

Catalytic production of hydroxymethylfurfural from sucrose using 1-methyl-3-octylimidazolium chloride ionic liquid

Jae-An Chun*, Jin-Woo Lee*, Young-Byung Yi*, Seong-Sig Hong**, and Chung-Han Chung*[†]

*Department of Biotechnology, Dong-A University, Busan 604-714, Korea

**National Institute of Horticultural & Herbal Science, RDA, Suwon 441-853, Korea

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Abstract—Hydroxymethylfurfural (HMF) is an important chemical intermediate, but it has not been widely used because of low yields and high production costs. Sucrose is available at lower costs than other sugars and thus could be a biomass-derived abundant source for HMF production. In this study, a catalytic process for efficiently producing HMF from sucrose was scrutinized using 1-methyl-3-octylimidazolium chloride ([MOIM]Cl) as a reaction solvent, and HCl and metal chlorides (CrCl₂ and ZnCl₂) as a catalyst. The rate of sucrose hydrolysis was relatively much faster in the reactions with HCl than without it. The hydrolysis of sucrose to fructose and glucose was affected by its reaction time. The mixed solvent of 50% [MOIM]Cl and 50% sucrose solution with HCl was more effective in HMF synthesis than single solvent alone. The addition of ZnCl₂ and CrCl₂ increased HMF yields by approximately 1.2-1.8-fold and its higher yield was found in the latter. The highest yield (82.0±3.9 wt%) in HMF production was achieved in the reaction mixture containing 5 g [MOIM]Cl and 5 mL of 20% sucrose solution with 0.5 M HCl plus CrCl₂ at 30 min reaction time. However, 0.3 M HCl was more effective for the HMF productivity than 0.5 M HCl.

Key words: Hydroxymethylfurfural, Ionic Liquid, Metal Chloride Catalyst, Sucrose Hydrolysis

INTRODUCTION

In recent studies, HMF has been highlighted as a key platform chemical for production of future liquid transportation biofuels [1]. In addition, HMF can be utilized not only as a good starting material for synthesis of precursors of some pharmaceuticals, liquid alkanes, thermo-resistant polymers and complex macrocycles but also as an intermediate for synthesis of some flavor agents and cosmetic components [2]. In spite of this usefulness of HMF, it has not been widely used because of low yields and high production costs. Until now, HMF has been synthesized principally from some hexose substrates by chemical processes via the thermal dehydration reaction in acidic solvent media using diverse catalysts [2]. Many attempts have been made to increase the yield of HMF at lower production cost by improving the chemical processes of HMF synthesis. The major parameters of these processes include the source of feedstock sugars, reaction conditions, solvent media and catalysts [3]. For improvement of HMF synthesis by these parameters, a wide variety of solvent systems with various catalysts have been introduced using biomass-derived carbohydrates as renewable feedstocks [4-8]. Some recent studies advanced the reaction process of HMF synthesis by using fructose and glucose as a feedstock substrate [9,10]. Nonetheless, its low productivity and high production costs still remain problematic.

Sucrose (α -D-glucopyranosyl β -D-fructofuranoside, commonly called table sugar), which is a disaccharide sugar linked by an α -1,2-glycosidic bond between two monomeric hexoses of glucose and fructose (Fig. 1), is one of the abundant carbohydrates synthesized in plants, and thus can be utilized as a renewable resource in the sustainable chemical industry. This sugar is hydrolyzed to glu-

ose and fructose by catalytic reactions in the presence of acidic solvents such as hydrochloric acid, sulfuric acid and other acidic media [11]. The sucrose hydrolysates (mainly fructose and glucose) can be further transformed into versatile organic compounds by catalytic thermo-decomposition [11,12]. Recent studies demonstrated that fructose and glucose could be a major resource for high production of HMF [1,13,14]. However, sucrose is more favorable for industrial uses than fructose and glucose because of its relatively lower cost. Accordingly, when sucrose is used as a bio-feedstock, the efficiency of its hydrolysis into fructose and glucose could be an important factor in synthesizing hydroxymethylfurfural (HMF).

Recently, some ionic liquids that act as both catalyst and solvent have been employed to promote HMF production or to improve its reaction process. For example, Zhao et al. [9] reported a production process with high HMF yields from two hexose feedstocks of fructose and glucose by their thermal conversion to HMF in some ionic liquid solvents with metal chloride catalysts. Other studies also enhanced HMF yields by introducing some ionic liquids [4,7,9,15]. In general, ionic liquids have various properties favorable to chemical synthetic processes, such as high thermal stability, wide solvating properties in the solution, and low melting points [15-20]. An ionic liquid, 1-methyl-3-octylimidazolium chloride ([MOIM]Cl), is a derivative of disubstituted imidazolium chloride (Fig. 2), which has not been used as a solvent for sucrose hydrolysis and HMF synthesis. Accordingly, we here demonstrate a simple process for high yields of HMF from sucrose in the presence of [MOIM]Cl using two metal chloride catalysts and HCl in association with hydrolysis of sucrose (Fig. 1).

EXPERIMENTAL

1. Chemical Materials

1-Methyl-3-octylimidazolium chloride (Merck, Germany, 98%),

*To whom correspondence should be addressed.

E-mail: chchung@donga.ac.kr

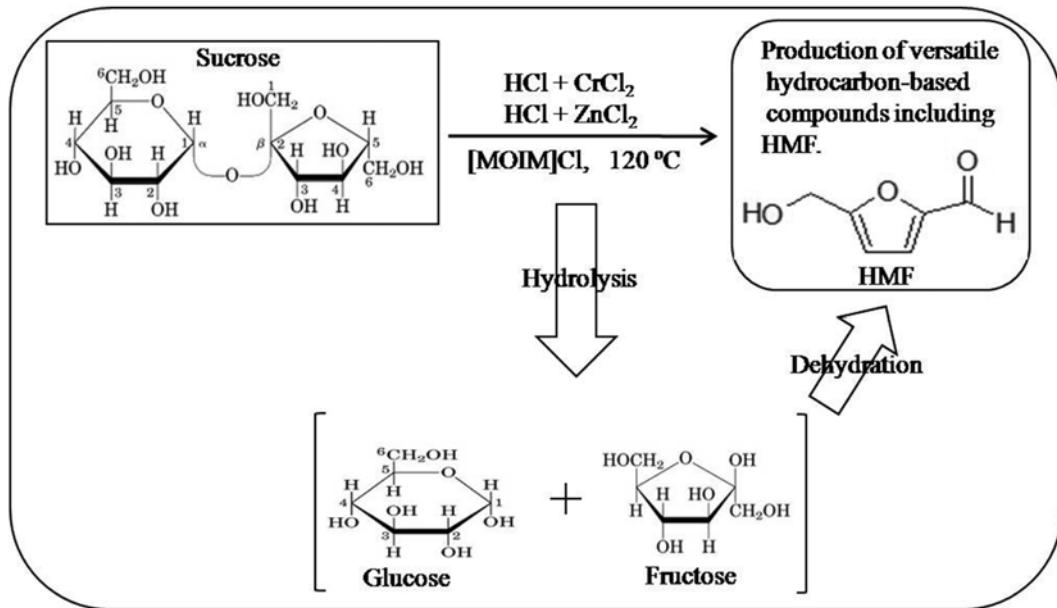


Fig. 1. Schematic strategy for sucrose exploitation in the production of hydroxymethylfurfural (HMF). It is assumed that HMF is synthesized through two sequential reactions of sucrose hydrolysis and then dehydration of its products (fructose and glucose). [MOIM]Cl; 1-methyl-3-octylimidazolium chloride.

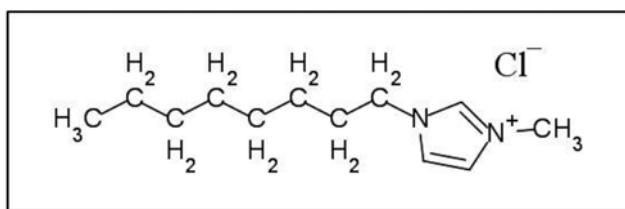


Fig. 2. The chemical structure of 1-methyl-3-octylimidazolium chloride ([MOIM]Cl).

chromium(II) chloride (Alfa Aesar, USA, 97%), zinc chloride (Sigma, USA, 98%), and hydrochloric acid (Sigma, USA, 37%) were used.

2. Reaction Procedures

For the acidic hydrolysis of sucrose in the presence of [MOIM]Cl, 10% (wt/v) sucrose solutions with each of four different HCl concentrations (0.0, 0.1, 0.3 and 0.5 M HCl) were used. The reactions were done on a heating mantle with gentle stirring at 120 °C for 150 min. At regular intervals of 30 min reaction time, the samples were taken for the analyses of sucrose, fructose and glucose.

For selection of an optimal reaction solvent, two groups of reaction mixture were prepared: 1) four different reaction mixtures containing 10 g [MOIM]Cl with each of four different HCl concentrations [0.0, 1.0, 3.0 and 5.0 weight % (wt/v)] (each HCl % (wt/v) in [MOIM]Cl corresponds to 0.0, 0.1, 0.3 and 0.5 M HCl in solution, respectively), and 2) four different reaction mixtures containing 5 g [MOIM]Cl and 5 mL of 10% (wt/v) sucrose solution with each of four different HCl concentrations. The solvent mixtures were reacted on a heating mantle for 90 min.

To evaluate the effect of metal chloride catalysts, CrCl_2 and ZnCl_2 were used. For this, the reaction solvents were divided into three groups: 1) four different reaction mixtures containing 5 g [MOIM]Cl and 5 mL of 10% (wt/v) sucrose solution with each of four differ-

ent HCl concentrations, 2) four different reaction mixtures containing 5 g [MOIM]Cl and 5 mL of 10% (wt/v) sucrose solution with each of four different HCl concentrations plus CrCl_2 , and 3) four different reaction mixtures containing 5 g [MOIM]Cl and 5 mL of 10% (wt/v) sucrose solution with each of four different HCl concentrations plus ZnCl_2 . The reactions were performed in a 25 mL flask containing the reaction mixtures. For the activation between the metal chlorides and [MOIM]Cl, the mix of 5 g [MOIM]Cl plus 0.2 g metal chloride was prereacted at 120 °C for ca. 10 min and then 5 mL of 10% (wt/v) sucrose solution with HCl was added. Thereafter, the reaction was processed at 120 °C for 120 or 150 min, and the samples were taken as described above for their analysis.

In the final procedure, five different sucrose concentrations [0, 10, 20, 30, 40 and 50% (wt/v)] were used to compare the effect of sucrose concentrations on HMF yield and its productivity. For this, the reaction mixtures were divided into four groups: Group 1) the reaction mixture containing 5 g [MOIM]Cl plus 0.2 g CrCl_2 and 5 mL of the given sucrose concentration solution [0%, 10%, 20%, 30%, 40% or 50% (wt/v)] dissolved in 0.3 M HCl solution, Group 2) the reaction mixture containing 5 g [MOIM]Cl plus 0.2 g CrCl_2 and 5 mL of the given sucrose concentration solution [0%, 10%, 20%, 30%, 40% or 50% (wt/v)] dissolved in 0.5 M HCl solution, Group 3) the reaction mixture containing 5 g [MOIM]Cl plus 0.2 g ZnCl_2 and 5 mL of the given sucrose concentration solution [0%, 10%, 20%, 30%, 40% or 50% (wt/v)] dissolved in 0.3 M HCl solution, and Group 4) the reaction mixture containing 5 g [MOIM]Cl plus 0.2 g ZnCl_2 and 5 mL of the given sucrose concentration solution [0%, 10%, 20%, 30%, 40% or 50% (wt/v)] dissolved in 0.5 M HCl solution. Their reactions were processed at 120 °C for 120 min as above and the samples taken as described previously.

3. Analyses of HMF and Sugars

HMF, sucrose, fructose and glucose were quantitated by high performance liquid chromatography (HPLC). A Waters HPLC sys-

tem, a Waters autosampler and a Waters refractometer were used for their analyses. HMF quantification was carried out with a Waters XBridge C₁₈ reversed-phase column (4.6 mm×150 mm, 5 μ m) at 320 nm using a gradient mobile phase at a flow rate of 0.7 mL/min. The gradient condition was as follows: 100% (v/v) water phase for 2 min, first transition and gradient phase in the ratio of 80% (v/v) water and 20% (v/v) methanol for 8 min, second transition and finally 100% (v/v) water for 20 min including transition time. For quantification of the sugars, a YMC-Pack Polyamine II column (4.6 mm×250 mm, 5 μ m, 12 nm, Japan) was used with a mobile phase (75:25, acetonitrile:water) at a flow rate of 1 mL/min.

4. Data Analysis

All measurements were estimated with the mean values of at least four independent reactions and expressed with standard deviation values. For the relative HMF productivity, a control measurement was calculated as a value of 1. The HMF yield for the control measurement was obtained by undertaking the reaction for 60 min in a reaction mixture containing 5 g [MOIM]Cl plus 0.2 g CrCl₂ and 5 mL of 10% (wt/v) sucrose solution dissolved in 0.3 M HCl solution.

RESULTS AND DISCUSSION

1. Reaction Behavior of Sucrose Hydrolysis

The overall result showed that HCl concentration significantly affected the reaction behavior of sucrose hydrolysis (Fig. 3). At higher concentrations of HCl (0.3 M and 0.5 M), sucrose was not detected at 30 min reaction time, but its products (fructose and glucose) were detectable (Fig. 3), indicating that the behavior of their conversion was apparently affected by its reaction conditions [6,7,12,21]. The rate of sucrose hydrolysis was relatively much faster in the reactions with HCl than without HCl. Furthermore, in the reaction mixture with no HCl, relatively high amounts of the sucrose products (fructose and glucose) remained even though sucrose almost disappeared (Fig. 3; 0.0 M HCl). These reaction results imply that HCl played an important role in their conversion behaviors. Kautz and Robinson [22] proposed the role of the activity of hydrogen ion in determining the rate of sucrose hydrolysis. Another research group [23] reported that the imidazolium ion can promote sucrose hydrolysis by acting as a polarizing mediator in the glycosidic bond of sucrose. Based on their studies, the activities of two ions of hydrogen (in

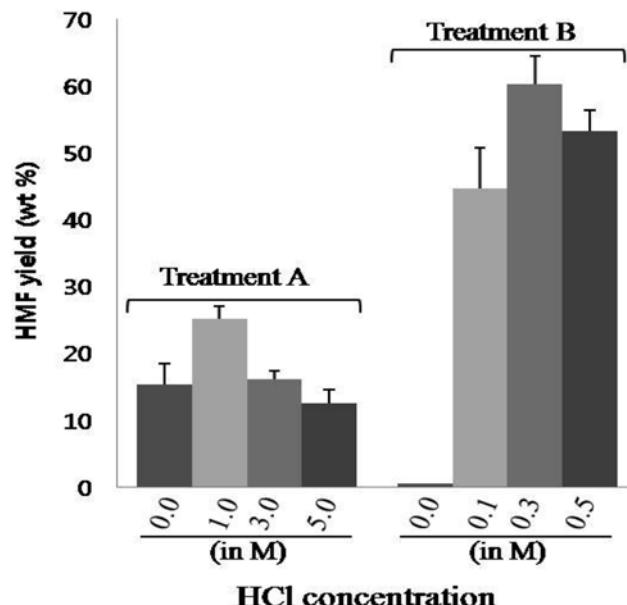


Fig. 4. The effect of the reaction mixture on HMF yields (see Methods for Treatment A and B).

HCl) and imidazolium (in [MOIM]Cl) might contribute to the behaviors of sucrose hydrolysis and further conversion of its products. In addition, our results showed that the reaction time, together with HCl and [MOIM]Cl solvent, affected the hydrolytic process of sucrose. Another interesting finding was observed at 0.1 M HCl treatment (Fig. 3). This treatment showed that sucrose was completely hydrolyzed at 60 min reaction time. As a result of its hydrolytic behavior, fructose was undetectable, whereas relatively high level of glucose was detected (Fig. 3; 0.1 M HCl). The reason for this undetectable fructose may be due to its much quicker conversion to other compounds than that of glucose, which is caused probably by its strong chemical reactivities of isomerization, dehydration, fragmentation or condensation reaction [11,12,24].

2. Effect of the Reaction Mixture on Production of HMF

Ionic liquids can serve as an excellent solvent in the synthetic reactions since they are non-volatile, non-flammable and thermo-stable, and have both properties of cation and anion [16,18]. To evaluate

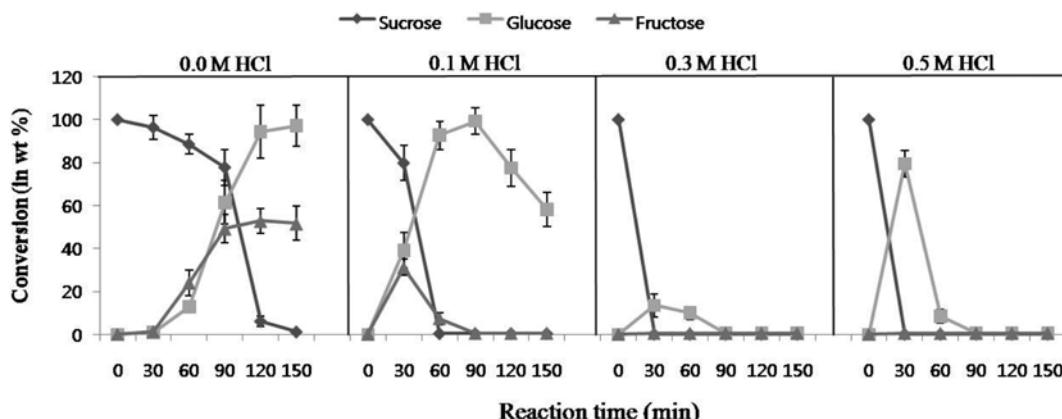


Fig. 3. The hydrolytic behavior of sucrose. Its reactions were processed at 120 °C in the given reaction solvents.

ate the effect of the solvent mixture on the HMF yields, it was divided into two groups (Treatment A and B) with four different HCl concentrations (see Experimental). In Treatment A, the highest HMF yield was observed in the reaction mixture of 100% [MOIM]Cl and 1 wt% HCl (Fig. 4). The others showed similar HMF yields. The average yield of HMF in Treatment A was 17.3 wt%. In contrast, in Treatment B, the highest yield of HMF was found in the reaction mixture containing 5 g [MOIM]Cl plus 5 mL of 10% sucrose solution with 0.3 M HCl. The average yield was 40.7 wt%, indicating that Treatment B was over two-fold greater in the average HMF yield than that of Treatment A (Fig. 4). This experimental evidence clearly suggested that Treatment B (50% [MOIM]Cl+50% of 10% sucrose solution with HCl) is likely to be more effective in the synthesis of HMF than Treatment A (10% sucrose in 100% of 10 g [MOIM]Cl with HCl). Another interesting result was that HCl as an acid catalyst is necessary in Treatment B, but not in Treatment A (Fig. 4; Treatment A and B). It is difficult to explain the reason for the above results because of limited information about the chemical reaction mechanism of HMF synthesis in the presence of ionic liquids. Nonetheless, it cannot be ruled out that the enhancement of HMF synthesis may be attributed to the cooperation of such chemical/physical properties present in the reaction mixture as the polarity of water molecules, the activity of H^+ ion from HCl and both cation/anion properties of ionic liquid [7,12,16,18,24].

3. Effect of $CrCl_2$ and $ZnCl_2$ Catalysts on Production of HMF

In this experiment, two metal chlorides, $CrCl_2$ and $ZnCl_2$, were used to examine their effect on the yields of HMF. Based on the previous results, the reaction solvent was fixed with a mix of 50% [MOIM]Cl and 50% of 10% sucrose solution with HCl. As shown in Table 1, both the chloride catalysts contributed to the promotion of HMF yields, although the degree of its yield promotion varied with the length of its reaction time, catalyst type and HCl concentration. Overall, the addition of the catalysts increased the yields of HMF by approximately 1.2-1.8-fold compared with those of the corresponding treatments of no catalyst addition. Furthermore, rel-

atively higher yields of HMF were observed in $CrCl_2$ than $ZnCl_2$. With the exception of no HCl addition, the optimal reaction time for the two catalysts was likely to be 60 min because the highest yields of HMF for both treatments of $CrCl_2$ plus 0.5 M HCl (78.5 ± 9.4 wt%) and $ZnCl_2$ plus 0.3 M HCl (68.4 ± 7.2 wt%) were obtained at 60 min reaction time (Table 1). This positive effect of the catalysts on the synthetic process of HMF may involve the complex formation between the metal chlorides and [MOIM]Cl, which in turn induces the sucrose products (fructose and glucose) to further rapid reactions such as isomerization and dehydration, resulting in high HMF synthesis [9,25]. On the whole, there was a decreasing trend in the yields of HMF after 90 min reaction time. This would be due to the conversion of HMF to rehydration products such as levulinic acid and formic acid, thus resulting in its decrease [2,10].

4. Effect of Sucrose Concentration on Production of HMF

Sucrose is a good source derived from plant biomass for production of HMF because it is available at lower costs than other sugars such as fructose and glucose. Some workers showed that the concentration of substrate sugars could affect the productivity of HMF [3,10]. So, in this section, the effect of sucrose concentration on the productivity of HMF was examined and their results were provided and discussed. Table 2 illustrates the differences in the yields of HMF between the concentrations of sucrose. The highest yield of HMF (82.0 ± 3.7 wt%) among all treatments was found in Solvent B containing 20% sucrose and $CrCl_2$ catalyst at 30 min reaction time (Table 2), and its relative productivity was 2.4-fold higher than that of the control (Fig. 5 and Experimental). The greatest relative productivity of HMF (a value of 4.7-fold higher) was identified in the reaction mixture containing 50% sucrose, 0.3 M HCl and $CrCl_2$ (Fig. 5). The overall patterns of HMF yield (Table 2) and its productivity (Fig. 5) showed: 1) It was assumed that the optimal reaction time was between 30-60 min, depending on the sucrose concentration because the highest yields of HMF in each treatment were observed both at 30 min and 60 min reaction time (Table 2), 2); as the reaction time elapsed, HMF yields were decreased (Table

Table 1. Results of HMF yield (in wt%) synthesized from sucrose at different concentrations of hydrochloric acid in the presence of $CrCl_2$ and $ZnCl_2$ catalysts

Catalyst	HCl (M)	Reaction time (min)				
		30	60	90	120	150
No catalyst	0.0	-	-	-	10.2 ± 3.3	17.5 ± 5.4
	0.1	-	33.4 ± 4.6	44.7 ± 6.1	40.0 ± 4.0	38.5 ± 5.1
	0.3	36.1 ± 8.1	43.2 ± 6.4	58.3 ± 5.1	42.0 ± 5.7	42.4 ± 2.8
	0.5	38.7 ± 8.7	54.8 ± 5.3	53.3 ± 3.1	42.4 ± 6.1	36.6 ± 4.6
$CrCl_2$	0.0	49.0 ± 8.4	61.5 ± 5.1	56.0 ± 7.2	49.0 ± 5.3	44.5 ± 5.3
	0.1	51.5 ± 8.8	61.5 ± 7.3	53.3 ± 6.5	48.7 ± 3.2	30.0 ± 9.4
	0.3	60.0 ± 8.1	65.0 ± 6.8	55.3 ± 7.1	50.0 ± 7.8	43.1 ± 6.6
	0.5	62.5 ± 9.1	78.5 ± 9.4	71.6 ± 8.9	64.4 ± 6.4	56.3 ± 8.1
$ZnCl_2$	0.0	-	-	9.0 ± 4.8	20.5 ± 6.0	28.5 ± 5.8
	0.1	8.3 ± 3.3	54.7 ± 3.1	59.3 ± 7.0	56.7 ± 3.5	56.5 ± 5.8
	0.3	62.3 ± 5.3	68.4 ± 7.2	64.6 ± 7.7	58.4 ± 8.7	53.2 ± 9.6
	0.5	53.9 ± 6.1	58.0 ± 2.7	53.1 ± 4.2	46.6 ± 5.9	42.2 ± 7.5

The reaction was done at 120 °C for 30 to 150 min in the reaction mixture consisting of 5 mL of 10% sucrose solution with or without HCl and 5 g [MOIM]Cl plus 0.2 g catalyst ($CrCl_2$ or $ZnCl_2$)

Each value is the means of at least four independent measurements with standard deviation

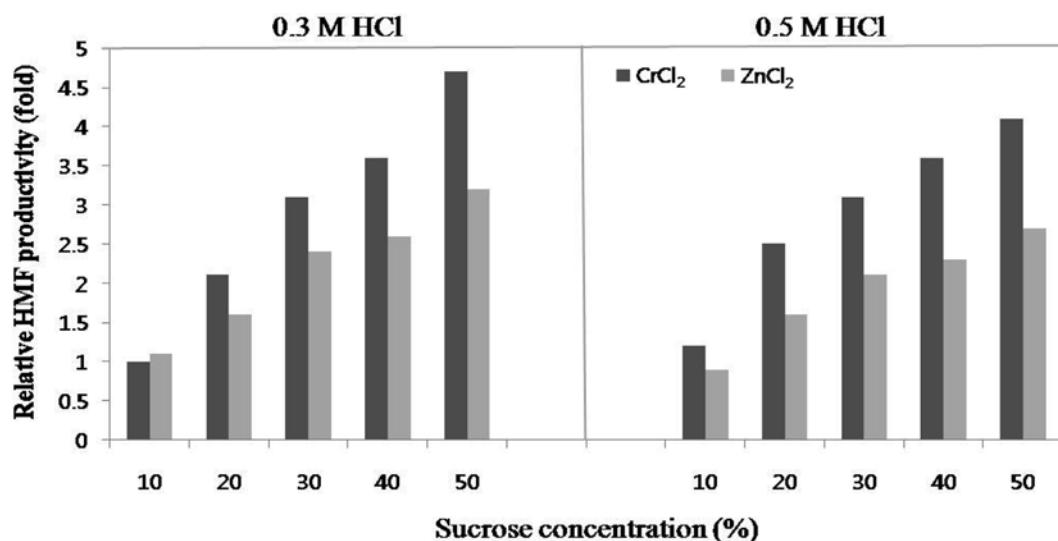
Table 2. Results of HMF yield (in wt%) synthesized in two solvents with different sucrose concentrations

Catalyst	Sucrose (%)	Solvent A				Solvent B			
		Reaction time (min)				Reaction time (min)			
		30	60	90	120	30	60	90	120
CrCl ₂	10	60.0±8.1	65.0±6.8	55.3±7.1	50.7±7.8	62.5±9.1	78.5±9.4	71.6±8.9	64.4±6.4
	20	68.7±8.7	63.0±3.8	51.2±4.8	39.5±3.1	82.0±3.7	71.5±3.4	57.5±3.0	42.3±4.0
	30	48.0±5.0	67.3±5.8	63.4±7.1	38.8±3.8	57.4±5.5	67.7±3.9	59.5±4.3	47.2±5.2
	40	48.3±2.7	59.3±8.1	51.5±4.4	40.0±3.9	44.3±3.3	59.0±3.5	53.3±5.9	47.0±4.8
	50	42.6±3.9	61.6±4.8	56.8±2.8	35.4±2.4	36.4±3.5	53.2±4.6	47.6±4.5	44.1±3.3
ZnCl ₂	10	62.3±5.3	68.4±7.2	64.6±7.7	58.4±8.7	53.9±6.1	58.0±2.7	53.1±4.2	46.6±5.9
	20	53.0±7.3	45.5±6.2	36.5±5.3	28.5±5.7	52.5±3.3	42.5±7.0	33.0±4.5	25.0±3.0
	30	48.9±6.5	52.8±3.7	46.8±3.3	35.9±4.0	42.0±5.5	45.5±3.7	39.5±5.1	29.2±3.8
	40	36.5±3.9	43.0±5.1	40.0±4.8	38.8±6.4	37.5±3.9	38.0±2.8	33.0±3.6	24.5±4.5
	50	39.4±2.8	42.2±6.2	40.0±3.7	34.8±3.5	34.8±4.0	35.2±5.4	33.4±3.4	27.6±3.4

Solvent A: The solvent containing 5 mL each of sucrose concentrations with 0.3 M HCl and 5 g [MOIM]Cl

Solvent B: The solvent containing 5 mL each of sucrose concentrations with 0.5 M HCl and 5 g [MOIM]Cl

The reactions were done at 120 °C for 30 to 120 min in the reaction mixture consisting of the above solvents and 0.2 g catalyst (CrCl₂ or ZnCl₂)
Each value is the means of at least four independent measurements with standard deviation

**Fig. 5. The effects of sucrose concentrations on HMF yields and its productivity.**

2), 3) HMF productivity was more effective in 0.3 than 0.5 M HCl on the whole (Fig. 5), 4) the addition of CrCl₂ or ZnCl₂ catalyst conducted to the enhancement of HMF yields, but the degree of its yields was slightly higher in the former (Table 2), and finally sucrose concentration and the length of reaction time greatly affected the yields of HMF and its productivity; on the whole, with the higher sucrose concentration and the longer reaction time, its yields were gradually decreased (Table 2 and Fig. 5). One particular finding was that the highest yields of HMF were achieved at 60 min reaction time for almost all treatments, while the treatments with 20% sucrose concentration showed their highest yields of HMF at 30 min reaction time (Table 2). The reason for this remains to be investigated for detailed explanation. Collectively, based on the above results, sucrose concentration would be an important parameter when it is considered for the efficient production of HMF.

CONCLUSIONS

The presence of [MOIM]Cl, HCl and the metal chlorides (CrCl₂ and ZnCl₂) in the reaction solvent positively affected the yields of HMF, although the degree of its enhancement varied with their combinations. The most efficient combination for the yields of HMF was examined in the reaction mixture containing 5 g [MOIM]Cl and 5 mL of 20% sucrose solution with 0.5 M HCl plus CrCl₂ at 30 min reaction time. In particular, the concentration of sucrose had influence on the yields and productivity of HMF. The greatest relative productivity of HMF was achieved in the reaction mixture containing 50% sucrose, 0.3 M HCl and CrCl₂. This result suggested that sucrose concentration could be a critical parameter for the commercial production of HMF. In addition, the addition of metal chloride catalysts and HCl concentration also acted as an important factor

for high production of HMF. On the whole, both factors of HCl and metal chlorides (CrCl_2 and ZnCl_2) greatly increased the yields of HMF. However, the choices of appropriate HCl concentration and the catalysts were dependent on the combination with other factors such as reaction time and sucrose concentration.

Our study showed that sucrose could be a biomass-derived chemical feedstock for the production of HMF in the presence of $[\text{MOIM}]\text{Cl}$ ionic liquid, HCl and metal chlorides. Our results also demonstrated that the proper combination between sucrose concentration and its reaction conditions could be an important parameter for cost-effective production of HMF.

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