Conversion of Glucose into HMF Catalyzed by CPL-LiCl Investigated using Dual-Wavelength UV Spectrophotometry

Yue Yuan,[1] Shuangquan Yao,[1] Shuangxi Nie, and Shuangfei Wang*

The process of dehydration of glucose to 5-hydroxymethylfurfural (HMF), using caprolactam-lithium chloride (CPL/LiCl) as a solvent, was investigated. Dual-wavelength ultraviolet spectrophotometry provides a new approach for the determination of glucose conversion rate and yield of HMF. Experiments were performed to demonstrate the accuracy and precision of this method. Various reaction parameters, such as the ratio of ionic liquid, reaction temperature, reaction time, catalyst dosage, and solid absorbent, were investigated in detail for the dehydration of glucose. The optimal conditions were explored. Finally, a possible mechanism for the dehydration of fructose to HMF was proposed.

Key words: Glucose; Caprolactam-lithium chloride (CPL/LiCl); 5-Hydroxymethylfurfural (HMF); Dual wavelength UV spectrophotometry

*Contact information: Department of Light Industrial and Food Engineering, Guangxi University, Nanning, 53004, China; *Corresponding author: wangsf@gxu.edu.cn; [1]these authors contributed equally to this work.*

INTRODUCTION

Most fuels and fossil resources are gradually being depleted. However, the rapid development of human society requires much more energy. Biomass is one of the most widely available resources; it can be converted into liquid fuels and chemicals, and it is a replacement for fossil resources-derived fuels and chemicals (Melero *et al.* 2012; Camarero Espinosa *et al.* 2013). 5-Hydroxymethylfurfural (HMF) is one of the new platform chemicals derived from biomass resources (Bahari *et al.* 2014; Zhang *et al.* 2015). In addition, the hydrolysis of HMF can furnish a variety of useful products and new polymeric materials such as plastic resins and diesel fuel additives (Bicker *et al.* 2003; David and Gross 2007). 5-Hydroxymethylfurfural can be obtained by acid-induced dehydration of glucose (Wang *et al.* 2011; Dunn *et al.* 2013). Fructose is usually selected as a preferred feedstock for the production of HMF (Zhang *et al.* 2012). However, it should be pointed out that fructose is expensive and uncommon in nature, which limits the large-scale and sustainable production of HMF (Hu *et al.* 2015). On the contrary, glucose has been considered an abundant and cheap resource for the production of HMF (Zhou *et al.* 2013; Xiao *et al.* 2014).

In recent decades, the dehydration of glucose has been reported using water, organic solvents, and ionic liquids as the reaction mediums for high HMF yields (Liu *et al.* 2015b). Water, as a green solvent, may accelerate the rehydration of HMF, bringing many unexpected side products and thus decreasing the selectivity of HMF formation in the dehydration reaction (Liu *et al.* 2015b). On the other hand, Ranoux *et al.* (2013) found that HMF synthesis from hexoses is autocatalyzed by formic acid, which is a by-product of the reaction. Complex preparation processes, expensive materials, and difficult recovery are the limitations of organic solvents in commercial applications (Alonso *et al.* 2010). The degradation of HMF can be effectively inhibited by the presence of H^+ ions in the system. Ionic liquids as solvents also provide the advantages of moderate reaction conditions and shorter times (Ohara *et al.* 2010). Therefore, many researchers have considered ionic liquids (ILs) to be the most convenient solvents and catalysts for the selective dehydration of fructose into HMF (Qu *et al.* 2012; Chinnappan *et al.* 2014; Jadhav *et al*. 2014).

The process of direct dehydration of hexoses to HMF is well known. Several mechanisms for the direct formation of HMF have been suggested in the literature. HMF was dehydrated of hexoses by elimination of three water molecules. The determination of HMF can be accomplished using high-performance liquid chromatography (HPLC) and ultraviolet (UV) spectrophotometry. Tao *et al.* (2011) analysed the HMF by HPLC on a Waters Alliance 2695 series chromatograph equipped with Waters 2996 PDA detector and an Intersil ODS-EP C18 reversed-phase column at 30 ºC. Hu *et al.* (2012) analysed the HMF on an Agilent 1200 series system equipped with a refractive index detector and a Bio-Rad Aminex HPX-87H ion exclusion column at 65 ºC. The concentration of HMF was calculated based on the standard curve obtained with known concentrations of the substance. Although HPLC is a relatively precise measurement, the analytical process is complex and more costly. Gürkan and Altunay (2015) used spectrophotometry coupled with ultrasonic-assisted cloud point extraction. This method was established as simple, cost-effective, and fast. De Andrade *et al.* (2016) investigated the HMF in corn and cane syrups by HPLC-UV for the first time. The method was accurate and precise and showed excellent performance with low limits; however the pretreatment for determination was complicated.

In this study, the HMF yield was investigated by means of dual-wavelength UV spectrophotometry, and the solvent used was the ionic liquid caprolactam-lithium chloride (CPL-LiCl). The effects of various process parameters, such as the ratio of ionic liquid, reaction temperature, reaction time, catalyst dosage, and solid absorbent, on glucose conversion and HMF yield were investigated. The optimal conditions and possible mechanism for the dehydration of fructose to HMF were also explored.

EXPERIMENTAL

Materials

D-glucose and HMF (99%) were supplied by Aladdin (Shanghai, China). Caprolactam (CPL) was purchased from Guanghua Technology Co. Ltd. (Guangzhou, China). Lithium chloride (LiCl), P_2O_5, $CaCl_2$, and Al_2O_3 were purchased from Kelong Chemical Co. Ltd. (Chengdu, China). All chemicals were of analytical grade.

Methods

Caprolactam (5.0 g) was added to a 50-mL flask followed by LiCl, keeping the molar ratios of LiCl/CPL at 1/2, 1/3, 1/4, and 1/5. The ionic liquid CPL/LiCl was obtained by oil-bath heating of the mixture (Liu *et al*. 2015a).

Absorbance measurements at the selected wavelengths were conducted on a UV-visible spectrophotometer (Agilent, USA) equipped with 1.0-cm quartz cells (Rather *et al*. 2015). The steps of the preparation process were as follows: five groups of HMF standards were prepared using water as solvent, and the concentrations were increased from 0.019 to 0.093 mM. The absorption spectra of standard solutions acquired using a quartz cuvette 5 mm in length were measured from 200 to 800 nm. The absorption spectra of the sample and actual ionic liquids were also measured to eliminate the absorbance interference from them (Barthwal *et al*. 2015). Glucose was added to the ionic liquid; the content of the glucose was 10% of the ionic liquid. To ensure completion of the reaction, the samples were pretreated for 3 h at 110 °C with continued stirring. Then, the liquid was examined by UV-visible spectroscopy.

To ensure the reliability of the results obtained, various reaction parameters for the glucose-to-HMF conversion were investigated. Various samples (5 mL) were respectively put in five test tubes, and the absorbance of the solutions at 284 and 450 nm were measured using dual-wavelength UV spectrophotometry.

RESULTS AND DISCUSSION

Dual-Wavelength UV Spectrophotometry of HMF

Figure 1 shows the UV analysis of HMF standard solutions of various concentrations when the wavelength was in the range of 200 to 800 nm. The standard solutions of HMF exhibited an obvious absorption peak at 284 nm. When the wavelengths were at 200 to 350 nm, HMF with various concentrations had a definite absorption. However, the absorbance was close to zero when the wavelength was beyond 350 nm.

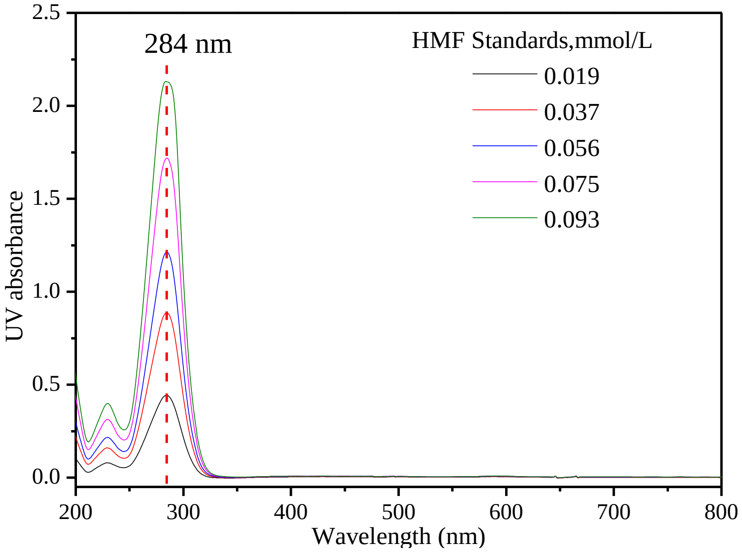

Fig. 1. UV analysis of HMF standards

Figure 2 reveals that the absorbance varies linearly with the concentration in accordance with the Beer-Lambert law (Rather *et al.* 2015). The relationship between the absorbance and concentration is:

$$\text{Absorbance (284 nm)} = 22.6 \times C \ (R^2 = 0.995). \qquad (1)$$

It can be detected by UV spectrophotometry that the maximum absorbance of HMF was at 284 nm.

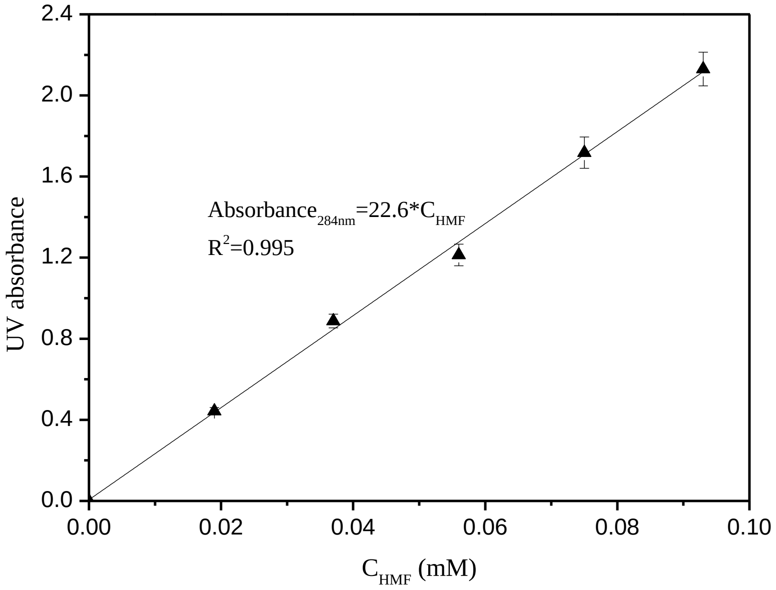

Fig. 2. UV analysis of HMF standard curve (284 nm)

The UV-visible analysis of HMF standards and the test sample is shown in Fig. 3. New, broad bands appeared in the test sample at 350 to 600 nm (*i.e.*, a red shift). This, as we speculate, was due to the presence of unsaturated bonds in ionic liquids (Liu and Chen 2012, 2013).

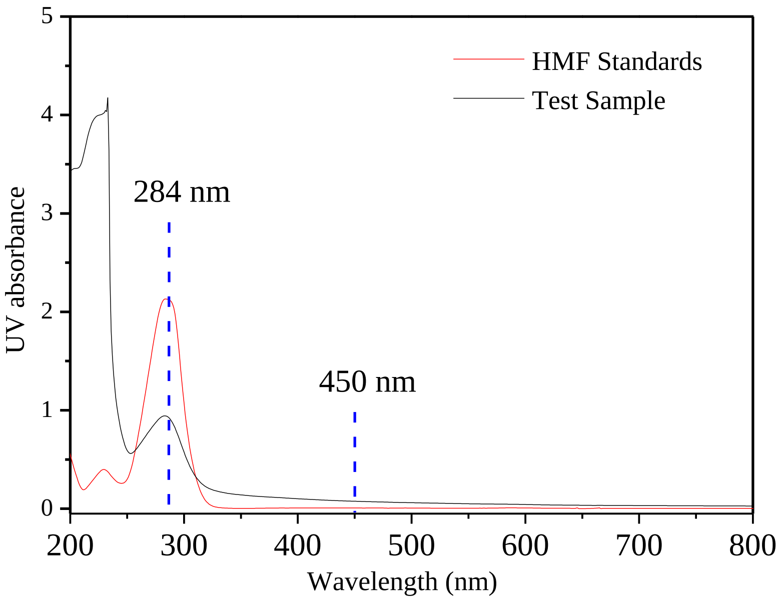

Fig. 3. UV analysis of HMF standards and test sample

According to Fig. 4, the CPL/LiCl ionic liquids have a certain absorbance at 350 to 600 nm, which is in agreement with the inference in Fig. 3. The absorption band at 284 nm of the ionic liquid itself will have an impact on absorbance. Therefore, the actual absorbance of HMF at 284 nm was the sum of the HMF and that of the ionic liquid.

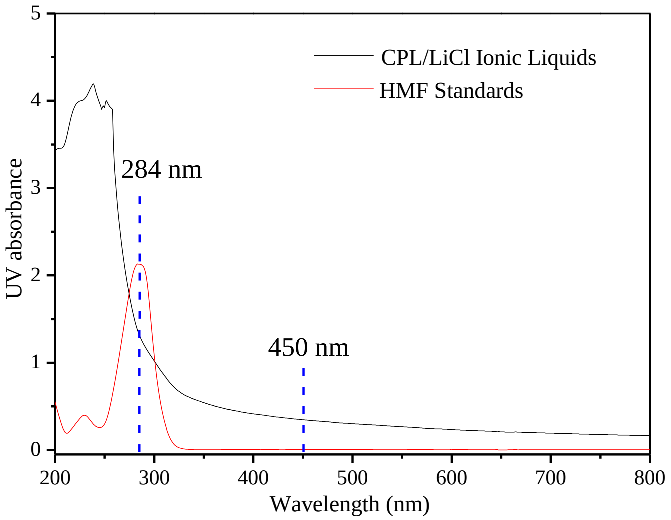

Fig. 4. UV analysis of HMF standards and CPL/LiCl ionic liquids

Computation of Dual-Wavelength UV

To remove the effect of interfering substances, dual-wavelength UV spectrophotometry was used to measure the absorbance of HMF. The method was established by taking the absorbances of ionic liquids into consideration. Consequently, the actual absorbance of HMF at 284 nm was evaluated as shown below:

$$A_{\text{HMF absolute 284}} = A_{\text{sample284}} - A_{\text{CPL/LiCl284}} = A_{\text{sample284}} - A_{\text{CPL/LiCl450}} \times K$$

$$K = A_{\text{CPL/LiCl284}} / A_{\text{CPL/LiCl450}} = 1.345/0.34748 = 3.871 \qquad (2)$$

In Eq. 2, $A_{\text{CPL/LiCl284}}$ and $A_{\text{CPL/LiCl450}}$ are the absorbances of CPL/LiCl at 284 and 450 nm, respectively. $A_{\text{HMF absolute 284}}$ is the absorbance of the sample HMF at 284 nm. $A_{\text{sample284}}$ is the absorbance of HMF standard sample at 284 nm. K is the ratio of absorbance for CPL/LiCl at 284 and 450 nm.

According to Beer-Lambert's law, there is a fixed proportion of the absorbance for the ionic liquid at 284 and 450 nm. Therefore, based on the absorbance of the sample at 450 nm, the absorbance at 284 nm can be obtained. In addition, the absorbance of HMF at 284 nm is the absorbance of the actual sample minus the absorbance of ionic liquids at 284 nm. Thus, the content of HMF can be calculated.

Precision and Accuracy of Dual-Wavelength Method

Five groups of recovery experiments were performed to demonstrate the accuracy and precision of the dual-wavelength UV method. The HMF yield is shown in Table 1. The HMF standards were added to the sample solution in quantities of 4.0, 8.0, 10.0, 15.0, and 20.0 μmol, respectively. The obtained recoveries were approximately 95.0%, 97.5%, 99.0%, 98.7%, and 97.0%, respectively. The recovery of standard material should be close to 100%. If the recovery is too high or too low, it illustrates that the method was unreliable. The results show that the measurement errors are in the extent permitted (error of ±0.5%) and the feasibility of dual-wavelength UV spectrophotometry was thus established.

Table 1. Recovery Rate of HMF

Assay	HMF(μmol)	
	HMF addition	HMF measured quality
1	3.5	3.9
2	7.8	7.6
3	10	9.9
4	15	14.9
5	20	19.6

The results suggest that dual-wavelength UV spectrophotometry is simple, rapid, has high precision, and no colour treatment to HMF measurement is required. The method can be of value in investigating the glucose-to-HMF conversion.

HMF Preparation by Glucose Dehydration with CPL/LiCl Catalyst

HMF was one of the main products of cellulose's degradation. And it has several different functional groups. Therefore, HMF was chosen and considered as a potential platform chemical in the future. It can be converted to 2,5-dimethylfuran, which is a biofuel just like gasoline and other important molecules such as levulinic acid, 2,5-furandicarboxylic acid, 2,5-diformylfuran, dihydroxymethylfuran, and 5-hydroxy-4-keto-2-pentenoic acid (Rosatella *et al.* 2011).

Effect of reaction time on glucose dehydration efficiency

The conditions for glucose dehydration were as follows: the ratio of CPL/LiCl was 5:1, the amount of glucose was 10% of the ionic liquid amount, and the reaction temperature was 110 °C. The effects of reaction time on glucose conversion rate and HMF yield are shown in Fig. 5A.

Figure 5A shows that the conversion rate of glucose increased with increasing time. It increased considerably in the first three hours. The conversion rate of glucose was 93.7% at 3 h. The upward trend of conversion rates began to slow down after 3 h of reaction time. The conversion of glucose was 98.6% after 4 h. The yield of HMF was unvaried at first and increased afterwards. It is respect to the increase in the conversion of glucose, the yield of HMF had a steady increase. This is probably due to the part of glucose converted to intermediate substances at 3 h and not yet converted to HMF until 4 h. The yield of HMF was 59.3% at 4 h. The optimal reaction time was found to be 4 h.

Effect of Reaction Temperature on Glucose Dehydration

Figure 5B shows the effect of reaction temperature on glucose conversion rate and HMF yield. The condition for glucose dehydration was as follows: the ratio of CPL/LiCl was 5:1, the amount of glucose was 10% of the ionic liquid amount, and the reaction time was 4 h.

Figure 5B shows that the glucose conversion rate and HMF yield increased as the temperature increased. The yield of HMF increased slowly below 110 °C. It can be concluded that conditions were not suitable for HMF production when the temperature was less than 100 °C.

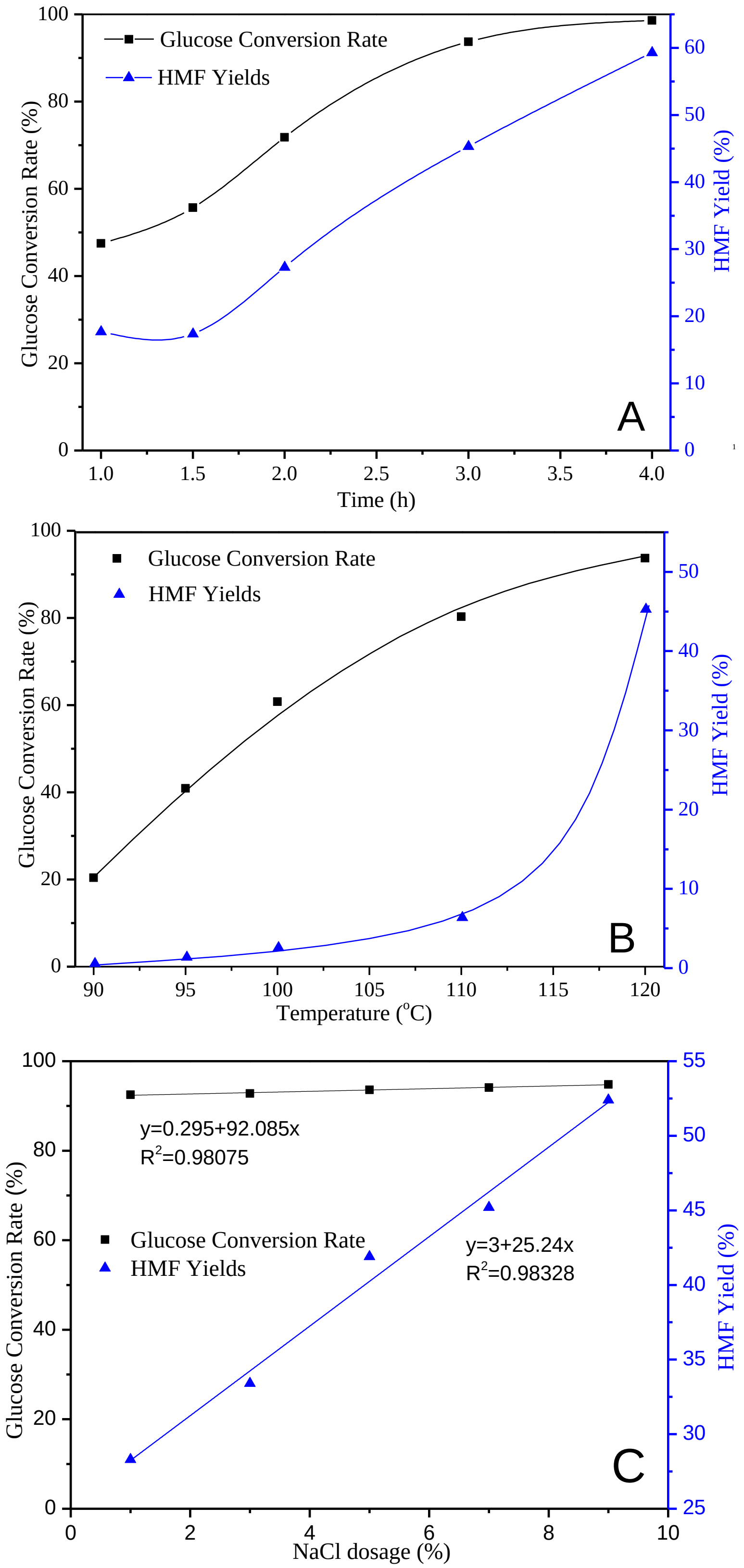

Fig. 5. Effect of reaction time, reaction temperature, and NaCl dosage on glucose conversion rate and HMF yield (A: reaction time on glucose conversion rate and HMF yield, B: reaction temperature on glucose conversion rate and HMF yield, C: NaCl dosage on glucose conversion rate and HMF yield)

The conversion rate of HMF increased rapidly when the temperature was over 110 °C. This increase was probably due to the glucose immediately being converted to HMF. The yield of HMF increased quickly when the intermediate material was transformed to HMF at 120 °C. The optimum reaction temperature was found be 120 °C.

Effect of Catalyst Dosage on Glucose Dehydration Efficiency

Marcotullio and De Jong (2010) found that metal salts have good catalytic effect on xylose dehydration with water as solvent. They conducted a comparative study of NaCl, KCl, $FeCl_3$, $CaCl_2$, $MgCl_2$, and other common metal salts. Figure 5C shows the effect of NaCl dosage on glucose conversion rate and HMF yield. The glucose dehydration conditions were as follows: the ratio of CPL/LiCl was 5:1, the amount of glucose was 10% of the ionic liquid amount, the reaction temperature was 120 °C, and the reaction time was 4 h.

Figure 5C shows that the amount of catalyst had little effect on glucose conversion. At the same time, the HMF yield greatly improved with increasing NaCl dosage. Considering the glucose conversion rate and HMF yield, the optimum dosage of NaCl was found to be 9%.

Effect of Solid Absorbent on Glucose Dehydration Efficiency

As it is reported that HMF is not stable in the presence of water, it was assumed that water produced during the dehydration process would result in the decomposition of HMF to formic acid, acetic acid, or other side products (Liu and Chen 2012; Zhang *et al.* 2012). To avoid the influence of water, solid absorbent materials such as P_2O_5, Al_2O_3, and $CaCl_2$ were added. Based on the results in generation of glucose, three molecules of water were taken off. The amount of adsorbents of P_2O_5, Al_2O_3, and $CaCl_2$ was, respectively, 1.155 g, 0.83 g, and 0.903 g. The yield of HMF was higher than without absorbent. The results reveal that adsorbents promote the reaction and these adsorbents do not react with other products.

Table 2. Influence of Dehydrating Agents on HMF Yield

CPL/LiCl, M/M	HMF (mol%)		
	P_2O_5	$CaCl_2$	Al_2O_3
2:1	74	44	14
3:1	79	51	20
4:1	86	59	34
5:1	90	74	72

Table 2 shows that the yield of HMF increased with the addition of P_2O_5, Al_2O_3, and $CaCl_2$; P_2O_5 was the best solid absorbent studied, as the yield of HMF (the ratio of CPL/LiCl was 5:1) increased from 46.2% to 89.67% with the addition of P_2O_5.

Reaction Mechanism for Glucose-to-HMF Conversion in CPL/LiCl

Figure 5 shows the HMF yield was greatly improved with increasing NaCl dosage. There were some by-products from the reaction. Roman *et al.* (2006) improved the two-phase system. They added DMSO and PVP into water to inhibit the side reaction. This method increased the selectivity of HMF. Moreover, the addition of MIBK and DCM can improve the extraction of organic phase to HMF (Chheda *et al.* 2007). These authors also studied glucose conversion process by using similar biphasic system. They found that the conversion rate, selection, and yield of HMF were increased. And the organic solvent after the product isolated can be recycled, thus reducing the cost.

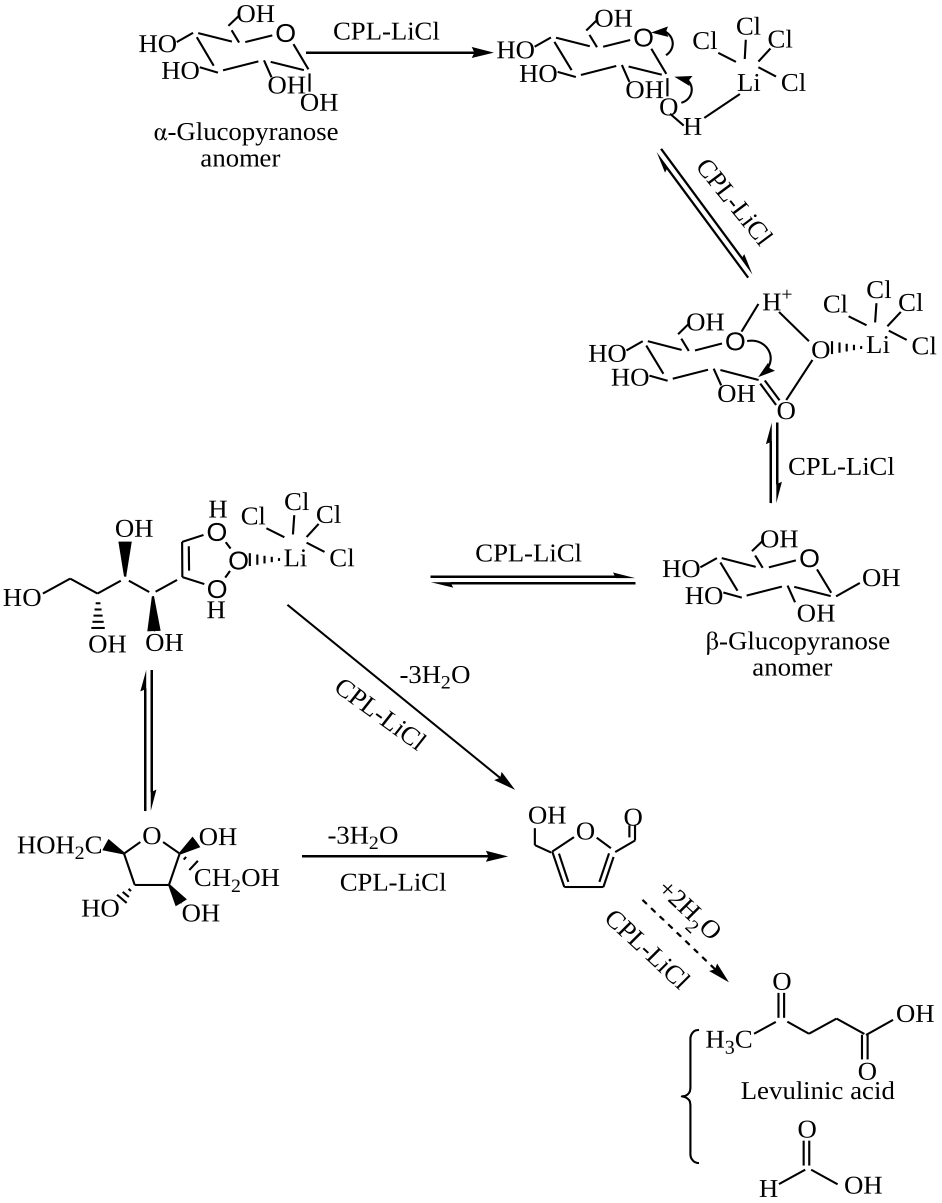

Fig. 6. Reaction mechanism for glucose-to-HMF conversion in CPL/LiCl

Figure 6 shows that the ring-opening reaction of α-glucose occurred when CPL/LiCl attacked the hydroxyl on the C^1 position. Then, the σ coordination bond was formed by the lone-paired electrons of oxygen atoms on hydroxyl groups of enol coordinating with Li^+. α-glucose turned into β-glucose, as the optical rotation of glucose changed. The ring-opening reaction of β-glucose then occurred. The product HMF was obtained when β-glucose isomerized to fructose or underwent a dehydration reaction. The fructose was dehydrated to HMF by catalysis. Solid absorbent was added to prevent the degradation of HMF in the glucose dehydration process, improving the HMF yield.

CONCLUSIONS

1. The standard solution of 5-hydroxymethylfurfural (HMF) was detected by dual-wavelength UV. The results showed that dual-wavelength method was feasible for determining the content of HMF. The method was simple, fast, without color treatment, and high recovery rate. It means that an effective means for detecting HMF produced by biomass hydrolysis was thus provided.
2. The condition of HMF production from glucose hydrolysis by CPL/LiCl catalysis was optimized. The optimal conditions: reaction time is 4 h, temperature is 120 ºC, NaCl dosage is 9%, and solid absorbent is P_2O_5. The best rate of HMF is 89.67%.
3. The mechanism of glucose dehydration catalyzed by CPL / LiCl was discussed. First, the ring-opening reaction of α-glucose occurred, and then α-glucose turned into β-glucose. The fact that the optical rotation of glucose changed implies that a ring-opening reaction of β-glucose is involved. The product HMF was obtained when β-glucose isomerized to fructose or underwent a dehydration reaction. The fructose was dehydrated to HMF by catalysis. Solid absorbent was added to prevent the degradation of HMF in the glucose dehydration process, thus improving the HMF yield.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the Innovation Project of Guangxi Graduate Education (YCBZ2015011) and the Guangxi Natural Fund (2013GXNSFFA019005).

REFERENCES CITED

Alonso, D. M., Bond, J. Q., and Dumesic, J. A. (2010). "Catalytic conversion of biomass to biofuels," *Green Chemistry* 12(9), 1493-1513. DOI: 10.1039/c004654j

Bahari, A., Baig, M. N., Leeke, G. A., Bowra, S., and Santos, R. C. D. (2014). "Subcritical water mediated hydrolysis of cider spent yeast: Kinetics of HMF synthesis from a waste microbial biomass," *Industrial Crops and Products* 61, 137-144. DOI: 10.1016/j.indcrop.2014.06.031

Barthwal, S., Ravi, P., and Vudayagiri, A. (2015). "UV–visible spectroscopic study of laser irradiated lithium colloids and ionic liquids," *Journal of Molecular Liquids* 208, 11-15. DOI: 10.1016/j.molliq.2015.03.052

Bicker, M., Hirth, J., and Vogel, H. (2003). "Dehydration of fructose to 5-hydroxy-methylfurfural in sub- and supercritical acetone," *Green Chemistry* 5(2), 280-284. DOI: 10.1039/b211468b

Camarero Espinosa, S., Kuhnt, T., Foster, E. J., and Weder, C. (2013). "Isolation of thermally stable cellulose nanocrystals by phosphoric acid hydrolysis," *Biomacromolecules* 14(4), 1223-1230. DOI: 10.1021/bm400219u

Chheda, J. N., Roman, L. Y., and Dumesic, J. A. (2007). "Production of 5-hydroxy-methylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides," *Green Chemistry* 9(4), 342-350. DOI: 10.1039/b611568c

Chinnappan, A., Jadhav, A. H., Kim, H., and Chung, W. -J. (2014). "Ionic liquid with metal complexes: An efficient catalyst for selective dehydration of fructose to 5-hydroxymethylfurfural," *Chemical Engineering Journal* 237, 95-100. DOI: 10.1016/j.cej.2013.09.106

David, R. D., and Gross, R. A. (2007). "Chemicals from biomass," *Science* 318, 1250-1251. DOI: 10.1126/science.1146356

De Andrade, J. K., Komatsu, E., Perreault, H., Torres, Y. R., da Rosa, M. R., and Felsner, M. L. (2016). "In house validation from direct determination of 5-hydroxymethyl-2-furfural (HMF) in Brazilian corn and cane syrups samples by HPLC–UV," *Food Chemistry* 190, 481-486. DOI: 10.1016/j.foodchem.2015.05.131

Dunn, E. F., Liu, D., and Chen, E. Y. X. (2013). "Role of N-heterocyclic carbenes in glucose conversion into HMF by Cr catalysts in ionic liquids," *Applied Catalysis A: General* 460-461, 1-7. DOI: 10.1016/j.apcata.2013.04.015

Gürkan, R., and Altunay, N. (2015). "Quantification of 5-hydroxymethylfurfural in honey samples and acidic beverages using spectrophotometry coupled with ultrasonic-assisted cloud point extraction," *Journal of Food Composition and Analysis* 42, 141-151. DOI: 10.1016/j.jfca.2015.03.012

Hu, L., Sun, Y., Lin, L., and Liu, S. (2012). "Catalytic conversion of glucose into 5-hydroxymethylfurfural using double catalysts in ionic liquid," *Journal of the Taiwan Institute of Chemical Engineers* 43(5), 718-723. DOI: 10.1016/j.jtice.2012.04.001

Hu, L., Tang, X., Wu, Z., Lin, L., Xu, J., Xu, N., and Dai, B. (2015). "Magnetic lignin-derived carbonaceous catalyst for the dehydration of fructose into 5-hydroxy-methylfurfural in dimethylsulfoxide," *Chemical Engineering Journal* 263, 299-308. DOI: 10.1016/j.cej.2014.11.044

Jadhav, A. H., Chinnappan, A., Patil, R. H., Kostjuk, S. V., and Kim, H. (2014). "Green chemical conversion of fructose into 5-hydroxymethylfurfural (HMF) using unsymmetrical dicationic ionic liquids under mild reaction condition," *Chemical Engineering Journal* 243, 92-98. DOI: 10.1016/j.cej.2013.12.054

Liu, D., and Chen, E. Y. X. (2012). "Ubiquitous aluminum alkyls and alkoxides as effective catalysts for glucose to HMF conversion in ionic liquids," *Applied Catalysis A: General* 435-436, 78-85. DOI: 10.1016/j.apcata.2012.05.035

Liu, D., and Chen, E. Y. X. (2013). "Polymeric ionic liquid (PIL)-supported recyclable catalysts for biomass conversion into HMF," *Biomass & Bioenergy* 48, 181-190. DOI: 10.1016/j.biombioe.2012.11.020

Liu, D., Li, Q., Zhao, A., Song, L., Wu, P., and Yan, Z. (2015a). "Hydro-liquefaction of sawdust and its three components in supercritical ethanol with [BMIM]Cl/NiCl2 catalyst," *Chemical Engineering Journal* 279, 921-928. DOI: 10.1016/j.cej.2015.05.052

Liu, H., Hua, C., Song, C., Dai, S., Wang, H., Zhu, W., and Li, H. (2015b). "Commercially available ammonium salt-catalyzed efficient dehydration of fructose to 5-hydroxymethylfurfural in ionic liquid," *Inorganica Chimica Acta* 428, 32-36. DOI: 10.1016/j.ica.2015.01.016

Marcotullio, G., and De Jong, W. (2010). "Chloride ions enhance furfural formation from D-xylose in dilute aqueous acidic solutions," *Green Chemistry* 12(10), 1739-1746. DOI: 10.1039/B927424C

Melero, J. A., Iglesias, J., and Garcia, A. (2012). "Biomass as renewable feedstock in standard refinery units. Feasibility, opportunities and challenges," *Energy and Environmental Science* 5(6), 7393. DOI: 10.1039/c2ee21231e

Ohara, M., Takagaki, A., Nishimura, S., and Ebitani, K. (2010). "Syntheses of 5-hydroxymethylfurfural and levoglucosan by selective dehydration of glucose using solid acid and base catalysts," *Applied Catalysis A: General* 383(1-2), 149-155. DOI: 10.1016/j.apcata.2010.05.040

Qu, Y., Huang, C., Zhang, J., and Chen, B. (2012). "Efficient dehydration of fructose to 5-hydroxymethylfurfural catalyzed by a recyclable sulfonated organic heteropolyacid salt," *Bioresource Technology* 106, 170-172. DOI: 10.1016/j.biortech.2011.11.069

Ranoux, A., Djanashvili, K., Arends, I. W. C. E., and Hanefeld, U. (2013). "5‑Hydroxymethylfurfural synthesis from hexoses is autocatalytic," *ACS Catalysis* 3, 760-763. DOI: 10.1021/cs400099a

Rather, M. A., Rather, G. M., Pandit, S. A., Bhat, S. A., and Bhat, M. A. (2015). "Determination of CMC of imidazolium based surface active ionic liquids through probe-less UV–vis spectrophotometry," *Talanta* 131, 55-58. DOI: 10.1016/j.talanta.2014.07.046

Roman, L. Y., Chheda, J. N., Dumesic, J. A. (2006). "Phase modifiers promote efficient production of hydroxymethylfurfural from fructose," *Science* 312(5782), 1933-1937. DOI: 10.1126/science.1126337

Tao, F., Song, H., and Chou, L. (2011). "Hydrolysis of cellulose in SO_3H-functionalized ionic liquids," *Bioresource Technology* 102(19), 9000-9006. DOI: 10.1016/j.biortech.2011.06.067

Wang, P., Yu, H., Zhan, S., and Wang, S. (2011). "Catalytic hydrolysis of lignocellulosic biomass into 5-hydroxymethylfurfural in ionic liquid," *Bioresource Technology* 102(5), 4179-4183. DOI: 10.1016/j.biortech.2010.12.073

Xiao, S., Liu, B., Wang, Y., Fang, Z., and Zhang, Z. (2014). "Efficient conversion of cellulose into biofuel precursor 5-hydroxymethylfurfural in dimethyl sulfoxide-ionic liquid mixtures," *Bioresource Technology* 151, 361-366. DOI: 10.1016/j.biortech.2013.10.095

Zhang, Z., Liu, B., and Zhao, Z. (2012). "Conversion of fructose into 5-HMF catalyzed by GeCl4 in DMSO and [Bmim]Cl system at room temperature," *Carbohydrate Polymers* 88(3), 891-895. DOI: 10.1016/j.carbpol.2012.01.032

Zhang, M., Su, K., Song, H., Li, Z., and Cheng, B. (2015). "The excellent performance of amorphous Cr2O3, SnO2, SrO, and graphene oxide–ferric oxide in glucose conversion into 5-HMF," *Catalysis Communications* 69, 76-80. DOI: 10.1016/j.catcom.2015.05.024

Zhou, L., Liang, R., Ma, Z., Wu, T., and Wu, Y. (2013). "Conversion of cellulose to HMF in ionic liquid catalyzed by bifunctional ionic liquids," *Bioresource Technology* 129, 450-455. DOI: 10.1016/j.biortech.2012.11.015

Article submitted: July 19, 2015; Peer review completed: October 18, 2015; Revised version received and accepted: January 3, 2016; Published: January 26, 2016.
DOI: 10.15376/biores.11.1.2381-2392