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Direct Conversion of Mono- and Polysaccharides into 5-Hydroxymethylfurfural Using Ionic-Liquid Mixtures

Sviatlana Siankevich,[a] Zhaofu Fei,[a] Rosario Scopelliti,[a] Philip G. Jessop,[b] Jiaguang Zhang,[c] Ning Yan,*[c] and Paul J. Dyson*[a]

Platform chemicals are usually derived from petrochemical feedstocks. A sustainable alternative commences with lignocellulosic biomass, a renewable feedstock, but one that is highly challenging to process. Ionic liquids (ILs) are able to solubilize biomass and, in the presence of catalysts, convert the biomass into useful platform chemicals. Herein, we demonstrate that mixtures of ILs are powerful systems for the selective catalytic transformation of cellulose into 5-hydroxymethylfurfural (HMF). Combining ILs with continuous HMF extraction into methylisobutyl ketone or 1,2-dimethoxyethane, which form a biphase with the IL mixture, allows the online separation of HMF in high yield. This one-step process is operated under relatively mild conditions and represents a significant step forward towards sustainable HMF production.

Introduction

It is envisaged that renewable commodity chemicals derived from lignocellulosic biomass could eventually replace petrochemical derived feedstocks.[1] Currently, a wide and diverse range of different chemicals may be obtained from biomass and many processes are under development. The conversion of various cellulosic derivatives to 5-hydroxymethylfurfural (HMF) represents a key route as HMF can be subsequently transformed into many useful compounds (Figure 1).[1a, 2] Breaking down lignocellulosic polymers is challenging and most of the synthetic routes employed require harsh reaction conditions. In this context, ionic liquids (ILs) are promising solvents for the transformation of carbohydrates[3] as they are able to dissolve biomass[4] and, consequently, facilitate biomass pretreatment and breakdown. Certain ILs may even be derived from lignocellulosic materials.[5]

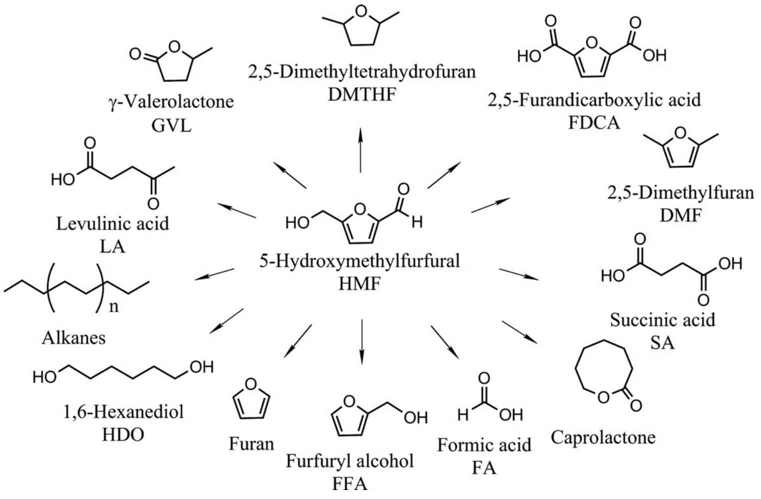

Figure 1. Examples of commodity chemicals derived from HMF.

The synthesis of HMF from fructose and glucose may be enhanced when ILs are employed as the reaction media relative to other classes of solvents.[1a,c,d,4,6] Notably, imidazolium chloride ILs have an exceptionally high capacity for dissolving carbohydrates, attributable to the formation of extensive hydrogen bonding interactions that disrupt the macromolecular structure.[3b,7] When ILs are combined with transition metal catalysts, for example, chromium(II) chloride, HMF can be efficiently generated from simple sugars.[1c,8] However, despite the ability of ILs and IL/catalyst mixtures to solubilize cellulose and transform simple sugars, the direct conversion of cellulose into HMF in IL/$CrCl_2$ solutions has proven elusive.

Cellulose possesses significant thermal and chemical stability and its transformation into chemical products is challenging with only a limited number of solvent systems having been found to facilitate the conversion of cellulose into sugar monomers. Examples include lithium chloride in *N*,*N*-dimethylacetamide,[9] *N*-methyl-2-pyrrolidine,[10] 1,3-dimethyl-2-imidazolidinone,[11] dimethyl sulfoxide/paraformaldehyde,[12] *N*-methylmor-

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[a] *Dr. S. Siankevich, Dr. Z. Fei, Dr. R. Scopelliti, Prof. P. J. Dyson*
Institut des Sciences et Ingénierie Chimiques
Ecole Polytechnique Fédérale de Lausanne (EPFL)
1015, Lausanne (Switzerland)
E-mail: paul.dyson@epfl.ch

[b] *Prof. P. G. Jessop*
Department of Chemistry
Queen's University
Kingston, Ontario K7L 3N6 (Canada)

[c] *Dr. J. Zhang, Prof. N. Yan*
Department of Chemical and Biomolecular Engineering
National University of Singapore
4 Engineering Drive 4, 117585, Singapore (Singapore)
E-mail: ning.yan@nus.edu.sg

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pholine-*N*-oxide,[13] molten salt hydrates including $LiClO_4·3H_2O$ and $LiSCN·2H_2O$,[14] and some aqueous solutions containing, for example, cadmium or nickel complexes.[15] However, these systems are often based on toxic and volatile solvents, which are difficult to recover and reuse, and some of the systems are unstable. Consequently, none of the solvents mentioned above are, to the best of our knowledge, currently used to produce sugar monomers from cellulose on an industrial scale, although *N*-methylmorpholine-*N*-oxide and water are used to manufacture regenerated cellulose fibers and films.[16] Nevertheless, the high temperatures required to dissolve and degrade cellulose in *N*-methylmorpholine-*N*-oxide result in solvent decomposition and high operating costs.

In contrast, aqueous solutions comprising NaOH/urea, NaOH/thiourea, and LiOH/urea dissolve cellulose at relatively low temperatures.[17] Another promising system is based on an inexpensive mixture of γ-valerolactone/water/H_2SO_4 that dissolves biomass, including the lignin fraction.[18] Interestingly, γ-valerolactone can be obtained by the catalytic hydrogenation of levulinic acid which itself is accessible from the hydrolysis of lignocellulosic biomass.[2b,19]

As alternatives to conventional mineral acids (e.g., H_2SO_4 and HCl), the hydrolysis of cellulose with solid acid catalysts is perceived to be a more environmentally benign approach as their use simplifies downstream processing.[20] In this context, ILs containing acidic units[21] may potentially dissolve and selectively deconstruct biomass while simultaneously catalyzing reactions.[22] Sulfonic acid ($-SO_3H$) functionalized ILs and catalysts are highly efficient for the selective conversion of simple sugars into HMF,[21a] and their activity may be modulated by immobilization on different support structures.[3a,23] Many other ILs have also potential to convert simple sugars into HMF in combination with $CrCl_2$ employed as a catalyst.[24] However, to the best of our knowledge, complex polysaccharides and cellulose cannot be converted using IL/$CrCl_2$ systems, thus necessitating an additional step to first generate simple sugars from cellulose, which leads to significantly higher production costs.

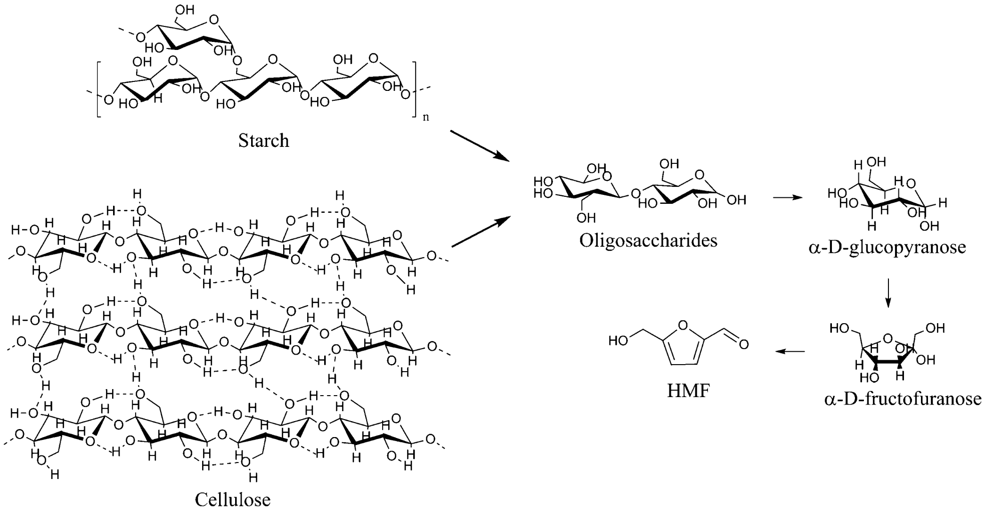
Herein, we show how the application of a combination of appropriately functionalized ILs with $CrCl_2$ affords HMF from glucose under mild conditions in high yield and suppresses the formation of unwanted by-products. This one-step process operates under relatively mild conditions and represents a significant step towards a renewable route for HMF production from cellulose.

Results and Discussion

Initial studies were conducted with glucose (rather than cellulose itself) as glucose is the predominant building unit of the most abundant carbohydrate polymers and an intermediate in the dehydration process (Scheme 1). The imidazolium-based IL, **IL 1** (see Figure 2), combined with $CrCl_2$ in [C_2OHmim]Cl was previously shown to catalyze the dehydration of glucose to HMF in good yield (i.e., 63%).[8b] Therefore, we investigated a series of ILs with various modified imidazolium cations under similar conditions to those used previously. Absolute trends are difficult to determine from the data. For example, the acidic 2-proton in **IL 2** does not appear to be essential to give a high yield of HMF as the yield obtained in **IL 3** (with a methyl group instead of the 2-proton) leads to a slightly higher yield of HMF (73 vs. 62%) under the same reaction conditions. However, the reverse trend is observed for the IL pair **IL4** and **IL5**, where the former IL with a 2-proton gives a considerably higher yield of HMF (92 vs. 70%).

The introduction of an additional $-CH_2CH_2Ph$ group on the imidazolium cation enhances HMF formation with the application of **IL 4** considerably, enhancing the yield of HMF (92% after 2 h reaction). Others ILs were explored, that is, **IL 5**–**IL 8**, but none improved the catalytic activity to the same extent as **IL 4**.

A kinetic analysis of the [C_2OHmim]/**IL 1** and [C_2OHmim]/**IL 4** systems was performed (Figure 3) revealing differences between the conversion of glucose to fructose and subsequent dehydration of fructose to HMF. For the system with **IL 4**, complete consumption of glucose was achieved within 2 h with



Scheme 1. Dehydration of cellulose and starch to HMF.

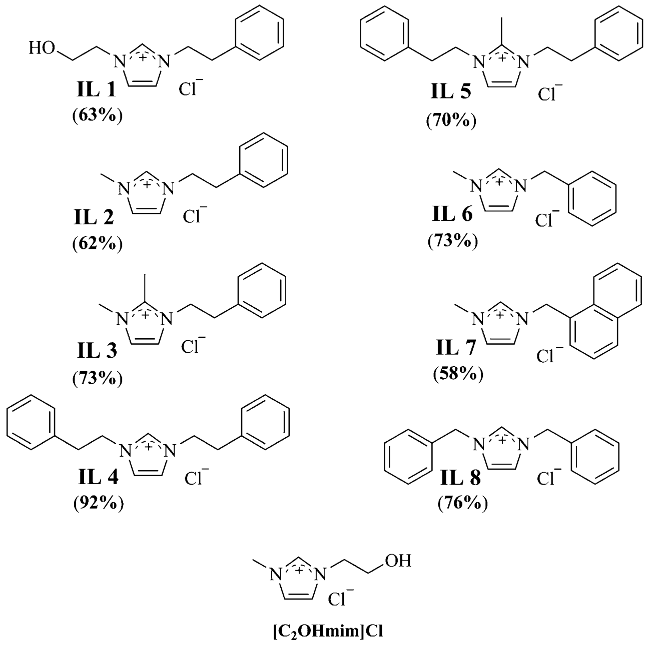


Figure 2. Modified ILs combined with [C$_2$OHmim]Cl and CrCl$_2$ evaluated in the dehydration of glucose to HMF. Yield of HMF obtained from glucose is given in parenthesis. Conditions: [C$_2$OHmim]Cl (450 mg) IL (50 mg), glucose (0.28 mmol, 50 mg), CrCl$_2$ (0.019 mmol, 2.3 mg), 100 °C, 2 h.

the maximum concentration of fructose observed after only 20 min. In contrast, with the system incorporating **IL 1**, 25 % of glucose remains unconverted at 2 h and the concentration of fructose peaks around 45 min. At longer reaction times, the [C$_2$OHmim]/**IL 1** system results in the formation of humins. Moreover, in the [C$_2$OHmim]/**IL 4** system, HMF displays outstanding stability properties and is less prone to decomposition (see the Experimental Section for further details).

NMR studies were performed using C$_6$- and C$_1$-enriched ^{13}C glucose to elucidate the influence of the –CH$_2$CH$_2$Ph groups in **IL 4** on the reaction mechanism. Taking into account the stability of HMF in the reaction medium and the proposed reaction mechanism (Scheme 2),[9] it may be assumed that either the isomerization of glucose to keto-fructose or the isomerization

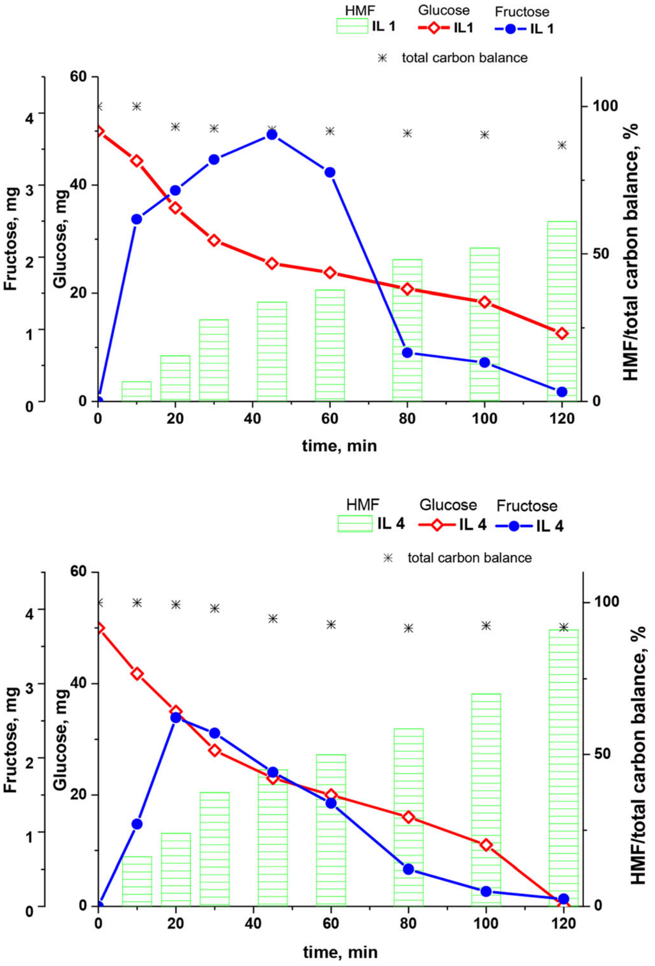
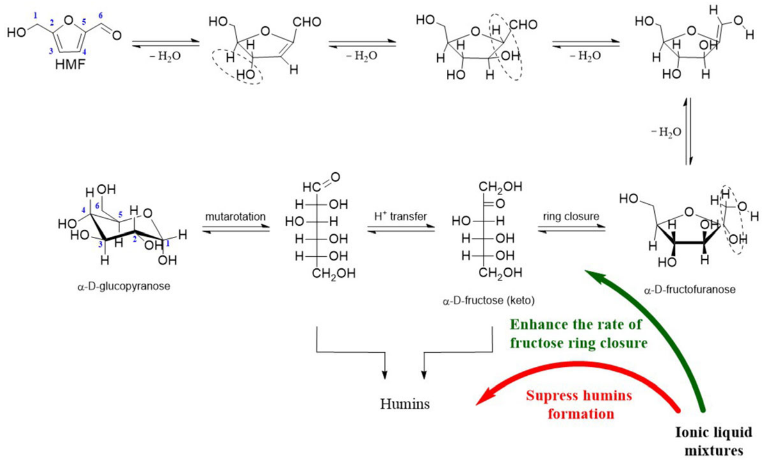


Figure 3. Conversion of glucose/formation of fructose and its dehydration to HMF as a function of time for [C$_2$OHmim]Cl with **IL 1** (top) or **IL 4** (bottom). Conditions: [C$_2$OHmim]Cl (450 mg) and functionalized IL (50 mg), glucose (0.28 mmol, 50 mg), CrCl$_2$ (0.019 mmol, 2.3 mg), 100 °C, 2 h.



Scheme 2. Reaction pathways for the dehydration of glucose to fructose and subsequent transformation to HMF through a pathway involving a cyclic fructofuranosyl intermediate. The labeling schemes for the carbon atoms in glucose and HMF are also provided.

of keto-fructose to fructofuranose is a key step favoring the condensation reaction and the formation of humins. In contrast, the condensation reaction may be suppressed if the isomerization from the linear form of fructose to the furanosyl form is very fast.

There are clear differences between the ^{13}C NMR spectra obtained in catalyst solutions containing [C_2OHmim]Cl and [C_2OHmim]Cl containing **IL 4** (Figure 4 and S3 in the Supporting Information). In the former, a peak at approximately 215 ppm is observed that may be attributed to fructose in the linear form.[25] In contrast, this peak is not observed in the catalyst solution containing [C_2OHmim]Cl and **IL 4**. The system containing **IL 4**, with the C_1-enriched ^{13}C glucose substrate, a signal is observed at approximately 205 ppm, which may be tentatively attributed to the C_1 aldose form of glucose,[26] whereas for the fully ^{13}C-enriched glucose substrate, a signal at approximately 190 ppm is observed, which indicates that the C_1 and C_2 of the aldose interact strongly with **IL 4**.[27] The corresponding peak is also present in the [C_2OHmim]Cl system, but it is of much lower relative intensity. The apparent interaction between the substrate and **IL 4** presumably enhances the rate of fructose isomerization from the linear to the furanosyl form leading to an increase in the reaction rate. Moreover, the fructofuranosyl form disfavors humins formation as it does not contain a carbonyl group, which is responsible for the aldol condensation mechanism required for the generation of humins.

X-ray absorption spectroscopy at the CrK edge was employed to provide insights on the electronic state of the Cr^{II} ion, as well as on its coordination sphere in different ILs. Samples were prepared by quenching the reaction mixture after 10 min. In the X-ray absorption near-edge structure (XANES) data (Figure 5, top), the white line intensity (i.e., the height of the peak at around 6008 eV in Figure 5, top) of the Cr species in [C_2OHmim]Cl or **IL4** are similar, being in between the Cr metal foil and Cr_2O_3 reference samples, indicative of the maintenance of Cr^{II} ions in the ILs. Moreover, the introduction of glucose into these systems does not significantly change the white line intensity, indicating that only ligand exchange processes take place during the reaction. The extended X-ray ab-

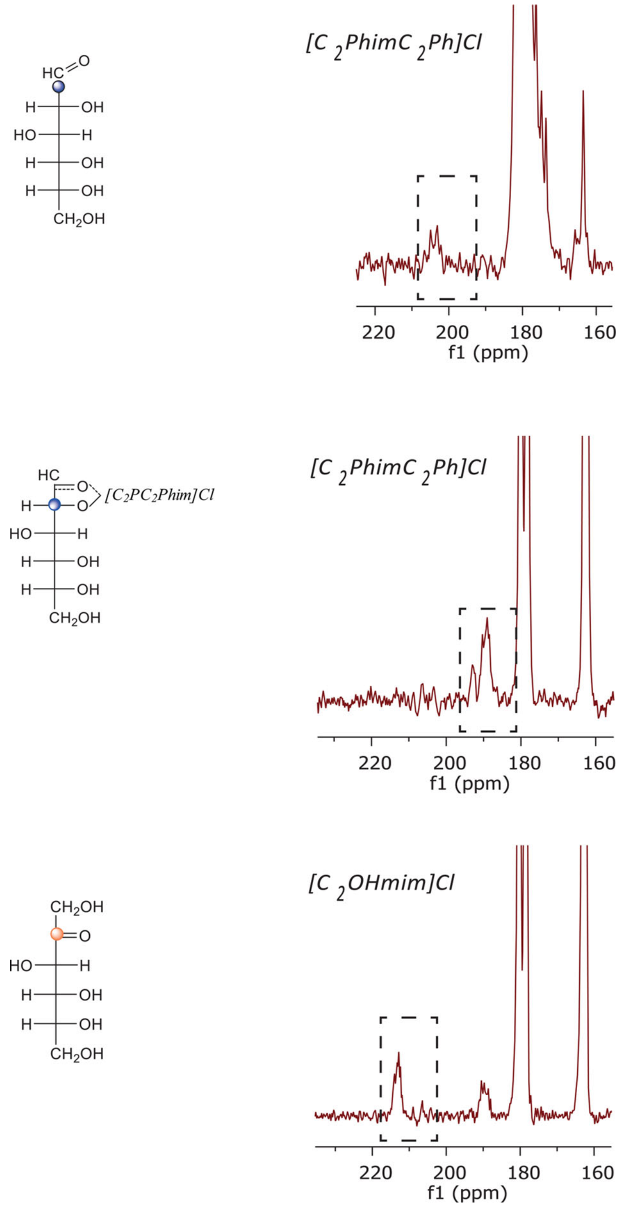


Figure 4. ^{13}C NMR spectra for the transformation of C_6-enriched ^{13}C glucose into HMF in [C_2OHmim]Cl (bottom) and [C_2OHmim]Cl/**IL 4** (middle), and C_1-enriched ^{13}C glucose into HMF in [C_2OHmim]Cl/**IL 4** (top) in presence of $CrCl_2$. Conditions: [C_2OHmim]Cl (450 mg) and functionalized IL (50 mg), glucose (0.28 mmol, 50 mg), $CrCl_2$ (0.019 mmol, 2.3 mg), 87 °C, 1 h.

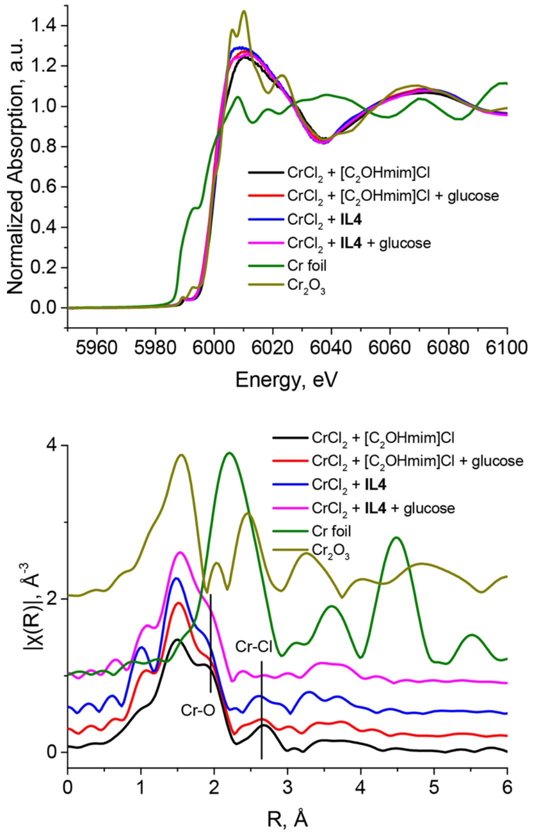


Figure 5. XANES (top) and FT-EXAFS (bottom) spectra of $CrCl_2$ in [C_2OHmim]Cl, $CrCl_2$ with glucose in [C_2OHmim]Cl, $CrCl_2$ in **IL4**, and $CrCl_2$ with glucose in **IL4**. The spectra of Cr foil and Cr_2O_3 are included as references.

sorption fine structure (EXAFS) spectra (Figure 5, bottom) of the IL/$CrCl_2$ systems exhibit a peak at approximately 2.6 Å, which does not correspond to the Cr–O bond (at ≈1.5 Å) or the Cr–Cr bond (at ≈2.5 Å). We tentatively attribute the peak to the presence of a Cr–Cl bond based on prior literature.[28] In [C_2OHmim]Cl, this peak is still present after adding glucose, although with a lower relative intensity, whereas in **IL4** in the presence of glucose it disappear completely. This observation is consistent with the higher activity observed in reaction mixtures containing **IL4**.

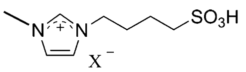
Transformation of polysaccharides into HMF

The conversion of polysaccharides is considerably more challenging than glucose and other simple sugars, combining the hydrolysis of the carbohydrates into oligomers followed by formation of monosaccharides, which then undergo dehydration to HMF (Scheme 1). Nevertheless, the catalyst solutions comprising $CrCl_2$ in [C_2OHmim]Cl containing **IL 1** or **IL 4** efficiently transform starch to HMF in 40 and 51 % yield, respectively (see Table 1). Similarly, using cellulose as a substrate, following pretreatment by ball milling to reduce the crystallinity and increase the specific surface area of cellulose (see Figure S2),[29] both systems, that is, $CrCl_2$ in [C_2OHmim]Cl/**IL 1** or [C_2OHmim]Cl/**IL 4**, afford HMF in 35 and 38 % yield, respectively.

Table 1. Dehydration of starch and cellulose to HMF.[a]

Substrate	IL	$CrCl_2$ [mg]	Brønsted IL	HMF [%]
Starch	**IL 1**	16	–	40
	IL 4	16	–	51
Cellulose	**IL 1**	10	–	35
	IL 4	10	–	38
	IL 1	10[b]	–	41
	IL 4	10[b]	–	44
	IL 1	–	**IL 9**	6
	IL 4	–	**IL 9**	6
	IL 1	10	**IL 9**	31
	IL 4	10	**IL 9**	31
	–	10[b]	**IL 9**	48
	IL 1	10[b]	**IL 9**	48
	IL 4	10[b]	**IL 9**	51
	IL 4	10[c]	**IL 9**	62
	IL 1	10[b]	**IL 10**	45
	IL 4	10[b]	**IL 10**	47
	IL 1	10[b]	**IL 11**	41
	IL 4	10[b]	**IL 11**	46

[a] Conditions: [C_2OHmim]Cl (900 mg), **IL 1** or **IL 4** (100 mg), acidic IL (11 mg, where specified), starch (50 mg) or cellulose (100 mg), 140 °C, 4 h. [b] MIBK (methyl-isobutyl ketone) extraction. [c] DME (1,2-dimethoxyethane) extraction.



IL 9: X=CF_3SO_3
IL 10: X=HSO_4
IL 11: X=Cl

Figure 6. Imidazolium-based acidic (–SO_3H containing) ILs employed.

Addition of Brønsted acidic ILs, that is, functionalized with a –SO_3H group (Figure 6), to the IL medium was evaluated as ILs containing –SO_3H groups have been shown to be more efficient solvents for the dissolution and hydrolysis of cellulose compared to simple inorganic acids.[21a] These properties have been attributed to the ability of sulfonic acids to catalyze the cleavage of β-1,4 glycosidic bonds in cellulose.[21d] It should be noted that in the absence of $CrCl_2$ very low yields of HMF were obtained.

Inclusion of **IL 9** to the catalyst solutions comprising $CrCl_2$ in [C_2OHmim]Cl containing **IL 1** or **IL 4** slightly lowered the yield of HMF (31 % in both cases). However, the overall conversion of cellulose was higher, suggesting that the Brønsted acidic IL facilitates cellulose hydrolysis, but also enhances the formation of unwanted by-products. To overcome this obstacle the HMF was continuously extracted into an organic phase from the ILs mixture as it forms. Methyl-isobutyl ketone (MIBK) is commonly used for the continuous extraction of HMF,[30] and using this solvent, HMF was obtained in 51 % yield from cellulose after 4 h (Table 1). However, using 1,2-dimethoxyethane (DME) in place of MIBK (presumably owing to the greater hydrogen-bond accepting ability, as measured by Kamlet–Taft's solvents parameters, in particular $\beta = 0.41$[31] for DME versus 0.12[32] for MIBK), HMF was obtained from cellulose in 62 % yield. Additionally, the recycling study showed that HMF yield of more than 50 % can be recovered from DME phase multiple times. The other Brønsted acidic ILs evaluated, that is, **IL 10** and **IL 11** did not lead to as high yields of HMF.

Conclusions

Herein, we show that cellulose may be transformed into 5-hydroxymethylfurfural (HMF) in high yield in a single step using a $CrCl_2$ catalyst immobilized in a mixture of ionic liquids (ILs). To the best of our knowledge the yield obtained is unprecedented for ILs, which are typically completely inactive or are able to transform simple sugars, such as glucose. Moreover, we are not aware of any organic solvent-based systems that offer similar yields of HMF directly from cellulose. Each IL in the optimized catalyst mixture plays a specific role. It has previously been shown that the IL with a hydroxyl group, [C_2OHmim]Cl, forms a strong hydrogen bond with glucose, which weakens and activates the C–O bond to lower the activation energy of the reaction.[8b] The aryl rings present in **IL 4** facilitate closure of the fructose ring, which in turn favors the condensation reaction and helps to suppress humins formation. The sulfonic acid group in **IL 9** increases cellulose solubility and accelerates the reaction. Moreover, it has been shown that cellulose may be dissolved more effectively in IL mixtures than in a single IL,[33] and hence, it is possible that combining ILs derived from biomass with specific designer ILs, such as those described here, may afford inexpensive systems for the conversion of cellulose into key platform chemicals, such as HMF.

Experimental Section

All starting materials including **IL 6** were obtained from commercial sources and used as received. [C_2OHmim]Cl, **IL 1** and **IL 7**–**IL 11** were prepared using literature procedures.[8b,34] Electrospray ionization mass spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ Deca XP Plus quadrupole ion trap instrument in positive ion mode.[35] NMR spectra were recorded on a Bruker DMX 400 instrument. Elemental analysis was performed at the Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne.

Ball milling pretreatment of cellulose

Microcrystalline cellulose (1 g) was loaded in a ball mill (Retsch MM 400) equipped with a steel jar (10 mL) and two steel balls (12 mm diameter) and operated at 30 Hz for 24 h. FTIR spectra of microcrystalline and ball-milled cellulose were recorded using a PerkinElmer FTIR 2000 spectrometer. For each spectrum, 16 scans were averaged from 4500 to 500 cm^{-1}.

Synthesis of IL 2

1-Methylimidazole (0.1 mol, 8.2 g) and (2-chloroethyl)benzene (0.1 mol, 14.1 g) were stirred at 80 °C for 48 h. The resulting IL was washed with diethyl ether (3×10 mL) and dried under vacuum (yield = 90%). ^{1}H NMR (400 MHz, DMSO, 25 °C): $\delta = 9.31$ (s, 1H), 7.80 (s, 1H), 7.72 (s, 1H), 7.24–7.33 (m, 5H), 4.46 (t, $J = 8$ Hz, 2H), 3.84 (s, 3H), 3.15 ppm (t, $J = 8$ Hz, 2H), ^{13}C NMR (DMSO, 25 °C): $\delta =$ 137.4, 137.2, 129.2, 129, 127.3, 123.9, 122.8, 50.1, 36.2, 35.9 ppm. ESI-MS (*m/z*) 187.12 [cation]$^+$. Elemental analysis (%) for $C_{12}H_{15}ClN_2$ (222.09): calcd. C 64.72, H 6.79, N 12.58; found: C 64.73, H 6.74, N 11.48.

Synthesis of IL 3

IL 3 was prepared with the same method as **IL 2** using 1,2-dimethylimidazole (1 equiv.) and (2-chloroethyl)benzene (1 equiv.) as starting materials. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.86$ (s, 1H), 7.72 (s, 1H), 7.04–7.28 (m, 5H), 4.53 (t, $J = 8$ Hz, 2H), 3.91 (s, 3H), 3.15 (t, $J = 8$ Hz, 2H), 2.26 ppm (s, 3H), ^{13}C NMR ($CDCl_3$, 25 °C): $\delta =$ 143.9, 136.3, 129.1, 128.9, 127.6, 123.3, 121.5, 50.4, 36.6, 35.8, 9.8 ppm. ESI-MS (*m/z*) 201.14 [cation]$^+$. Elemental analysis (%) for $C_{13}H_{17}ClN_2$ (236.11): calcd. C 65.95, H 7.24, N 11.83; found: C 65.87, H 7.19, N 11.93.

Synthesis of IL 4

1-(Trimethylsilyl)imidazole (0.028 mol, 3.985 g) and (2-chloroethyl)-benzene (0.057 mol, 7.97 g) were stirred at 80 °C for 48 h. The resulting IL was that was washed with diethyl ether (3×10 mL) and dried under vacuum (yield = 90%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 11.2$ (s, 1H), 7.3–7.37 (m, 5H), 4.61 (t, $J = 7$ Hz, 2H), 3.25 ppm (t, $J = 7$ Hz, 2H), ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 143.9$, 136.3, 129.1, 128.9, 127.6, 123.3, 121.5, 50.4, 36.6, 35.8, 9.8 ppm. ESI-MS (*m/z*) 277.17 [cation]$^+$. Elemental analysis (%) for $C_{19}H_{21}ClN_2$ (312.14): calcd. C 72.95, H 6.77, N 8.95; found: C 72.98, H 6.64, N 9.09.

Synthesis of [$CH_3C_2PhC_2Phim$]Cl IL 5

2-Methylimidazole (0.122 mol, 10 g) and NaOH (0.122 mol, 4.87 g) were stirred at 150 °C for 5 h. The resulting salt (0.067 mol, 7.015 g) and (2-chloroethyl)benzene (0.135 mol, 19 g) were stirred at 80 °C for 48 h. The resulting IL was washed with diethyl ether (3×10 mL) and dried under vacuum (yield = 90%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.62$ (s, 1H), 7.3–7.37 (m, 5H), 4.48 (t, $J = 6$ Hz, 2H), 3.11 (t, $J = 6$ Hz, 2H), 1.93 ppm (s, 1H), ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 143.7$, 136.2, 129.1, 128.8, 127.7, 121.9, 50.4, 36.3, 9.4 ppm. ESI-MS (*m/z*) 291.19 [cation]$^+$. Elemental analysis (%) for $C_{20}H_{23}ClN_2$ (299.13): calcd. C 73.49, H 7.09, N 8.57; found: C 73.29, H 7.01, N 8.29.

Conversion of glucose to HMF

In a typical reaction, glucose (0.28 mmol, 50 mg), $CrCl_2$ (0.019 mmol, 2.3 mg,), [C_2OHmim]Cl (450 mg), and a second IL (50 mg) were placed in a glass vial. The vial was sealed and the reaction mixture was then heated to 100 °C for the required time. After reaction the mixture was cooled to RT and the mixture diluted with water and methanol (4:1, 25 mL) for analysis.

Dehydration of starch

In a typical reaction starch (50 mg), $CrCl_2$ (16 mg), IL [C_2OHmim]Cl (900 mg), **IL 1** (100 mg) or **IL 4** (100 g) were placed in a glass vial. The vial was sealed and the reaction mixture was heated to 140 °C for 4 h. After reaction the mixture was cooled to RT and diluted with water and methanol (3:1, 10 mL) for analysis.

Conversion of cellulose to HMF

In a typical reaction cellulose (100 mg), $CrCl_2$ (10 mg), [C_2OHmim]Cl (900 mg), **IL 1** (100 mg) or **IL 4** (100 mg), and the acidic IL (11 mg) were placed in a glass vial. The vial was sealed and the reaction mixture was then heated to 140 °C for the desired time. After reaction the mixture was cooled to RT and diluted with water and methanol (4:1, 25 mL) for further analysis. When necessary, MIBK or DME (6 mL) was added to the reaction vessel. After 80 min the organic solvent (upper layer) was removed with a syringe and another 6 mL of solvent added. At the end of the reaction the mixture was cooled to RT, the phases were combined and diluted with water and methanol (4:1, 25 mL) for MIBK or water (for DME) for analysis. The purity of the HMF was evaluated by ^{1}H NMR spectroscopy following air drying and dissolving in water and extraction into ethyl acetate (Figure S4). In the recycling study the upper DME phase was collected every hour and a new portion of solvent was added for 6 cycles. A new portion of cellulose was added every 4 h. Each collected sample was analyzed immediately.

Stability tests

HMF (0.16 mmol, 20 mg) and $CrCl_2$ (0.019 mmol, 2.3 mg,) were placed in a glass vial containing [C_2OHmim]Cl (500 mg), [C_2OHmim]Cl/**IL 1** (500/50 mg) or [C_2OHmim]Cl/**IL 4** (450/50 mg). The vial was sealed and the reaction mixture was heated to 100 °C for 1 h. After this time the mixture was cooled to RT and diluted with water and methanol (4:1, 25 mL) for analysis. The initial amount of HMF was recovered in all systems. Next, glucose (0.028 mmol, 5 mg) was added to each vial described above and tested under identical reaction conditions. With [C_2OHmim]Cl, HMF was recovered in 43% yield and for the mixture of [C_2OHmim]Cl/**IL**

1 the yield of HMF is 63%. The mixture with $[C_2OHmim]Cl$/**IL 4** afforded exclusively HMF.

Analysis

HMF was analyzed by HPLC on an Agilent 1260 Infinity instrument with a UV/Vis detector and equipped with a Poroshell 120 EC-C18 column (3.0×100 mm, 2.7 μm) using water-acetonitrile (97:3) as the mobile phase at a flow rate 0.5 mL min^{-1} at 30 °C. Glucose and fructose were determined with a refractive index detector and a Hi-Plex H, 300*7.7 column at 60 °C and acidified water (0.004 M H_2SO_4) as the eluent (0.5 mL min^{-1} flow rate).

CrK edge X-ray absorption spectra (XAS) were recorded on the BL01B1 beamline at the SPring-8 (Japan Synchrotron Radiation Research Institute, Hyogo, Japan) in fluorescence mode at ambient temperature. Samples were prepared as follows: $CrCl_2$ was mixed with 10 equivalents of $[C_2OHmim]Cl$ or **IL4**, in the absence or presence of 1 equivalent of glucose in a glove box. Each mixture was heated at 100 °C for 10 min, then deposited in PTFE molds and sealed with transparent tape.

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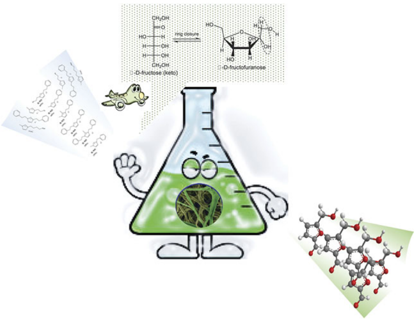

S. Siankevich, Z. Fei, R. Scopelliti,
*P. G. Jessop, J. Zhang, N. Yan,**
*P. J. Dyson**

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Direct Conversion of Mono- and Polysaccharides into 5-Hydroxymethylfurfural Using Ionic-Liquid Mixtures