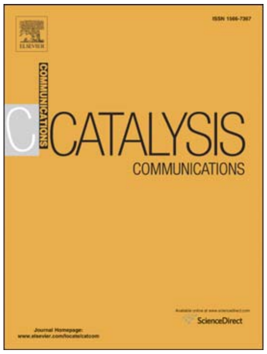

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# Catalytic Conversion of Fructose and Sucrose to 5-Hydroxymethylfurfural Using Simple Ionic Liquid/DMF Binary Reaction Media

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## ABSTRACT

The production of 5-hydroxymethylfurfural (HMF) from carbohydrates has been reported intensively in recent years. HMF is believed to be a versatile platform chemical and the focus of synthesizing it has especially been on the development of efficient catalysts, such as Lewis and Brønsted Acid. On the contrary, herein, we report a novel catalytic system that consists of 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) and N,N-Dimethylformamide (DMF) without any additional metal salts or acids, which leads to reasonable HMF yields (84.9%) and selectivities. In addition, the degradation mechanism of fructose catalyzed by [AMIM]Cl is also proposed in this communication.

**Keywords:** 5-hydroxymethylfurfural, fructose, ionic liquid, N,N-Dimethylformamide, system

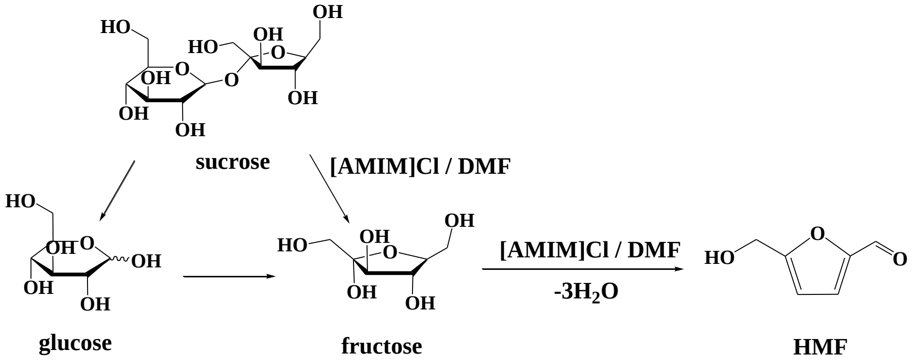
## 1. Introduction

Biomass is regarded as a potential abundant and renewable source to produce energy, chemicals and materials[1, 2]. Carbohydrates represent 75% of the annual renewable biomass. Fructose and sucrose are considered as superior carbohydrate compounds from which various furan chemicals can be obtained[3]. For example, 5-Hydroxymethylfurfural (HMF), which is considered to be one of the top 12 bio-based building blocks listed by the U.S. Department of Energy[4].

The awareness that it will become necessary to produce HMF from sugars to take place of fossil raw materials has led to an enormous increase in researching the conversion process. It is significant to find a simple and efficient catalytic system to convert monosaccharides and disaccharides into HMF. Therefore, various catalytic systems including solid acids[5], mineral acids[6], alkaline[7] and acidic ionic liquids[8] have been developed to achieve efficient transformation of sugars to HMF. The dehydration of fructose and sucrose to HMF has been performed in many different media, including (acidified) water[4, 9, 10], organic solvents[11], multicomponent mixtures[12] and ionic liquids[13, 14]. In addition, metal chloride salts are also applied to act as (co-)catalysts in the conversion, such as $GeCl_4$[15] and $SnCl_4$[16]. Originally, acidic catalysts are generally regarded as the important and essential compounds during the degradation of fructose, however, both Lewis Acid and Brønsted Acid are found to have a lot of shortcomings: corrosive (HCl, $H_2SO_4$, and $CH_3SO_3H$), toxic ($SnCl_4$ and $CrCl_3$), and difficult to recycle. Moreover, the post-processing is intractable due to the relative low selectivity of HMF, which is unstable in the acidic[10] and high temperature[17] environment. For the aqueous medium, because of the presence of water, levulinic acid (LA) and formic acid (FA) are formed, which decreased the selectivity of HMF[4].

Thus, it is urgent to build a catalytic system to convert fructose and sucrose efficiently that does not contain any metal salts or acids. Interestingly, some comparative trials[18, 19] have recently revealed that the neutral ionic liquid [BMIM]Cl had a small catalytic activity, even both the yield and selectivity are really not satisfied. Moreover, as reported by Moreau *et al.*, ~80% HMF yield was achieved from fructose catalyzed by Amberlyst-15 in [BMIM]$BF_4$ and [BMIM]$PF_6$ with DMSO as co-solvent within 24 h[20]. We herein systemically investigated a novel and simple process for HMF formation from fructose and sucrose by using [AMIM]Cl/DMF binary reaction system (Scheme 1 and Table S1). We hope this work could provide a simple, efficient and environmentally friendly way for the production of HMF from sugars.

**Scheme 1. Fructose and Sucrose Conversion into HMF.**



## 2. Experimental

### 2.1 Preparation of [AMIM]Cl catalyst

N-methylimidazole and allyl chloride at a molar ratio 1:1.25 were added to a round-bottomed flask fitted with a reflux condenser for 8 h at 55℃ with stirring. The unreacted chemical reagents and other impurities, such as water, were removed by vacuum distillation, and the obtained product [AMIM]Cl was further purified using ethyl acetate and ether. After further evaporation of volatiles, the product was dried in a vacuum oven at 60℃ for 2 days. $^1$H NMR ($D_2O$): δ=3.92 (s, 3H; $-CH_3$), 4.83 (d, *J* 6.0 Hz, 2H, $-CH_2$), 5.43 (dd, *J* 29.6 13.7 Hz, 2H, -CH), 6.07 (dq, *J* 11.4 6.1 Hz, 1H, -CH ), 7.48 (d, *J* 5.4 Hz, 2H; $-CH_2$), 8.74 (s, 1H; -CH). $^{13}$C NMR (DMSO): δ=36. 26 ($-CH_3$), 51.02 ($-CH_2$), 120.49 ($-CH_2$), 122.76 (-CH), 124.19 (-CH), 132.47 (-CH), 137.34 (-CH).

### 2.2 General procedure for synthesis of HMF from fructose

The reaction was carried out in a stainless steel autoclave with glass liner tube that was heated in the oil-bath. A mixture of fructose (1.0 mmol) and [AMIM]Cl/DMF media (5 ml) was placed in the tube, then heated and stirred at 100℃ for 45 min. After reaction, the resultant mixture was cooled in the ice bath, then diluted with deionized water and analyzed by HPLC.

## 3. Results and discusion

### 3.1 Effect of reaction time and temperature on dehydration

Temperature and time as the most critical parameters were initially investigated in the systematic evaluation process. To confirm the best conditions, the degradation of fructose in the [AMIM]Cl/DMF media was studied. As is shown in Figure 1, both too high temperature and too long time were not conducive to the stable of HMF due to the side-reaction. The highest yield of HMF was 84.4% obtained at 100℃ for 45 min. This yield was exceptional and comparable to the results obtained in many Lewis and Brønsted Acid systems[11, 21]. It should be noted that the selectivity of HMF in the present system was perfect (not shown here) and other by-products (furfural, LA and formic acid) were found to be particularly low and was not considered.

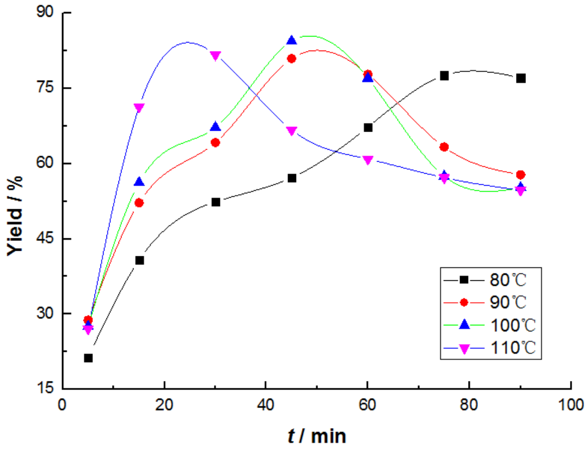


**Figure 1.** HMF synthesis from fructose in [AMIM]Cl/DMF binary reaction system. Conditions: Fructose (1 mmol), [AMIM]Cl (2 mL), DMF(3 mL).

### 3.2 Effect of volume ratio of [AMIM]Cl and DMF on dehydration

In order to confirm the roles of [AMIM]Cl and DMF played in the system, and more importantly, to confirm the effect of volume ratio of [AMIM]Cl and DMF, we then examined this condition. A series of volume ratios from 0 : 5 ([AMIM]Cl : DMF) to 5 : 0 and reactions in pure DMF and pure water as blank reactions were screened (Table 1 and S1). Both of the two solvents were not available for fructose degradation. Different volume ratios of [AMIM]Cl and DMF had different effects on the yield of

HMF, the results are presented in Table 1. It can be seen that HMF yield improved fast when increasing the ratio of [AMIM]Cl, but it began to shrink when enhancing the concentration of IL continually that exceeding 1/2. Meanwhile, a volume ratio of [AMIM]Cl/DMF greater than 2 : 3 was required for efficient transformation of fructose into HMF, and a volume ratio of 2.5 : 2.5 showed the best catalytic performance (84.9%). Actually, from the cost point of view, the volume ratio of 2 : 3 was considered to be more appropriate due to the close yields of entry 3-5. In addition, DMF revealed a significant function on reducing the viscosity of ionic liquid and enhancing heat transfer effect, and HMF became more stable in the presence of DMF in [AMIM]Cl.

**Table 1. HMF yields according to volume ratio of [AMIM]Cl and DMF[a].**

| Entry | *t* (min) | *T* (℃) | [AMIM]Cl (mL) | DMF (mL) | Conversion (%) | HMF Yield (%) |
|---|---|---|---|---|---|---|
| 1 | 45 | 100 | 0 | 5 | 10 | 0.5 |
| 2 | 45 | 100 | 1 | 4 | 85 | 39.6 |
| 3 | 45 | 100 | 2 | 3 | 97 | 84.4 |
| 4 | 45 | 100 | 2.5 | 2.5 | 99 | 84.9 |
| 5 | 45 | 100 | 3 | 2 | 99 | 81.3 |
| 6 | 45 | 100 | 4 | 1 | 93 | 77.1 |
| 7 | 45 | 100 | 5 | 0 | 95 | 76.8 |

[a]Conditions: Fructose (1 mmol), *T*=100℃, *t*=45 min.

### 3.3 Effect of impurities (water) in the system

Next, we found that in the presence of impurities in the system, particularly water, the yield of HMF decreased sharply. Figure 2 shows the degradation of fructose to HMF, the addition of water clearly lead to a serious decrease of HMF yield. From our research, with the growing of deionized water added into the reaction system, the HMF yield declined seriously. We speculated that water impaired the dissolution capacity of solvent and the stable balance of binary reaction media, causing the declined catalytic activity of [AMIM]Cl. Moreover, with the presence of water, the dehydration process of fructose was restrained seriously. To some extent, these findings agree with our previous work[22] that the water in [BMIM]Cl had negative effects on cellulose hydrolysis. In conclusion, strict purification procedures for [AMIM]Cl/DMF system are required to ensure the dehydration of fructose effectively.

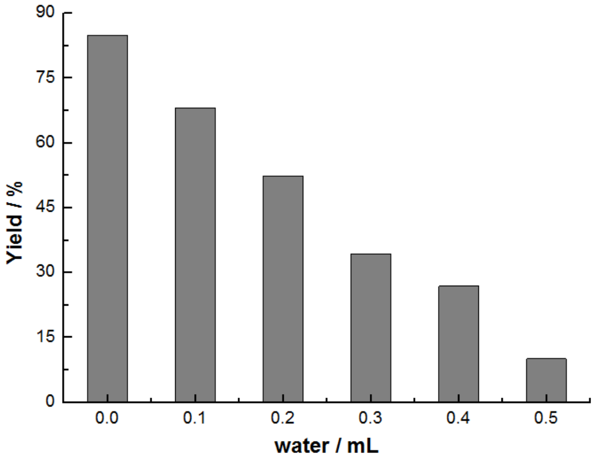


**Figure 2.** Effect of $H_2O$ added into system on the degradation of fructose. Conditions: Fructose (1 mmol), [AMIM]Cl (2 mL), DMF(3 mL), *T*=100℃, *t*=45 min.

### 3.4 HMF synthesis from various substrates

We then sought to explore the substrate scope in this simple catalytic system. When disaccharides were converted, HMF yield was equal to $\mathrm{mol}_{(\mathrm{HMF})}$ / $\mathrm{mol}_{(\mathrm{total\ monomer})}$. HMF was obtained in 40.3 % yield when sucrose was used as substrate (Table 2 and Figure S2). This result may be not comparable to the previous work by using Lewis Acid catalysts (compared, for example, with 55.4% yield and ~98% conversion were obtained at 120℃ for 30 min from sucrose in the presence of $GeCl_4$[23]). However, it is still acceptable due to the absence of metal salts and acids from the environmental viewpoint. When inulin was utilized as feedstock in the same reaction conditions, HMF yield of 53.7% was obtained. When other sugars were used, HMF yield was clearly lower and even cannot be detected. We reasoned that [AMIM]Cl/DMF-based system can hardly promote aldose (glucose) into ketose (fructose): the isomerization process. Sucrose is a disaccharide consisting of glucose and fructose, so only the ketose product could convert into HMF. Interestingly, the yield of HMF from sucrose was exactly a half of the yield that obtained from fructose, which confirmed our inference further.

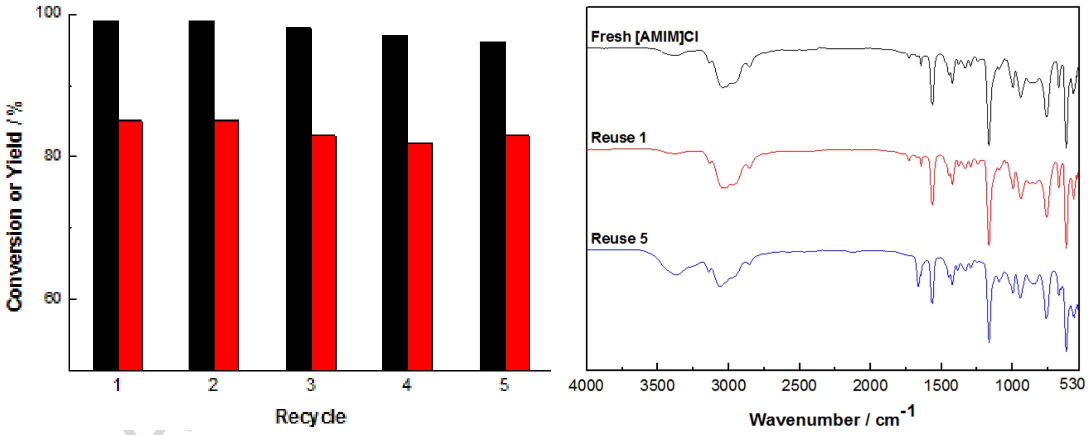
**Table 2. HMF synthesis from sugars in [AMIM]Cl/DMF system[a].**

| Entry | Substrate | *t* (min) | *T* (℃) | HMF Yield[c] (%) |
|---|---|---|---|---|
| 7 | Sucrose | 45 | 100 | 36.5 |
| 8 | | 60 | 100 | 40.3 |
| 9 | | 90 | 100 | 33.1 |
| 10 | Glucose | 45 | 100 | 0.5 |
| 11 | | 60 | 100 | 0.8 |
| 12 | | 90 | 100 | 0.9 |
| 13 | Maltose | 45 | 100 | ND[b] |
| 14 | Lactose | 45 | 100 | ND[b] |
| 15 | Galactose | 45 | 100 | ND[b] |
| 16 | Inulin | 60 | 100 | 53.7 |

[a]Conditions: Substrate (1mmol), [AMIM]Cl (2 mL), DMF (3mL). [b]ND = Not Detected. [c]HMF yield was equal to $\mathrm{mol}_{(HMF)}$ / $\mathrm{mol}_{(total\ monomer)}$.

### 3.5 Recycling and reutilization of reaction media

Reutilization of the catalyst is highly preferable in terms of green chemistry. Thus, the recycling experiments of [AMIM]Cl/DMF system were carried out using the synthesis of HMF from fructose as a model reaction. After reaction, the reaction mixture was first distilled under reduced pressure. Pure DMF was collected and the remaining mixture was extracted with ethyl acetate after water was added, similar to other procedures in the literature[8]. The obtained mixture after extraction was heated at 80℃ for 12 h in a vacuum oven to remove water and residual ethyl acetate. [AMIM]Cl was then used directly in the next run by adding the distilled DMF and an equal amount of fructose. As is shown in Figure 3(a), in a test of five cycles, the catalyst could be reused without any significant loss of catalytic activity (84.8% yield in the first cycle *versus* 80% in the fourth cycle). In order to further verify the stability of [AMIM]Cl, a FT-IR characterization experiment was also carried out. As can be seen in Figure 3(b), [AMIM]Cl remained stable after five cycles. Comparing the reused [AMIM]Cl with the fresh [AMIM]Cl, no distinct difference was observed.



(a) (b)

**Figure 3.** (a) Recycle experiments of [AMIM]Cl/DMF system. Balck bar: Fructose conversion, red bar: HMF yield. (b) FT-IR characterization of the reused [AMIM]Cl with the fresh [AMIM]Cl.

### 3.6 Mechanism of the fructose dehydration catalyzed by [AMIM]Cl

Much effort has been devoted to reveal the mechanism of the conversion of fructose into HMF catalyzed by Lewis and Brønsted Acids. However, the catalytic system that without $H^+$ or $M^{n+}$ (metal ions) was remained not fully studied. As is shown in Figure 4, chloride ion played an important role in the conversion process. Firstly, a molecule of water removed when compound **IM1** formed via the attachment of $Cl^-$ to the two OH groups on C1 and C2. Then an enediol intermediate (**IM2)** is formed and rapidly isomerizes into its isomers aldehyde **(IM3)**. Next, with the formation of another molecule of water which released from **IM3**, the product **IM4** is formed. Then following the similar route above, the third water molecule is removed. Finally, both IL and $H_2O$ are dissociated from **IM5** to give the target product.

It is suggested that in salt solutions with small, strong polarizing cations and large polarizable anions, intensive interactions with OH occur[24]. In comparison with [BMIM]Cl, we speculate that the cation $[AMIM]^+$ is conducive to the attack on OH groups due to the smaller ion size and a double bond in the cation of [AMIM]Cl. Moreover, the less electronic chemical structure caused by allyl group also enhances the interaction between cations in [AMIM]Cl and hydroxyl. Further investigations on the capture of the intermediates are underway.

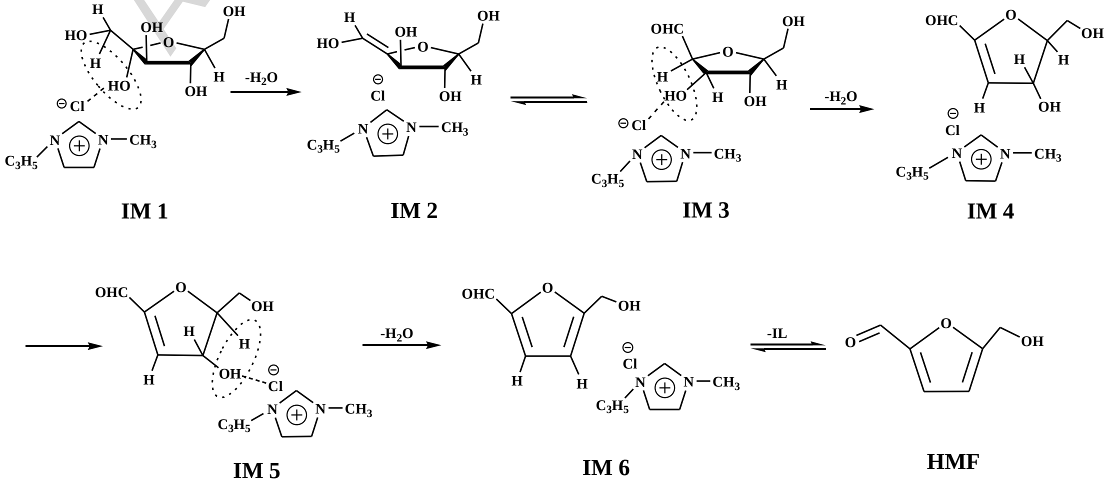


**Figure 4.** Possible mechanism for the dehydration of fructose. $–C_3H_5$ = Allyl.

## 4. Conclusions

In summary, we demonstrated that [AMIM]Cl/DMF binary reaction media was an excellent combination for the conversion of fructose and sucrose to HMF. High HMF yield was obtained in this simple and efficient catalytic/solvent system. [AMIM]Cl played an important role in the fructose conversion process and the possible mechanism for the dehydration of fructose was proposed. We believe that, the efficient, cheaper and reusable catalytic system has great potential for application in future.

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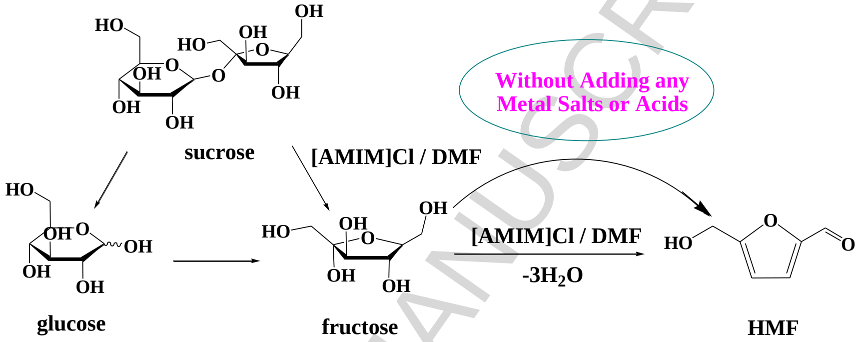
# Graphical Abstract

## TOC



## Highlights

- Simple and efficient ionic liquid/DMF binary reaction media is used.
- A high yield (84%) of HMF is obtained from fructose.
- Investigation of recovery method for HMF from media.
- [AMIM]Cl played an important role in the fructose conversion mechanism.