that approximately 13%–15% higher yields are provided by the NMR spectroscopy method (where the ionic liquid is used as the internal standard) compared to the HPLC technique which uses an external standard. It is not entirely clear why this should be the case. It is also worth noting that the yields calculated by both methods (NMR spectroscopy and HPLC) were consistent in showing that both reaction conditions tested yielded similar molar concentrations of HMF.