CONVERSION OF FRUCTOSE TO 5-HYDROXYMETHYLFURFURAL WITH A FUNCTIONALIZED IONIC LIQUID

Hao Ma,[a] Bo Zhou,[a] Yiqun Li,[a,]* and Dimitris S. Argyropoulos [b,c,]*

Fructose can be efficiently converted to 5-hydroxymethylfurfural by using the functionalized ionic liquid 3-(2-chloroethyl)-1-methylimidazolium chloride as both solvent and catalyst in the presence of water. This work advances the field and is distinct from earlier efforts in the sense that the observed yields of HMF from fructose are rather high and the reaction conditions rather mild and neutral in the complete absence of acidic additives (HMF yield 76% at 100 ^{o}C in 40 minutes).

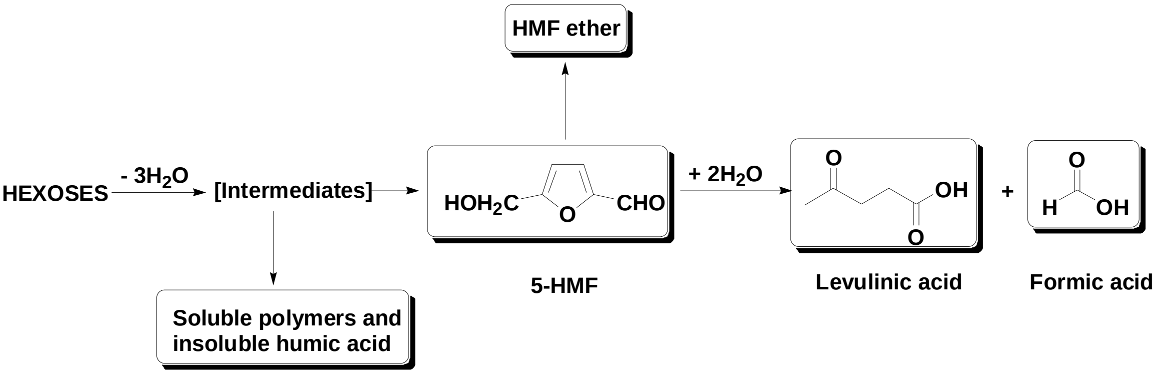
Keywords: D-Fructose; 5-Hydroxymethylfurfural; 1-(2-Chloroethyl)-3-methylimidazolium chloride; Catalytic conversion; Ionic liquid

*Contact information: a: Department of Chemistry, Jinan University, Guangzhou 510632,China; b: Department of Forest Biomaterials, North Carolina State University, Raleigh, North Carolina, 27695-8005, USA; c: Department of Chemistry, University of Helsinki, PO BOX 55, 00014, Helsinki, Finland; * Corresponding author: dsargyro@ncsu.edu; tlyq@jnu.edu.cn*

INTRODUCTION

5-hydroxymethylfurfural (HMF), an important valuable intermediate for fine chemicals, pharmaceuticals, and furan-based polymers has been of interest since the last decade of the 19th century (Lewkowski 2001; Zhao et al. 2007). HMF can be further transformed into levulinic acid and 2,5-disubstituted furan derivatives, with the latter being potential building blocks for the production of plastics and fine chemicals (Lewkowski 2001; Kuster 1990; Cukalovic et al. 2010; Huber et al. 2006; Zakrzewska et al. 2011). Moreover, HMF can be converted into molecules such as 2,5-dimethylfuran and other liquid alkanes, which make it suitable for its directly utilization as biofuel within diesel engines (Zakrzewska et al. 2011; Mascal et al. 2009; Roman-Leshkov et al. 2007; Thananatthanachon et al. 2010; Yang and Sen 2010). Routes towards the facile transformation of carbohydrates into bio-based chemicals and biofuels are, therefore, of the utmost significance.

HMF originates from hexoses, mainly fructose, by the loss of three molecules of water in an acid-catalyzed reaction. In aqueous mixtures HMF enters into a consecutive reaction, taking up two molecules of water to yield levulinic and formic acid (Lewkowski 2001; Zhao et al. 2007; Zakrzewska et al. 2011; Asghari and Yoshida 2007) (Scheme 1). The efficient conversion of fructose to HMF is a key step in utilizing carbohydrates for the production of liquid fuels and value-added chemicals. Recent research has shown that HMF can be obtained by the dehydration of carbohydrates, such as fructose, glucose, and cellulose, catalyzed by mineral acids (HCl, H_2SO_4, and H_3PO_4) (Chheda et al. 2007), solid acid catalysts (SO_4^{2-}/ZrO_2 and $SO_4^{2-}/ZrO_2–Al_2O_3$) (Yan et al. 2009), and even strongly acidic resins (Dowex 50wx8-100) (Qi et al. 2008) in good yields in a variety of solvents, such as water, aqueous-organic mixtures, pure organic solvents, as well as supercritical solvents. However, such systems have drawbacks in term of conversion, product selectivity, catalyst and solvent recycling, HMF stability, or equipment corrosion limitations. These disadvantages significantly increase the cost of raw material and product purification. For example, HMF decomposes in water to levulinic acid and formic acid under acidic conditions, while levulinic acid is particularly difficult to separate from HMF. Therefore, if one is to obtain HMF in high yields *via* an acid-catalyzed dehydration reaction of fructose, the presence of water needs to be avoided.



Scheme 1. Products from the acid catalyzed dehydration of hexoses and rehydration of HMF

Ionic liquids in conjunction with various Lewis acids, such as $CuCl_2$ (Qi et al. 2009), $SnCl_4$ (Hu et al. 2009), WCl_6 (Chan et al. 2009), $CrCl_2$ (Yong et al. 2008), $CrCl_3$ (Yong et al. 2008; Qi et al. 2010; Cao et al. 2011), etc. or Bronsted acids, such as HNO_3 (Li et al. 2010), H_2SO_4 (Li et al. 2010; Sievers et al. 2009; Cao et al. 2011), H_3PO_4 (Li et al. 2010), etc. have been shown to catalytically promote the conversion of HMF. More recently, ionic liquid coupled with microwave irradiation has been shown to be an efficient protocol to convert fructose to HMF (Li et al. 2011). Unfortunately, these ionic liquid systems have also shown at least one of the following limitations: low or moderate conversions and yields, unavailability of the ionic liquids, long reaction times, harsh reaction conditions, tedious work-up procedures, need the additional catalyst or microwave irradiation, and the requirement of water-free handling, etc. Consequently, the optimum combination of solvents and catalysts is essential for the technically feasible conversion of carbohydrates to HMF.

In this paper we describe our efforts aimed at minimizing the aforementioned limitations for the conversion of fructose to HMF by using the sugar-solubilizing ionic liquid 3-(2-chloroethyl)-1-methylimidazolium chloride ([ClC$_2$mim]Cl), acting as both the solvent and the catalyst.

EXPERIMENTAL

Materials

D-Fructose supplied by Amresco (Purity>99%), [ClC$_2$mim]Cl and other ionic liquids were prepared according to the literature (see below) and confirmed by ^{1}H NMR.

All of other chemicals were of analytical grade and purchased from commercial resources. They were used directly without any pretreatment.

3-(2-chloroethyl)-1-methylimidazolium Chloride [ClC$_2$mim]Cl

[ClC$_2$mim]Cl could be easily prepared by the reaction of 1-methylimidazole in the presence of a large excess of 1,2-dichloroethane as reported by Nachtigall et al. (Nachtigall et al. 2008; Song et al. 2008). A mixture of 1-methylimidazole (30 mL, 0.38 mmol) and 1, 2-dichloroethane (150 mL, 1.91 mmol) was heated to reflux for 10 h. The product was separated by removal of residual 1,2-dichloroethane under vacuum, and then it was dissolved in a mixture of isopropanol (30 mL) and acetone (90 mL), allowing the removal of the dicationic byproduct 1,2-bis(3-methylimidazolium-1-yl)ethane dichloride. This solution was then kept in a freezer overnight to allow the crystallization of the dicationic byproduct. The solid byproduct was then filtered, and the filtrate was concentrated in a rotary evaporator to afford the desired crude product as a pale amber solid. Finally, the crude product was dissolved in hot acetonitrile (400 mL). After cooling, the mixture was kept in a freezer overnight to further precipitate any residual dicationic by-product. After filtration, while the solution was cold, evaporation of the acetonitrile was carried out under reduced pressure, and a nearly pure product was obtained. This was further purified by allowing any residual solvents to evaporate using a vacuum drying oven set at 100 ^{o}C until a constant weight was obtained. The product was sufficiently pure and stored in a sealed container at room temperature prior to use. Its structure and purity were confirmed using ^{1}H and ^{13}C NMR as follows:

^{1}H NMR (400 Hz, DMSO-*d*$_6$) (ppm) showed the following: δ: 9.60 (s, 1H; CH imidazolium); 7.99 (s, 1H; CH imidazolium); 7.85 (s, 1H; CH imidazolium); 4.60 (t, *J* = 5.2 Hz, 2H; CH$_2$Cl); 4.12 (t, *J*= 5.2 Hz, 2H; NCH$_2$); 3.90 (s, 3H; NCH$_3$). ^{13}C NMR (100 Hz, DMSO-*d*$_6$) showed δ: 137.3 (CH imidazolium); 123.7 (CH imidazolium); 122.5 (CH imidazolium); 50.2 (CH$_2$Cl); 43.2 (NCH$_2$); 35.8 (NCH$_3$).

3-(2-chloroethyl)-1-methylimidazolium tetrafluoroborate [ClC$_2$mim]BF$_4$

[ClC$_2$mim]BF$_4$ was prepared by mixing NaBF$_4$ (21.8g, 0.2 mmol) with a solution which contained 50 mL of acetonitrile and [ClC$_2$mim]Cl (18.1g, 0.1 mmol) at room temperature with magnetic stirring for 48 h (Suarez et al. 1996). The precipitated salts were separated by filtration, and the desired crude product was obtained by solvent removal. Then, the crude product was centrifuged at 4000 rpm for 30 min to separate the suspended NaBF$_4$ impurities. The upper layer was then separated and dried in vacuum to remove all residual solvents and water at 100 ^{o}C until a constant weight was obtained. The product was stored in a sealed container at room temperature prior to use. Its structure was confirmed using ^{1}H and ^{13}C NMR as follows:

^{1}H NMR (400 Hz, DMSO-*d*$_6$) (ppm) δ: 9.13 (s, 1H; CH imidazolium); 7.78 (m, 1H; CH imidazolium); 7.71 (m; 1H; CH imidazolium); 4.54 (t, *J* = 5.6 Hz, 2H; CH$_2$Cl); 4.05 (t, *J* = 5.6 Hz, 2H; NCH$_2$); 3.87 (s, 3H; NCH$_3$). ^{13}C NMR (100 Hz, DMSO-*d*$_6$) δ: 137.2 (CH imidazolium); 123.8 (CH imidazolium); 122.5 (CH imidazolium); 50.4 (CH$_2$Cl); 43.1 (NCH$_2$); 35.9 (NCH$_3$).

3-(2-chloroethyl)-1-methylimidazolium nitrate [ClC_2mim]NO_3

[ClC_2mim]NO_3 was prepared by adding $AgNO_3$ (17.0g, 0.1mol) to a mixture of 50 mL methanol and [ClC_2mim]Cl (18.1g, 0.1mol) at room temperature under magnetic stirring for 10 h (Wilkes and Zaworotko 1992). The AgCl precipitate was removed by filtration and the filtrate was evaporated under vacuum. The desired product was further dried and freed of solvents under vacuum as mentioned above. The product was stored in a sealed container at room temperature prior to use. Its structure was confirmed using ^{1}H and ^{13}C NMRas follows:

^{1}H NMR (400 Hz, DMSO-*d*$_6$) (ppm) δ: 9.25 (s, 1H; CH imidazolium); 7.83-7.84 (m, 1H; CH imidazolium); 7.75-7.76 (m, 1H; CH imidazolium); 4.56 (t, *J*= 5.6 Hz, 2H; CH2Cl); 4.07 (t, *J* = 5.6 Hz, 2H; NCH_2); 3.88 (s, 3H; NCH_3). ^{13}C NMR (100 Hz, DMSO-*d*$_6$) δ: 137.2 (CH imidazolium); 123.8 (CH imidazolium); 122.5 (CH imidazolium); 50.3 (CH_2Cl); 43.1 (NCH_2); 35.8 (NCH_3).

3-butyl-1-methylimidazolium chloride ([C_4mim]Cl) and 3-(2-hydroxylethyl)-1-methyl imidazolium chloride ([HOC_2mim]Cl)

[C_4mim]Cl and [HOC_2mim]Cl were prepared conveniently according to the reported procedure (Branco et al. 2002; Li and Zhao 2007).

Water Content of Ionic Liquids

The water content of ionic liquids was determined by using a Karl-Fischer Moisture Titrator (MKS-520/MKA-520, KEM, Japan) according to GB/T 606-2003 standard method of the China National Analytical Center (Guangzhou).

Typical Procedures for the Conversion of Fructose into 5-hydroxymethylfurfural

Briefly, specified amounts of fructose, catalyst ([ClC_2mim]Cl), and water were put into a round-bottomed flask (25 mL) equipped with magnetic stirrer and reflux condenser. And the mixture was heated in oil bath at the controlled temperature for the specific time. Then the mixture was quenched immediately after cooling to ambient temperature by flowing water.

HMF Quantitative Analysis Procedure

The reaction mixture produced from the above procedure was thoroughly extracted with ethyl acetate for five times. The combined organic extracts were dried over fresh anhydrous $MgSO_4$. After removal of the solvent, the product was purified by chromatography (silica gel, dichloromethane/ethyl acetate=10/3) and the structure was confirmed by ^{1}H and ^{13}C NMR spectroscopies as follows:

^{1}H NMR (400 Hz, $CDCl_3$) (ppm) δ: 9.52(s, 1H; CHO); 7.18(d, *J* = 3.6 Hz, 1H; CH); 6.47(d, *J* = 3.6 Hz, 1H; CH); 4.67(s, 2H; CH_2). ^{13}C NMR (100 Hz, $CDCl_3$) δ: 177.7 (CHO); 160.8 and 152.2 (C); 123.1 and 110.0 (CH); 57.4 (CH_2).

The HMF yield (mol%) of each carbon compound was determined from its carbon basis, using the following equation:

$$Y = \frac{\text{Moles of carbon in product}}{\text{Moles of carbon loaded as fructose}} \times 100\% \qquad (1)$$

Determination of Residual Fructose

The amount of residual fructose was determined using the DNS sugar determination method. A mixture of 1.0 ml DNS reagent (Li and Zhao, 2007) and 1.0 mL of the reaction mixture (HMF was extracted with ethyl acetate for five times) was heated for 5 min in a boiling water bath, then cooled to room temperature, and mixed with 8 mL of deionized water. The color intensity of the mixture was measured with a visible spectraphotometer (721, Jinghua, China) set at 540 nm. The concentration of the total reducing sugars was calculated based on a calibration curve obtained using pure fructose ensuring that any background absorption from the solvent and the ionic liquid was subtracted.

Fructose conversion (mol%):

$$X = \left(1 - \frac{\text{Fructose concentration in product}}{\text{Fructose concentration in the loaded sample}}\right) \times 100\% \qquad (2)$$

RESULTS AND DISCUSSION

Influence of H_2O in Ionic Liquid System

The purity of ionic liquids available today is a serious problem nowadays. One of the major purity considered is the water. Since the water content is known to have an adverse effect on the conversion rate and the product yields, we first determined the water content in ionic liquids. The results are tabulated in Table 1.

Table 1. Water Content in Purified Ionic Liquids

Samples	[ClC_2mim]Cl	[C_4mim]Cl	[HOC_2mim]Cl	[ClC_2mim]BF_4	[ClC_2mim]NO_3
Water content (mass %)	0.69	0.41	0.85	0.28	0.069

Table 1 indicates that the purified ionic liquids still contained trace amounts of water after drying using the vacuum drying oven operated set at 1 mm Hg. These levels of initial water content were thus used in our catalytic systems.

The influence of water content was then evaluated relative to the dehydration of fructose to HMF within the functionalized ionic liquid [ClC_2mim]Cl system (Fig. 1). The data in Fig. 1 show that as the molar ratio of H_2O/[ClC_2mim]Cl varied from 0 to 1.263, the conversion of fructose remained nearly quantitative (nearly 100%). However, as the molar ratio of H_2O/[ClC_2mim]Cl was further increased from 1.263 to 6.313, the fructose conversion monotonically decreased from 100% to 40.7%.

These results lead to the conclusion that water contents below 25wt%, i.e. a molar ratio of H_2O/[ClC_2mim]Cl lower than 2.525, had no effect on HMF yield, while higher molar ratios of water were detrimental to both fructose conversion and HMF yields. In accordance with Scheme 1, side products may also be formed as the reaction proceeds.

The possibility of formation of side product is known to increase the accumulation of intermediates as the process of forming HMF proceeds (Lewkowski 2001; Zhao et al. 2007; Zakrzewska et al. 2011). Small amounts of water (0 to 1.0g, molar ratio of water and ionic liquid less than 2.525) present were tolerated in this system, whereas water contents that exceeded a molar ratio of 2.525 (>1.0g), diluted the concentration of the ionic liquid and consequently lowered its catalytic activity and its capacity to scavenge the water. This resulted in a decrease of both fructose conversion and HMF yields.

Interestingly, unlike previously reported data, a small amount of water appears to have negligible effects on the reactivity of the examined system. It is likely that the ionic liquid [ClC_2mim]Cl may also serve as water scavenger so as to promote the conversion of fructose at levels below molar ratio of 2.525.

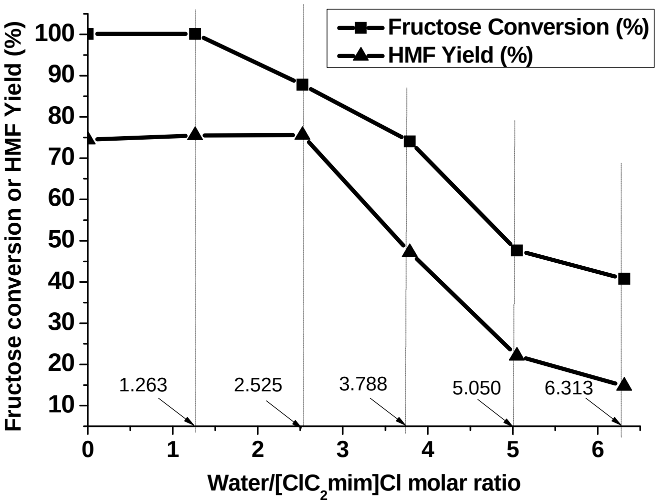


Fig. 1. Influence of H_2O existed into [ClC_2mim]Cl system on fructose conversion and HMF yields. Reaction conditions: [ClC_2mim]Cl 4.00g (0.022 mol), D-fructose 0.50g (0.0028 mol), 100°C oil bath, 40 min

Influence of Reaction Temperature and Time

In an effort to further understand the variables of significance affecting the reaction under examination, we further investigated the role of temperature (*T*) and time (*t*). Temperature is seen to have had a very significant effect on both the conversion of fructose and HMF yield (Fig. 2). Below 60 °C, the conversion of fructose and the yield of HMF were seen to be rather low, while higher elevated temperatures significantly improved both fructose conversion and the yield of HMF. More specifically, the fructose conversion increased from 24.6% to 87.8% and the HMF yield increased from 0.8% to 75.6% when the temperature was raised from 60 °C to 100 °C. Increasing the temperature beyond 100 °C is deemed unnecessary, due to the observed high degrees of conversion at 100 °C.

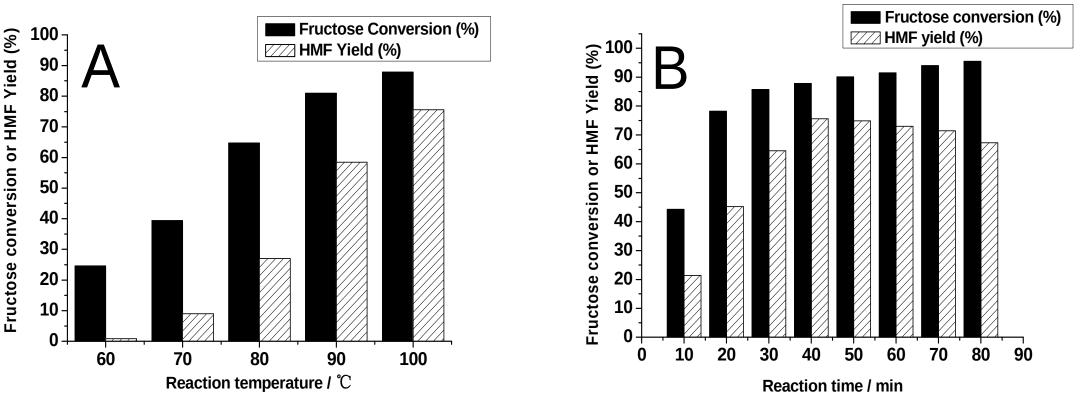


Fig. 2. The influence of reaction temperature (A) and time (B) in [ClC$_2$mim]Cl system. Reaction conditions: (A) [ClC$_2$mim]Cl 4.00g (0.022 mol), *D*-fructose 0.50g (0.0028 mol), H_2O 1.00g (0.056 mol), 40 min; (B) [ClC$_2$mim]Cl 4.00g (0.022 mol), *D*-fructose 0.50g (0.0028 mol), H_2O 1.00g (0.056 mol), 100^{o}C oil bath

Figure 2B shows that as the reaction time increased from 0 to 80 min, the conversion of fructose increased from 0 to 95.5%. However, the yield of HMF increased from 0 to 75.6% as the reaction time increased from 0 to 40 min and decreased to 67.3% as the reaction time was further prolonged to 80 min. This yield decrease in HMF may be due to a preponderance of side reactions caused by the presence of water (Lewkowski 2001; Zhao et al. 2007; Asghari and Yoshida 2007) (see Scheme 1). Despite the fact that the ionic liquid [ClC$_2$mim]Cl may play a significant role in scavenging water and thus reducing somewhat unwanted side reactions, prolonged reaction times create rather unfavorable conditions that cannot be mitigated by the nature of the ionic liquid alone.

Effect of Weight of Fructose and Recycling in the [ClC$_2$MIM]Cl System

The effect of fructose concentration (Fig. 3A) and the potential recyclability of the [ClC$_2$MIM]Cl system (Fig. 3B) were also investigated.

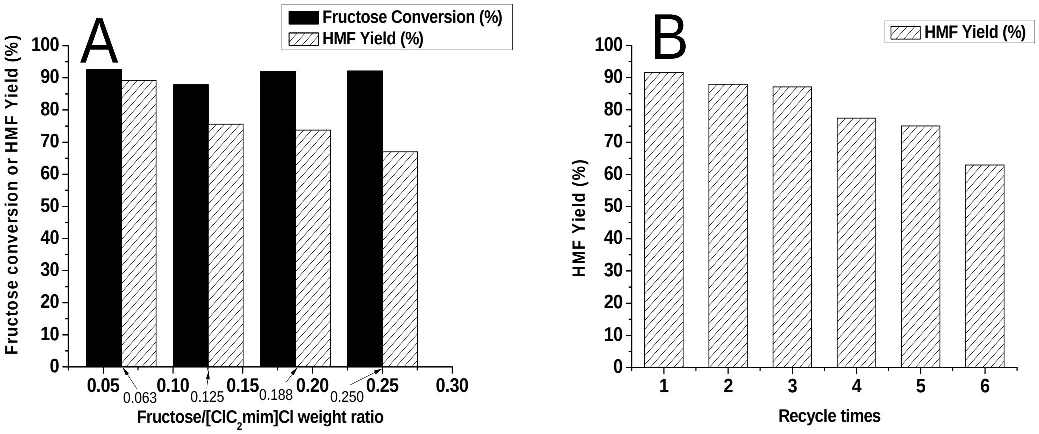


Fig. 3. The influence of weight of fructose (A) and the recycle times in [ClC$_2$mim]Cl system(B). Reaction condition: (A) [ClC$_2$mim]Cl (0.022 mol), H_2O 1.00g (0.056 mol), 40 min, 100 ^{o}C oil bath; (B) [ClC$_2$mim]Cl 4.00g (0.022 mol), *D*-fructose 0.20g (0.0011 mol), 40 min, 100 ^{o}C oil bath.

The concentration of fructose feedstock is seen to have had minor influence on its conversion, this variable being kept approximately constant (at about 92%) at the examined concentration levels. The yield, however, of HMF was seen to slightly decline as the concentration of fructose increased. As the concentration of fructose increased it is assumed that the concentration of intermediates also increased, resulting in a concomitant decrease of HMF within the system.

Since the primary objective of this work is to aid in the development of technology that promotes green chemistry, an understanding of the recyclability of the used ionic liquid was of paramount significance. Consequently, our work focused on examining such variables. After each experiment, the reaction mixture was thoroughly extracted (×5), using ethyl acetate as the extractant. The remaining aqueous mixture of the ionic liquid was then re-used in another experimental run without purification or any additional treatment. The accumulated data for describing the efficacy of recycling the ionic liquids are presented in Fig. 3B. Based on HMF yields, the data indicate partial recyclability of the ionic liquid during the first three cycles of use, since these exhibited reductions in yield to 91.7%, to 88.0%, and to 87.1%, respectively. The yields of HMF, however, after the third cycle were reduced to 77.4%, with the sixth cycle being only about 63%. The observed progressive reduction of HMF yields may be due to the accumulation of side products and water produced in previous cycles. It is likely that after each cycle the accumulated water diluted the concentration of the ionic liquid and consequently greatly lowered its catalytic activity and its capacity to scavenge more water according to the data displayed in Fig. 1.

The Effect of the Nature of the Cation and the Anion in the Ionic Liquid

Since our work so far has shown the critical significance the functionalized ionic liquid plays toward defining the overall reaction efficiency in terms of fructose conversion and HMF yields, it became important to further investigate the effect of the nature of the cation and anion of the ionic liquid toward the reaction efficiency. In accordance with earlier literature data (Swatloski et al. 2002; Feng and Chen 2008; Brandt et al. 2010; Zakrzewska et al. 2010; Luo et al. 2005), the concerted effect of the cation and the anion in an ionic liquid determines the dissolution characteristics of sugars within it. With respect to the structure of the examined ionic liquid (HOC$_2$mim]Cl) the hydroxyl group present within the cation serves both as a hydrogen-bond acceptor (Luo et al. 2005) (since the hydrogen atom of the OH group may serve as an electron pair acceptor) or a hydrogen-bond donor (since the oxygen atom within it may serve as an electron pair donor). Alternatively, the chloride anion within the ionic liquid only serves as a hydrogen-bond acceptor, since it may donate an electron pair. The binary nature of the OH group facilitates the interaction of the IL with the hydroxyl groups present within carbohydrates molecules, thus enhancing its ability to dissolve carbohydrates. Detailed research of the influence of halides on the formation of 5-HMF from carbohydrates has been carried out by Binder and Raines (2009), and it has been shown that the addition of the ionic liquid [C$_2$mim]Cl to both the DMA-LiCl-CuCl or the DMA-H$_2$SO$_4$ system significantly promoted 5-HMF yields. Furthermore, the reaction appeared to proceed better with the loosely held ion-paired chloride as afforded by the ionic liquids than with the more tightly bound chloride within lithium chloride. These data motivated us to synthesize and screen a series of ionic liquids, systematically varying the electronic characteristics of the cation that contains the hydroxyl group. More specifically we examined 3-(2-chloroethyl)-1-methylimidazolium ([ClC$_2$mim]) and 3-(2-hydroxylethyl)-1-methylimidazolium ([HOC$_2$mim]) with a range of anions varying from the small hydrogen-bond donor (Cl) to larger non-coordinating [BF$_4$] and [NO$_3$] (Table. 2). The data shown in Table 1 indicate that the ionic liquid ([ClC$_2$mim]Cl]) containing a chloride atom both within the cation and the anion showed by far the most pronounced effects toward the conversion of fructose to HMF amongst all the examined ionic liquids. Apparently there seems to be a synergistic effect for the chloride acting as a hydrogen-bond donor and a nucleophile causing to the efficient dehydration of fructose based on the mechanism proposed by Binder and Raines (2009) to indicate the importance of the halide in the conversion. Furthermore, the presence of chloride within both the cation and the anion seems to further promote the hydrogen-bond donor effect.

Table 2. Conversion of Fructose into HMF in Different Ionic Liquid [a]

Entry	Catalysts	Weight of catalysts[g][b]	Reaction time [min]	Yield of HMF[%][c]
1	[ClC$_2$mim]Cl	4.0	40	75.6
2	[C$_4$mim]Cl	3.8	60	0
3	[HOC$_2$mim]Cl	3.6	60	0
4	[ClC$_2$mim]BF$_4$	5.1	60	20.8
5	[ClC$_2$mim]NO$_3$	4.6	60	trace

[a] Reaction conditions: D-fructose 0.50g (0.0028 mol), H_2O 1.0g (0.056 mol)， 100°C oil bath. [b] equiv. 0.022 mol. [c] The product was purified by chromatography.

CONCLUSIONS

1. A chloro-functionalized ionic liquid 3-(2-chloroethyl)-1-methylimidazolium chloride ([ClC$_2$mim]Cl) was shown to be an efficient, recyclable solvent and a catalytic promoter for the direct conversion of fructose into HMF in the presence of water.
2. The presence of the chlorine atom within both the cation and the anion of this ionic liquid seem to play a key role in this reaction.
3. This work advances the field and is distinct to earlier efforts in the sense that the observed yields of HMF from fructose are rather high and the reaction conditions rather mild and neutral in complete absence of acidic additives (HMF yield 76% at 100 °C in 40 minutes).

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