Carbohydrate Research 346 (2011) 2019–2023

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Note

# Catalytic conversion of glucose to 5-hydroxymethyl furfural using inexpensive co-catalysts and solvents

Zhongshun Yuan [a,b], Chunbao (Charles) Xu [a,b,*], Shuna Cheng [c], Mathew Leitch [c]

[a] Department of Chemical Engineering, Lakehead University, Thunder Bay, ON, Canada P7B 5E1
[b] Department of Chemical & Biochemical Engineering, The University of Western Ontario, London, ON, Canada N6A 5B9
[c] Faculty of Forestry and Forest Environment, Lakehead University, Thunder Bay, ON, Canada P7B 5E1

ARTICLE INFO

*Article history:*
Received 21 April 2011
Received in revised form 1 June 2011
Accepted 6 June 2011
Available online 12 June 2011

*Keywords:*
5-Hydroxymethyl furfural
Glucose
Chromium dichloride
Chromium trichloride
Ionic liquids

ABSTRACT

Efficient conversion of glucose to 5-hydroxymethyl furfural (5-HMF), a platform chemical for fuels and materials, was achieved using $CrCl_2$ or $CrCl_3$ as the catalysts with inexpensive co-catalysts and solvents including halide salts in dimethyl sulfoxide (DMSO) and several ionic liquids. 5-HMF (54.8%) yield was achieved with the $CrCl_2$/tetraethyl ammonium chloride system at mild reaction conditions (120 °C and 1 h). The 5-HMF formation reaction was found to be faster in ionic liquids than in the DMSO system. Effects of water in the reaction system, chromium valence and reaction temperature on the conversion of glucose into 5-HMF were discussed in this work.

In the past 150 years, fossil fuels (petroleum, coal, and natural gas) have been the dominant sources for energy and chemicals.[1] However, due to the rapid economic development and population growth, fast consumption of these resources has accelerated their depletion. The global concerns over energy security, the environmental issues related to the use of fossil fuels, as well as the sustainability of the economic development have intensified the efforts in seeking alternative resources for energy and chemical production. Biomass, with a total annual production of $2.74 \times 10^{19}$ Btu equivalent of about eight times of the energy consumed each year in the world, offers an immense, renewable, and carbon-neutral source for fuels and chemicals.

Glucose is the main building block of biomass, for example, cellulose and starch. Although it has been successful in bio-conversion of cellulose and starch to ethanol fuel, the process to convert a 6-C glucose molecule into two molecules of ethanol (plus two molecules of $CO_2$) has an inherently lower efficiency with respect to energy and carbon utilization efficiency. Moreover, ethanol is not an ideal transportation fuel because of its low energy density (23 M J/L),[2] high volatility, and its readiness in water absorption from air. The ethanol-fueled vehicles have only about 66% of efficiency compared with those fueled with gasoline. In this regard, it is urgently needed to explore conversion technologies to convert plentiful biomass resources into bio-fuels with higher energy contents. 5-Hydroxymethyl furfural (5-HMF), is a dehydration intermediate product in glucose fermentation processes.[3] 5-HMF can be easily converted to dimethylfuran (DMF) with further improved energy content through hydrogenation.[4] The energy content of DMF (31.5 M J/L) is comparable to that of gasoline (35 M J/L) and 40% greater than that of ethanol.[2] Furthermore, DMF (bp = 92–94 °C) is less volatile than ethanol (bp = 78 °C) and is immiscible with water, making it a better candidate for alternative liquid transportation fuels. 5-HMF can also be a platform chemical for a variety of synthetic materials.[5]

The conversion of fructose to 5-HMF is a readily straightforward process that has been demonstrated in water and organic solvents,[6] in multiphase systems,[7,8] and in ionic liquids.[9,10] However, fructose is not an abundant building block in cellulose and starch, although fructose can be produced from glucose via some expensive isomerization processes. Obviously, direct conversion of glucose into 5-HMF offers a better economic value. Zhao et al.[10] have successfully produced 5-HMF from glucose at a high yield (69%) with chromium chlorides as the main catalysts combined with expensive alkylimidazolium chloride ionic liquids, such as 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl), as the co-catalyst. Separation of 5-HMF product from the ionic liquids may be achieved by solvent extraction with low boiling point organic solvents followed by evaporation and purification. Li et al.[11] obtained a surprisingly high yield (91%) of 5-HMF from glucose using the same catalyst/co-catalyst system as was used by Zhao et al.,[10] but under the microwave irradiation conditions. While promising, this catalytic method has

---

[*] Corresponding author. Tel.: +1 519 661 2111x86414.
*E-mail address:* cxu6@uwo.ca (C. (Charles) Xu).

0008-6215/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2011.06.007

limitation in the process economics due to the use of a large amount of expensive ionic liquid solvents. Binder and Raines[5] demonstrated that with chromium chlorides as the main catalyst, polar aprotic organic solvent combined with some halide (Cl, Br) salts could replace ionic liquid as a co-catalyst to convert glucose to 5-HMF at a high yield up to 80%. The drawbacks of this approach may be the difficulty in separation of the 5-HMF product from the high boiling point solvents and recovery of large amount of halide salts used in the process (the addition amount of these salts was over 10% of solvent in weight).

The main objective of the present research was to produce 5-HMF from glucose using $CrCl_2$ or $CrCl_3$ as the main catalysts with different inexpensive co-catalysts and solvents including halide salts in dimethyl sulfoxide (DMSO) and several new ionic liquids synthesized by ourselves.

## 1. Experimental

### 1.1. Materials

The raw materials and chemicals used in this research mainly include: glucose, fructose, dimethyl sulfoxide (DMSO), chromium dichloride ($CrCl_2$), chromium trichloride ($CrCl_3$), tetraethyl ammonium chloride (TEAC), epichlorohydrin, pyridine, dimethyl sulfate, lithium chloride, potassium bromide, zinc chloride, $H_2SO_4$-pretreated zeolite as a solid ultra acid, 5-HMF standard, and 0.005 M $H_2SO_4$ HPLC-grade water. All the raw materials and chemicals as listed above were ACS reagent-grade chemicals from Sigma–Aldrich and were used as received without further treatment.

Several new ionic liquids were synthesized and tested as the reaction co-catalysts and solvents. (3-chloro-2-hydroxypropyl) pyridinium chloride (CHPPC) was synthesized following Zhao's procedure.[12] That is, to a stirred solution of pyridine in ethanol at room temperature was added concentrated hydrochloric acid. After addition of the acid, the mixture was cooled to room temperature, and epichlorohydrin was added dropwise with stirring. Then the reactor flask was irradiated in the water bath of a laboratory ultrasonic cleaner at 25 °C for 2 h. Upon completion, the solvent was removed by evaporation under reduced pressure with heating at 60 °C, followed by vacuum drying to yield a colorless liquid of CHPPC. (3-chloro-2-methoxypropyl) pyridinium chloride (CMPPC) was synthesized by reacting CHPPC with dimethyl sulfate in the presence of barium hydroxide at room temperature for 8 h.[13] Poly(triethylammonium methylene ethylene oxide) (PTEAMEO) salt was synthesized by first cationic polymerization of epichlorohydrin with $BF_3$ plus ethanol as the initiator at 0 °C,[14] then reacting polyepichlorhydrin with triethylamine in ethanol under reflux for 10 h.[15] The synthetic procedures for these ILs are depicted schematically in the following Scheme 1.

### 1.2. Experimental methods for conversion of glucose to 5-HMF

In a typical run for the synthesis of 5-HMF in DMSO, a 100 mL three-neck reactor was equipped with Dean-stark trap, a condenser, a purge gas (nitrogen) inlet, nitrogen outlet and a thermometer in the three necks, respectively. The reactor was first evacuated and purged with nitrogen, then 25.00 g DMSO, 5.00 g glucose, and 0.110 g $CrCl_2$ (0.03 M), 0.150 g (0.03 M) tetraethyl ammonium chloride, and 3.0 mL of benzene (as a stripping reagent for water removal via azeotropic evaporation) were added to the reactor. The Dean-stark was filled with benzene. The reactor was put into an oil bath preheated at 130 °C. The reaction mixture was stirred with a magnetic stirrer under nitrogen protection for 2 h. The reaction mixture was analyzed with HPLC to determine the contents of remaining glucose and 5-HMF in the product.

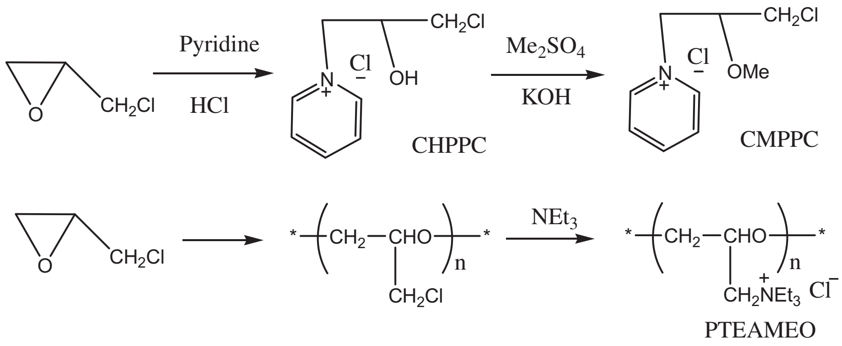
Synthesis of 5-HMF from glucose in ionic liquid solvents was conducted following the similar procedure as above in a 50 mL three-neck reactor with nitrogen purge or a 15 mL sealed reactor with nitrogen protection. In a typical run, 1.00 g glucose and 5.00 g ionic liquid and 0.03 M chromium chloride ($CrCl_2$ or $CrCl_3$) were reacted at 120 °C for 1 h. The reported yield of 5-HMF was calculated to be % of the moles of 5-HMF actually produced in each test to the theoretical maximum moles of 5-HMF if assuming 100% conversion. Duplicate tests were performed for most reaction conditions, and the maximum relative errors were ensured within 10%, as demonstrated in Figure 1.

The reaction products were analyzed by HPLC and quantified with calibration curves generated from commercially available standards. As the typical measurement procedure, the product mixture was first diluted with HPLC grade 0.005 M $H_2SO_4$ water, filtered with 0.45 μm filters, and analyzed using a Waters Breeze GPC–HPLC (gel permeation chromatography–high performance liquid chromatography) instrument (1525 binary pump with refractive index (RI) and UV detector). The analysis was conducted with Bio-Rad HPX-87H column (300 × 7.8 mm) using HPLC grade 0.005 M $H_2SO_4$ water solution as the eluent at a column temperature of 65 °C and a flow rate of 0.8 mL/min. Glucose and 5-HMF were detected with an RI detector and a UV detector, respectively. The reaction mixtures (diluted with methanol) were also analyzed by GC–MS (Varian 1200 Quadrupole GC/MS (EI), Varian CP-3800 GC) using a silicon column with temperature programming from an initial temperature of 65 °C to a final temperature of 280 °C at 10 °C/min with 2 min of initial and final time, to verify the formation of 5-HMF.

## 2. Results and discussion

### 2.1. Catalytic conversion of glucose to 5-HMF in DMSO

Zhao et al.[10] reported that $CrCl_2$ combined with an expensive ionic liquid ([EMIM]Cl) as a co-catalyst or solvent could effectively



**Scheme 1.** Synthesis of ionic liquids of CHPPC, CMPPC, and PTEAMEO.

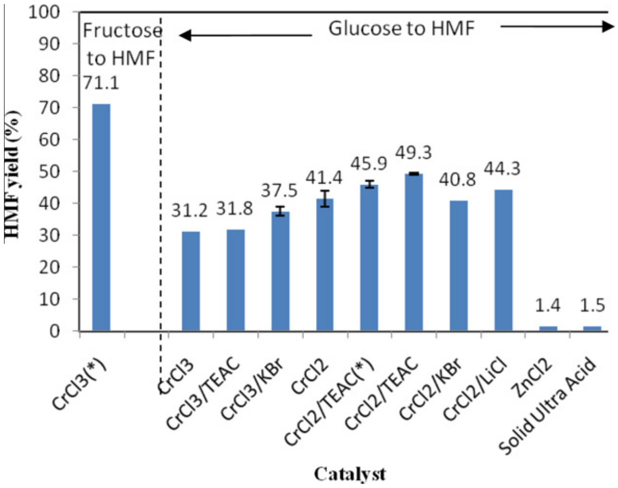


**Figure 1.** Conversion of fructose and glucose to 5-HMF with various catalysts. Reaction conditions: 5.00 g glucose in 25.0 mL DMSO at 130 ± 5 °C for 3 h with 2–3 mL of benzene to remove water by azeotropic distillation. The concentration of the catalyst ($CrCl_2$, $CrCl_3$ or other co-catalysts) was 0.03 M. (∗): without addition of the azeotropic solvent.

convert glucose to 5-HMF. Binder and Raines[5] reported that chromium chloride(II, III) combined with many less expensive co-catalysts such as a variety of halides in dimethyl acetamide produced similar or even better results than the ionic liquid system used by Zhao et al.[10] We began with our investigation of converting glucose and fructose to 5-HMF in dimethyl sulfoxide solution. Compared with the work of Binder and Raines,[5] we used a higher concentration of glucose (about two times) and a lower concentration of cocatalysts (1/15th to 1/10th). Figure 1 presents the yields from the tests for conversion of glucose (or fructose) to 5-HMF in DMSO with $CrCl_2$ or $CrCl_3$ as the main catalyst and KBr, tetraethylammonium chloride (TEAC), LiCl as a co-catalyst. The results in Figure 1 show that $CrCl_2$ is a more active catalyst than $CrCl_3$ as similarly demonstrated by Zhao et al.[10] Among different halides as the co-catalysts, TEAC led to the highest HMF yield from glucose, that is, 49.3% with $CrCl_2$ as the main catalyst. This could be owing to the fact that TEAC has higher solubility and weaker ionic bonding in the DMSO solvent. Without the addition of a co-catalyst, the conversion of glucose into 5-HMF was much lower, which could be explained with the glucose conversion mechanism proposed by Zhao et al.[10] and Binder and Raines.[5] That is, conversion of glucose to 5-HMF is through a fructose intermediate: glucose was first isomerized to fructose followed by conversion of fructose into 5-HMF.[10] The halide anion could act as a chelating ligand to coordinate with chromium ion in the transition state for the transformation of glucose to fructose. The presence of a co-catalyst could promote this isomerization process, hence enhance the HMF yield. As clearly shown in Figure 1, the 5-HMF yield from fructose was very high, 71.1% in the test with $CrCl_3$ catalyst, more than double that from glucose using the same catalyst. Fructose might be the key intermediate in the reaction of converting glucose into 5-HMF, as trace of fructose was detectable by HPLC in the final reaction mixture. Compared with $CrCl_2$ or $CrCl_3$, the use of other Lewis acid catalysts, that is, $ZnCl_2$ and the solid ultra acid (acidified zeolite) produced very low yield of 5-HMF (<2%). Thus, chromium salts played a crucial catalytic role in the conversion of glucose or fructose to 5-HMF.

5-HMF is well known to be unstable and it can undergo hydrolytic decomposition when being heated in the presence of water. For instance, Shimizu et al.[16] reported that mild evacuation of water from the reaction process could significantly increase the 5-HMF product yield from fructose. As shown in Figure 1, the use of benzene as a azeotropic solvent to remove water produced in the reaction process did increase 5-HMF yield from glucose by 3–5%.

## 2.2. Conversion of glucose to 5-HMF in ionic liquids

Since 5-HMF has a very high boiling point (114 °C at 1 bar) and is easy to transform to levulinic acid, it renders a challenge in separation of 5-HMF from a high boiling point aprotic solvent like DMSO. In this regard, employing ionic liquid (salts in liquid state or salts whose melting point is below 50 °C) as the reaction co-catalyst and solvent could be advantageous, since the 5-HMF product can be separated by extraction using low boiling point solvents (acetone, ethyl acetate, diethyl ether, etc.). After the product separation, the ionic liquid and catalyst may be recycled and reutilized. Since the ionic liquids used by Zhao et al.,[10] such as 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl), are very expensive, four inexpensive ionic liquids (three of them were prepared by ourselves in the lab) were investigated in this work for the conversion of glucose to 5-HMF.

### 2.2.1. Effects of ionic liquids

Figure 2 shows the results of synthesis of 5-HMF from glucose with $CrCl_2$ as the main catalyst in various ionic liquids as reaction solvents. The reaction was carried out in a 15 mL sealed reactor with 1.00 g glucose in 5.00 g ionic liquid with 0.03 M $CrCl_2$ at 120 °C for 1 h under $N_2$ protection. The ionic liquids (ILs) tested include tetraethyl ammonium chloride (TEAC), (3-chloro-2-hydroxypropyl) pyridinium chloride (CHPPC), (3-chloro-2-methoxypropyl) pyridinium chloride (CMPPC), and poly(triethylammonium methylene ethylene oxide) chloride (PTEAMEO). Among the four ILs, TEAC (a commercial ionic liquid) produced the best results with 51.6% 5-HMF yield and 100% glucose conversion. The other three self-prepared ionic liquids (as displayed in Scheme 1), that is, CHPPC, CMPPC, and PTEAMEO, produced 100% glucose conversion too, but a lower 5-HMF yield of 29.6%, 38.3%, and 48.4%, respectively, suggesting that more side reactions occurred in these ionic liquid systems. Especially for CHPPC, the hydroxyl group in the molecule may not be stable and easy to undergo dehydration to form double bond and subsequently undergo polymerization. König et al.[17] used a similar catalyst choline chloride combined with $CrCl_2$ for this transformation with an optimal yield of 45% achieved. Comparing the structure of the two ionic liquids, CHPPC is more likely undergo dehydration.

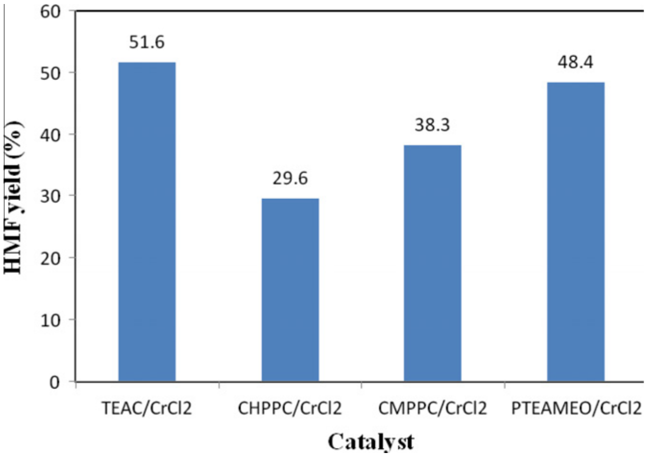


**Figure 2.** Conversion of glucose to 5-HMF with $CrCl_2$ catalyst in various ionic liquids. Reaction conditions: 1.00 g glucose in 5.00 g ionic liquid with 0.03 M $CrCl_2$ at 120 °C for 1 h under $N_2$ protection in a closed system.

**Table 1**
Glucose conversion and 5-HMF yields from the tests using different reactor configurations[a]

| Reactor configuration | Glucose conversion (%) | 5-HMF yield (%) |
|---|---|---|
| 15 mL sealed reactor | ~100 | 51.6 |
| Three necked 50 mL reactor under high vacuum | ~100 | 49.7 |
| Three necked 50 mL reactor under continuous nitrogen purge | ~100 | 54.8 |

[a] Reaction conditions: 1.00 g glucose in 5.00 g TEAC with 0.03 M $CrCl_2$ at 120 °C for 1 h.

### 2.2.2. Effects of water in the reaction system

Water is a by-product of the reaction. The presence of water was believed to promote the decomposition of 5-HMF to levulinic acid.[18] Removal of water could suppress two undesired reactions: hydrolysis of 5-HMF to levulinic acid, and the reactions that partially dehydrate the intermediates into condensation products. In contrast, Shimizu, et al[16] found in the conversion of fructose to 5-HMF under acidic condition, full removal of water decreased the 5-HMF yield while mild evacuation could improve the 5-HMF yield. In this study several special experiments were designed in order to investigate the influence of water in the reaction mixture on the conversion of glucose into 5-HMF. The tests were performed with three different reactor configurations as follows: in a 15 mL sealed reactor, in a three-neck 50 mL reactor under high vacuum, and in a three-neck 50 mL reactor under continuous nitrogen purge. In all tests, the conversion of glucose were all around 100% after 1 h at 120 °C, while the 5-HMF yield varied with different reactor configurations as presented in Table 1. Although the 5-HMF yield (54.8%) was the highest in the three-neck 50 mL reactor under continuous nitrogen purge, the 5-HMF yield in the 15 mL sealed reactor was 51.6%, even higher than that (49.7%) in the three-neck 50 mL reactor under high vacuum. This implies that without the existence of water in the 50 mL three-neck reactor under high vacuum (water was removed under high vacuum), the 5-HMF yield actually reduced, being lower than that from a sealed reactor where water was always present. It should be noted, however, under the nitrogen purge condition water vapor could only be partially removed, and there should always be some water present in the reaction mixture. These results are thus in a good agreement with those reported by Shimizu et al.,[16] where mild evacuation of the reactor could improve the 5-HMF yield, but full removal of water decreased the 5-HMF yield. Thus, the presence of a small amount of water in the reaction system can help the reaction, probably because water can increase the solubility of chromium catalyst in the reaction medium.

### 2.2.3. Effects of chromium valence

Zhao et al.[10] first found that chromium chlorides were very effective catalysts for glucose to 5-HMF conversion and $CrCl_2$ (70%) gave a much better yield than $CrCl_3$ (45%). The study of Binder and Raines[5] showed that there was no difference in the activities of $CrCl_2$ and $CrCl_3$ for the glucose to 5-HMF conversion, which is very interesting due to the fact that the cost of $CrCl_3$ is much lower than $CrCl_2$, while their finding seems to be questionable. In the present study, $CrCl_2$ was found to be more effective than $CrCl_3$ for catalyzing the conversion of glucose to 5-HMF in ILs (TEAC and CMPPC). The use of $CrCl_2$ led to about 10% higher yields of 5-HMF at 120 °C for 1 h either in a closed reactor system under $N_2$ protection or in a three-neck reactor with continuous nitrogen purge, as shown in Figure 3. This probably because $CrCl_3$ is a strong Lewis acid, so it can cause glucose dehydration to oligomers. As such, for glucose to 5-HMF conversion in ionic liquids, $CrCl_2$ is a better catalyst than $CrCl_3$ with respect to the 5-HMF yield.

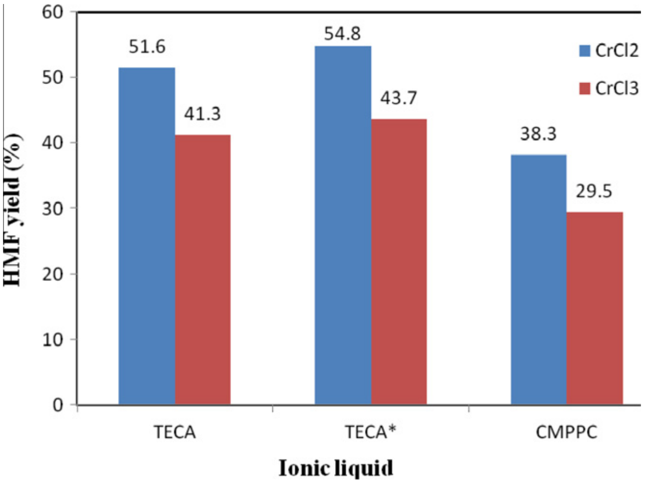


**Figure 3.** Conversion of glucose to 5-HMF in various ILs with $CrCl_2$ or $CrCl_3$ as the main catalyst. Reaction conditions: 1.00 g glucose in 5.00 g ionic liquid with 0.03 $CrCl_2$ or $CrCl_3$ at 120 °C for 1 h in a closed reactor system under $N_2$ protection or in a three-necked reactor with continuous nitrogen purge (∗).

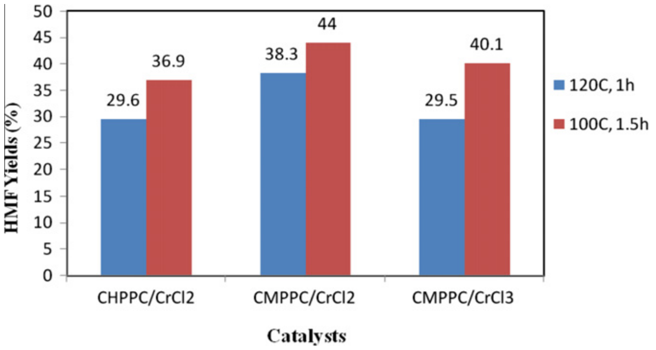


**Figure 4.** Conversion of glucose to 5-HMF at different temperatures. Reaction conditions: 1.00 g glucose in 5.00 g ionic liquids with 0.03 M $CrCl_2$ or $CrCl_3$ at 120 °C for 1 h or at 100 °C for 1.5 h in a closed reactor system under $N_2$ protection.

### 2.2.4. Effects of reaction temperature

Effects of reaction temperature on the glucose conversion to 5-HMF were investigated under the following reaction conditions: 1.00 g glucose in 5.00 g ionic liquids with 0.03 M $CrCl_2$ or $CrCl_3$ at 120 °C for 1 h or at 100 °C for 1.5 h in a closed reactor system under $N_2$ protection. The results are shown in Figure 4. Although in all tests at 120 °C for 1 h or at 100 °C for 1.5 h with the CHPPC/$CrCl_2$, CMPPC/$CrCl_2$ and CMPPC/$CrCl_3$ catalyst system, the glucose conversion attained 100%, the 5-HMF yields were about 6–10% higher at 100 °C than those at 120 °C. This result might suggest that although the reaction was faster at a higher temperature, more side reactions occurred, resulting in reduced yields of 5-HMF.

## 3. Conclusions

Efficient conversion of glucose to 5-HMF was achieved with $CrCl_2$ and $CrCl_3$ as the main catalysts in DMSO and several new ionic liquids as co-catalyst or solvents. When using DMSO, the highest 5-HMF yield obtained was ~50% with the $CrCl_2$/TEAC catalyst system. The yield of 5-HMF attained ~55% using $CrCl_2$ catalyst with TEAC ionic liquid as the co-catalyst or solvent. The reaction was faster in ionic liquids than in DMSO solvent. $CrCl_2$ was demonstrated to be more effective than $CrCl_3$ for converting glucose into 5-HMF in either DMSO or ionic liquids. Nitrogen purging to remove water from the reaction system could significantly enhance the 5-HMF yield, while complete removal of water reduced the HMF yield. In a closed reaction system with ionic liquids, the 5-HMF yields were higher at 100 °C than those at 120 °C.

## Acknowledgments

The authors are grateful for the financial support from the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA) through the New Directions Program Grant, as well as the funding from FedNor and NOHFC. One of the authors (C.X.) also acknowledges the funding from NSERC through the Discovery Grant.

## References

1. *Biorefineries—Industrial Processes and Products: Status Quo and Future Directions*; Kamm, B., Gruber, P. R., Kamm, M., Eds.; Wiley-VCH: Weinheim, Germany, 2006.
2. Román-Leshkov, Y.; Barrett, C. J.; Liu, Z. Y.; Dumesic, J. A. *Nature* **2007**, *447*, 982–986.
3. Martin, C.; Marcet, M.; Almazán, O.; Jönsson, L. J. *Bioresource Tech.* **2007**, *98*, 1767–1773.
4. Lichtenthaler, F. W. A. *Chem. Res.* **2002**, *35*, 728–737.
5. Binder, J. B.; Raines, R. T. *J. Am. Chem. Soc.* **2009**, *131*, 1979–1985.
6. Halliday, G. A.; Young, R. J., Jr.; Grushin, V. V. *Org. Lett.* **2003**, *5*, 2003–2005.
7. Román-Leshkov, Y.; Chheda, J. N.; Dumesic, J. A. *Science* **2006**, *312*, 1933–1937.
8. Chheda, J. N.; Román-Leshkov, Y.; Dumesic, J. A. *Green Chem.* **2007**, *9*, 342–350.
9. Moreau, C.; Finiels, A.; Vanoye, L. *J. Mol. Catal. A: Chem.* **2006**, *253*, 165–169.
10. Zhao, H.; Holladay, J. E.; Brown, H.; Zhang, Z. C. *Science* **2007**, *316*, 1597–1600.
11. Li, C.; Zhang, Z.; Zhao, Z. K. *Tetrahedron Lett.* **2009**, *50*, 5403–5405.
12. Zhao, S.; Zhao, E.; Shen, P.; Zhao, M.; Sun, J. *Sonochemistry* **2008**, *15*, 955–959.
13. Srivastava, H. C.; Singh, P. P.; Harshe, S. N.; Virk, K. *Tetrahedron Lett.* **1964**, *5*, 493–498.
14. Francis, A. U.; Venkatachalam, S.; Kanakavel, M.; Ravindran, P. V.; Ninan, K. N. *Eur. Polym. J.* **2003**, *39*, 831–841.
15. Nakanishi, T.; Komiyama, J.; Iijima, T. *J. Membr. Sci.* **1986**, *26*, 263–275.
16. Shimizu, K.; Uozumi, R.; Satsuma, A. *Catal. Commun.* **2009**, *10*, 1849–1853.
17. Ilgen, F.; Ott, D.; Kralisch, D.; Reil, C.; Palmberger, A.; König, B. *Green Chem.* **2009**, *11*, 1948–1954.
18. Huber, G. W.; Iborra, S.; Corma, A. *Chem. Rev.* **2006**, *106*, 4044–4098.