Preparation of 5-(Hydroxymethyl)furfural by the Catalytic Degradation of Cellulose in an Ionic Liquid/Organic Biphasic System

Heng Zhang,[a,b,]* Suxiang Li,[a] Xue Song,[a] Pengfei Li,[a] and Junxun Li [c]

This work has established the optimum reaction conditions in a biphasic system using microcrystalline cellulose as the raw material, an ionic liquid as the solvent, metal chloride as a catalyst, and an organic solvent as the extraction reagent. The optimum reaction conditions were microcrystalline cellulose:ionic liquid - 1:10 (mass ratio), chromium(III) chloride ($CrCl_3$) - 6.8 mol% (based on the glucose unit of cellulose molecule), reaction time - 3 h, temperature - 130 °C, and mass ratio of 1-butyl-3-methyl-imidazolium chloride ([BMIM]Cl) to methylbenzene - 1:4.4]. Under these conditions, the yields of glucose and 5-(hydroxymethyl)furfural (5-HMF) were 27% and 55%, respectively. The solvent [BMIM]Cl could be reused twice. The first recovery rate of [BMIM]Cl was approximately 70.9%. The product 5-HMF was obtained in 64.7% yield, which decreased after the first [BMIM]Cl recycling. The second recovery rate of [BMIM]Cl was 45%. The yield of 5-HMF was 39.6%, which decreased after the second recycling of [BMIM]Cl. In this paper, the energy consumption, operation, reutilization of [BMIM]Cl, and product yields of a one-phase system and a biphasic system were compared. Experimental results demonstrated that the biphasic solvent system was suitable for the degradation of cellulose to glucose and 5-HMF.

Keywords: Microcrystalline cellulose; Organic solvent; 5-HMF; Ionic liquid

*Contact information: a: College of Chemical Engineering, Qingdao University of Science & Technology, Qingdao, Shandong, 266042, China; b: State Key Laboratory of Pulp and Paper Engineering , South China University of Technology , Guangzhou, 510640, China; c: Tai'an Shengliyuan Bioengineering Co., Ltd, Tai'an,271000, China; *Corresponding author: hgzhang@sina.com*

INTRODUCTION

Fossil fuels such as oil, natural gas, and coal are important energy pillars for the survival of human society. This energy is closely related to the development of human life and social economy (Shuit *et al.* 2009). With the development of society, fossil fuels face the danger of exhaustion. As a sustainable resource, biomass resources are rich in quantity, easily sourced, cheap, biodegradable, and produce no pollution.

Cellulose is the largest biomass resource found in nature. An increasing number of researchers have focused attention on the preparation of the platform compound 5-(hydroxymethyl)furfural (5-HMF) from cellulose (Ragauskas *et al.* 2006). Numerous methods have been used to prepare 5-HMF using cellulose as raw material (Hattori *et al.* 2002; Binder and Raines 2009; Feridoun and Hiroyuki 2010). With cellulose as the raw material and ionic liquids as solvents, the yields of glucose and 5-HMF obtained are relatively high (Zhou *et al.* 2015). However, 5-HMF is highly unstable under acidic conditions and is easy to further hydrolyze to produce acetic acid and other by-products, resulting in difficult product extraction and declined yield (Holladay *et al.* 2007; Kim *et al.* 2013).

The selectivity and yield of the product can be improved through the timely separation of 5-HMF from the acidic ionic liquid reaction medium. Shen *et al.* (2014) added sodium chloride (NaCl) to a water/tetrahydrofuran (H_2O/THF) biphasic system with microcrystalline cellulose as raw material and found that the addition of NaCl can suppress the production of the by-product levulinic acid. Sun *et al.* (2015) added NaCl to a H_2O/THF biphasic system under microwave heating conditions, with bamboo fiber as a raw material, and the results demonstrated that the addition of NaCl can separate HMF from the water phase to the organic phase continuously. Using abundant cellulose biomass as raw material, Hou (2011) investigated the degradation of biomass to 5-HMF in a biphasic system of an organic extractant (acetone, benzene, toluene, *etc.*)–zinc chloride solution. The experimental results revealed that the reaction by-product yield was reduced. The biphasic reaction medium could be reused numerous times, and the highest yield of 5-HMF obtained was 63%.

In general, ionic liquids are miscible with liquids having medium-to-high dielectric constants and immiscible with liquids with low dielectric constants (Pagàn-Torres *et al.* 2012). A suitable organic solvent can form a biphasic system with an ionic liquid. Although the relatively high boiling point of organic solvents will often present certain difficulties in the separation and purification of 5-HMF, it can suppress the formation of by-products to a certain extent (Shimizu *et al.* 2009).

We selected a suitable ionic liquid–organic solvent (extraction agent) for building a biphasic reaction system, which was used to continuously extract 5-HMF generated in the ionic liquid to the extraction agent used. After the reaction, the extraction agent phase was subjected to vacuum distillation to obtain the target product. The biphasic system is expected to reduce the difficulty of product extraction, reduce the decomposition of the product, and improve the product yield. At the same time, an appropriate organic solvent not only exerts a swelling effect on cellulose but also can improve the speed and selectivity of the specific reaction. In addition, organic solvents and ionic liquids can also form a unique dual-functional system, soluble in several ionic liquids or ionic liquids almost insoluble in specific organic solvents. Organic solvents can reduce the viscosity of ionic liquids, which is conducive to the mass transfer process (Seddon *et al.* 2000). Moreover, decreased viscosity can speed up the reaction rate and improve the selectivity of the reaction. Combining the advantages of organic solvent and ionic liquid for catalytic reaction in ionic liquids, organic solvent-assisted extraction of products, and recycling of ionic liquids after the end of the reaction, one can achieve a green reaction process. Ionic liquids and organic biphasic media can possibly render an efficient conversion of cellulose to 5-HMF and the separation of the formed 5-HMF.

EXPERIMENTAL

Materials

Microcrystalline cellulose, methanol, methyl isobutyl ketone, ethyl acetate, acetone, and toluene were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methanol, methyl isobutyl ketone, ethyl acetate, acetone, and toluene were analytically pure. 1-Butyl-3-methylimidazolium chloride (referred to as [BMIM]Cl,

>99%) was purchased from Shanghai Cheng Jie Chemical Co. (Shanghai, China). All of these chemicals were used without further purification.

Methods

Selection of extraction agent

The optimum reaction conditions were microcrystalline cellulose:ionic liquid - 1:10, $CrCl_3$ - 6.8 mol%, reaction time - 3 h, temperature - 130 °C, and mass ratio of [BMIM]Cl to methylbenzene - 1:4.4. In a typical reaction, 1-butyl-3-methylimidazolium chloride was added to the reactor. The oil bath was heated to the desired temperature, and the ionic liquid was melted under stirring. Microcrystalline cellulose and $CrCl_3$ catalyst were then gradually added in sequence, and the system was timed after the additions were completed. After a set time, a definite amount of the reaction liquid was removed and mixed with the extraction agent (1:2.6) in an extractor. The concentration of reaction liquid before and after extraction and the extraction rate of the solvent were determined. The optimum extraction agent after comprehensive stratification and extraction rate was thus identified.

Preparation of glucose and 5-HMF

The reaction involves microcrystalline cellulose:[BMIM]Cl = 1:10 (mass ratio) and 6.8. mol% of $CrCl_3$. A certain amount of [BMIM]Cl was added to a 250-mL four-neck flask and the contents were heated in an oil bath set at to 100 °C under stirring. The temperature was increased to a specified value to melt the ionic liquid in the flask. Then, microcrystalline cellulose and $CrCl_3$ were added, followed by a set proportion of extraction agent in condensing equipment. After the reaction, a small amount of the upper liquid was removed to determine the concentration of 5-HMF, and the production rate was determined using an ultraviolet spectrophotometer. The remaining liquid was concentrated and dried to obtain 5-HMF. A small amount of the lower liquid was then taken for the determination of glucose concentration using an ultraviolet spectrophotometer. After the reaction, the remaining liquid of the lower liquid was heated at 100 °C to remove water for the next reaction recycle. Chromium always exist in the form of bivalent, trivalent, and hexavalent compounds. The toxicity of hexavalent chromium is strongest, followed by trivalent chromium, bivalent, and pure chromium, which has small toxicity. Trivalent chromium is used as catalyst, belong to the environmental protection series. But the recycle of the catalysis system still needs further improvement.

Feasibility of ionic liquid recycling

The extraction liquid was used as the extraction solvent, and the liquid from the bottom layer was filtered and washed using deionized water. The filtrate was vacuum-distilled at 60 °C in a rotary evaporator and then dried in a vacuum drying oven at 70 °C. The samples for analysis were prepared by the KBr compression method (Reich 2005), and the infrared spectrum of the sample was acquired.

Analysis

Product analysis

The products were quantitatively analyzed by a TU-1810 UV–Vis spectrophotometer (Beijing Puxi, Beijing, China). The measurement wavelength of 5-HMF was 284 nm. Glucose content was determined *via* the DNS method (Goncalves *et* *al.* 2010; Teixeira *et al.* 2012), and the measurement wavelength used was 540 nm. The content of 5-HMF was also confirmed by GC7890-C gas chromatograph (FID) (Shanghai, China), using a capillary column. The initial temperature of the column was 373 K, which was maintained for 3 min. The heating rate was 10 K/min, the final temperature was 473 K, the keeping time was 9 min, the gasification temperature was 513 K, the temperature of the detector was 523K, the flow rate of high purity N_2 was 1.0 mL/min, the split ratio was 30:1, and the sample size was 0.4 µL.

XRD characterization

Cellulose, which was dissolved in ionic liquid, was precipitated by adding acetone and ethanol which got mixed with ionic liquids easily, dried in an oven at 90 °C, and then ground to powder for further analysis. The cellulose thus obtained was placed in a DX—2700 model X-ray diffractometer (Ettlingen, Germany) and tested in the range of 5° to 50° (2θ).

Infrared characterization

The ionic liquid was removed in vacuum oven at 70 °C. An appropriate amount was obtained and tested using a 510P model FT-IR infrared spectrometer (Ettlingen, Germany) with a resolution of 4 cm^{-1} in the region of 4000 to 400 cm^{-1}.

Product yield calculation

Calculations for product yield attributes were carried out according to Eqs. 1 through 5.

1) Extraction rate:

$$X = \frac{C_1 - C_2}{C_1} \times 100\% \tag{1}$$

where X is the extraction rate, C_1 is the concentration of the sample before extraction and C_2 is the concentration of the sample after extraction.

2) Recovery rate of ionic liquid:

$$Y = \frac{m_2}{m_1} \times 100\% \tag{2}$$

where m_1 is the mass of unused ionic liquid and m_2 is the mass of the used ionic liquid.

3) Glucose yield:

$$Y_{\text{glucose}} = \frac{C_{\text{glucose}} \times V}{m} \times 100\% \tag{3}$$

where C_{glucose} is mass concentration of glucose, mg/ml; V is bulk after constant volume of reaction solution, ml; and m is mass of microcrystalline cellulose, mg.

4) 5-HMF yield:

$$Y_{\text{5 - HMF}} = \frac{C_{\text{5 - HMF}} \times 180V}{m \times 126} \times 100\% \tag{4}$$

where $C_{5\text{-HMF}}$ is mass concentration of 5-HMF, mg/ml; V is bulk after constant volume of reaction solution, ml; and m is mass of microcrystalline cellulose, mg.

5) Conversion yield of cellulose:

$$Y_C = \frac{M_{C0} - M_C}{M_{C0}} \times 100\% \tag{5}$$

where M_{C0} is the mass of cellulose before reaction, g; and M_C is the mass of cellulose after reaction, g.

RESULTS AND DISCUSSION

Extraction Effect of Various Extraction Agents

This study investigated the extraction efficiency of 5-HMF using acetone, ethyl acetate, methyl isobutyl ketone, toluene, and methanol as extractant solvents. The results are shown in Table 1.

Table 1. Extraction Effect of Various Extraction Agents

Extraction agent	Formation of different layers	Upper layer color	One-time Extraction (%)	Two-time extraction (%)
Acetone	Layer formation time was longer, fuzzy interface, bubbles	Dark brown	60	—
Ethyl acetate	Layer formation time was short, clear interface, less air bubbles	Light yellow	80.2	97
Methyl isobutyl ketone	Layer formation time was short, clear interface	Brown	84	—
Toluene	Layer formation time was short, clear interface	Light yellow	83	—
Methanol	No layer formation	—	—	—

The extraction of glucose was not investigated in this work because of the existence of ionic liquid in the bottom layer. Glucose was difficult to be extracted into the organic solvent from the remaining ionic liquid present in the lower layer with the continuous production of 5-HMF from the raw material.

As shown in Table 1, the standard samples were completely soluble in methanol, which did not exert any extraction effect. Extraction rate and stratification with acetone as the extraction agent were not ideal. Under normal conditions, 5-HMF should be light yellow in color, but the upper liquid extracted by acetone appeared dark brown. The results demonstrated the presence of other dark-colored impurities in the upper liquid. Higher extraction rates were obtained using methyl isobutyl ketone, toluene, and ethyl acetate as extraction agents, without apparent major difference among them.

The extraction conditions for isobutyl ketone, toluene, and ethyl acetate were determined. The color of the top-layer liquid was darker with methyl isobutyl ketone as solvent extractant. In addition, the vapor of the methyl isobutyl ketone (boiling point of 117 °C) can easily form an explosive mixture with air at higher temperature, and the risk was higher. Therefore, the test was not adopted because the reaction temperature was higher than 100 °C. Ethyl acetate possesses a boiling point of approximately 77 °C, which can easily evaporate at high temperature, thus increasing the difficulty of condensation. Therefore, the test was also not adopted.

In summary, toluene showed good extraction effect with higher boiling point, under satisfactory reaction conditions. Therefore, toluene was selected as the extracting agent in this work.

Effect of Ratio of Toluene/[BMIM]Cl on the Product Yield

The amount of extraction agent is an important factor that influences the extraction effect. In general, a greater extraction dose indicates a greater driving force for extraction and better extraction effect. However, excessive use of the extraction agent will lead to increased recycling costs for the extraction agent. Therefore, suitable extractant consumption should be selected.

Reaction conditions

The reaction conditions were as follows: microcrystalline cellulose:[BMIM]Cl = 1:10; content of $CrCl_3$ - 6.8 mol.% (IL ratio and amount of $CrCl_3$ were taken from single phase reactions that we had studied (Han 2014; Zhang *et al.* 2016)): temperature, 130 °C; reaction time, 3 h. The toluene/[BMIM]Cl ratio was adjusted to investigate the effects on the product yield. Experimental results are shown in Fig. 1.

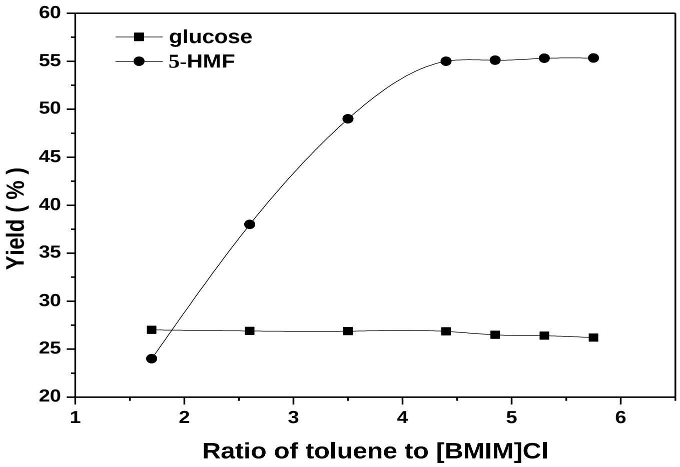


Fig. 1. Effect of the ratio of toluene to [BMIM]Cl on product yield

As shown in Fig. 1, the glucose yield slightly changed with the ratio of toluene/[BMIM]Cl because of the presence of glucose in the [BMIM]Cl phase. The yield of 5-HMF increased with an increase in the ratio of toluene to [BMIM]Cl. The yield reached the maximum when the ratio of toluene to [BMIM]Cl reached 4.4:1, and then remained steady. The formed 5-HMF was only partially extracted into the toluene phase, as the saturation point was immediately reached. The remaining part still existed in the

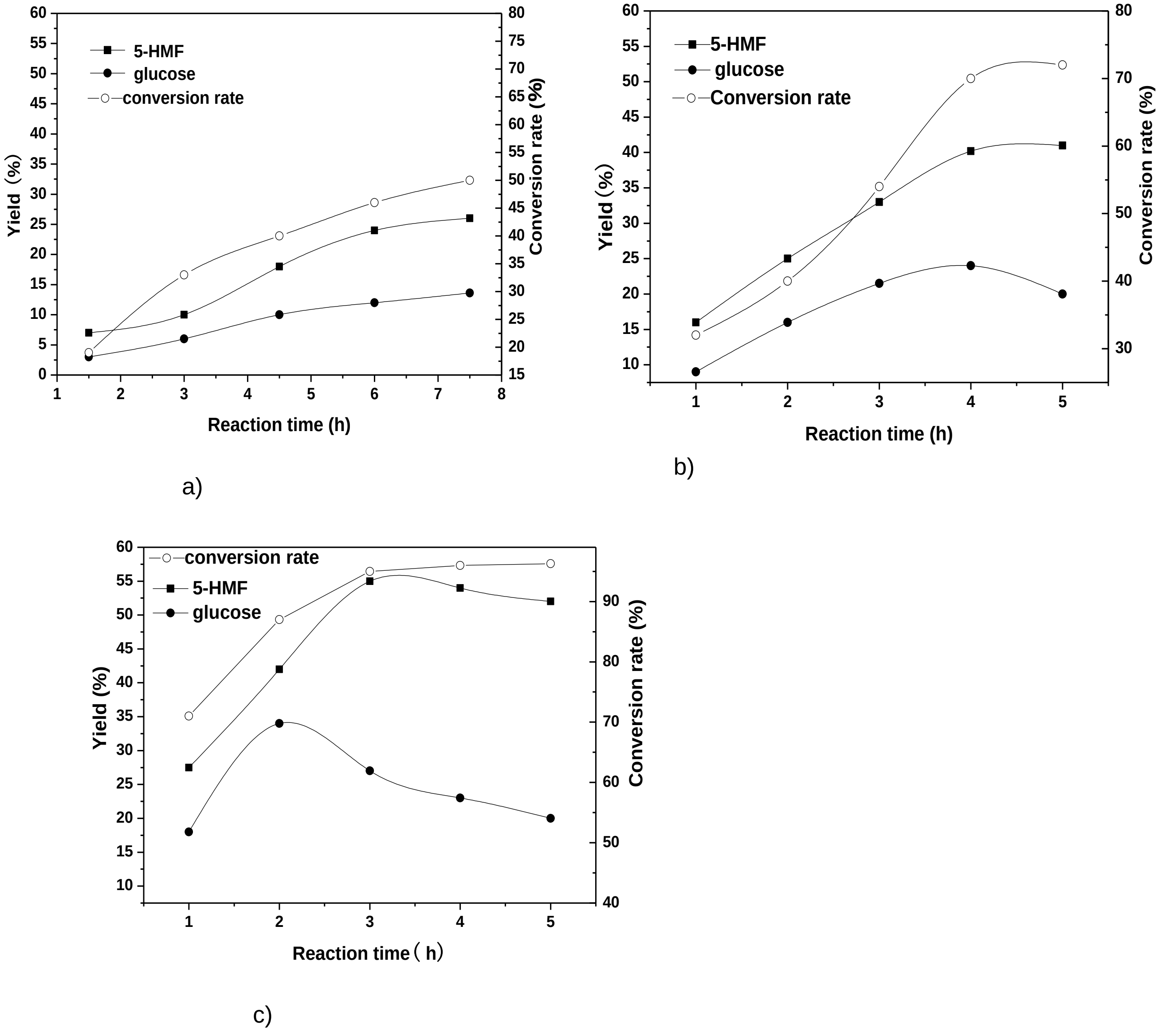
[BMIM]Cl system because of the limited amount of extraction agents when the dosage was relatively small. When the dosage was increased to 4.4:1, the formed 5-HMF was almost completely extracted into the toluene phase. A minimal effect on the yield of 5-HMF was seen when the amount of toluene/[BMIM]Cl was increased further.

To sum up, when the dosage ratio of toluene to [BMIM]Cl was 4.4:1, the yields of glucose and 5-HMF were 27% and 55%, respectively.

Effect of Reaction Temperature and Time on Product Yield

Reaction conditions

The reaction conditions were as follows: microcrystalline cellulose:[BMIM]Cl: toluene = 1:10:44; content of $CrCl_3$ - 6.8 mol.%; temperature - 110 °C, 120 °C, 130 °C, and 140 °C. The experimental results are shown in Figs. 2a to 2c:



a)

b)

c)

Fig. 2. Effect of reaction time on the yield of products at a) 110 °C, b) 120 °C, and c) 130 °C

As shown in Fig. 2a, the yields of glucose and 5-HMF increased with time at a temperature of 110 °C. However, the conversion rate of cellulose was low, only 50% when the reaction time reached 7.5 h, and the yields of glucose and 5-HMF were 13.6% and 26%, respectively. At this time, the yields of the two products still had not reached the highest value. Because the response time was too long, this result may not be taken into account. As shown in Fig. 2b, the conversion rate of cellulose at 120 °C was notably faster than that at 110 °C. The rate of accumulation of glucose, as the intermediate product of microcrystalline cellulose transformation to 5-HMF, increased with prolonged production time, reaching the maximum value at 4 h before decreasing. The yield of 5-HMF increased with time and became stable when the reaction time reached 5 h. Approximately 28% of the cellulose did not undergo any change, even when the reaction time was shortened. At 120 °C, the yields of glucose and 5-HMF improved markedly in comparison with those at 110 °C. As shown in Fig. 2c, the conversion rate of cellulose increased with time and was almost in a steady state after 3 h at 130 °C. The intermediate product of glucose reached the maximum yield at 2 h, and then was converted to 5-HMF rapidly. The yield of product 5-HMF showed an increasing trend with time, reached the maximum at 3 h, then showed a slight drop. At 130 °C, the product 5-HMF and organic solvents have begun to volatilize, and several by-products formed were not condensed efficiently through the condensation device, resulting in loss of a small amount of product.

We also investigated the changes in glucose and 5-HMF yields with time at 140 °C. However, this temperature considerably exceeded the boiling point of toluene and 5-HMF, and the reflux rate reached 130 drops/min, resulting in serious volatilization. Therefore, the results were not taken into consideration. To sum up, the best reaction time and temperature for the preparation of glucose and 5-HMF were 3 h and 130 °C in the toluene/[BMIM]Cl biphasic system, respectively. At this time, the conversion rate of cellulose was 95%, the yield of glucose was 27%, and the yield of 5-HMF was 55%.

Degradation of Cellulose

The degradation of cellulose to HMF by $CrCl_3$ can be seen from Fig. 3 (Zhou *et al.* 2015).

Recovery of Ionic Liquid

Feasibility of ionic liquid recovery

The recycling process of ionic liquid: The lower liquid was washed and filtered using deionized water after the reaction solution was extracted with the extraction agent, the filtrate was vacuum-distilled at 60 °C in a rotary evaporator and then dried in a vacuum drying oven at 70 °C.

The samples for analysis were prepared by the KBr compression method. The infrared analysis results on the recovery of ionic liquid are shown in Fig. 4. As revealed in Fig. 4 a), the stretching vibration peaks of C-H bond on the alkyl group were found at 2961.1 and 2871.6 cm^{-1}, the stretching vibration peak of C-N bond was at 1573.7 cm^{-1}, and the deformation and vibration peak of C-H bond in the imidazole ring plane was at 1170.6 cm^{-1}, respectively. Moreover, the rocking vibrations peak of C-H bond in the imidazole ring was at 854.8 cm^{-1}, the rocking vibrations peak of C-H bond outside the imidazole ring was at 756 cm^{-1}, and the vibration peak of imidazole ring frame was at 1637.4 cm^{-1}. The ionic liquid [BMIM]Cl, when recycled also presented strong absorption peaks at the characteristic wavelengths, illustrating that the [BMIM]Cl was not changed chemically and remained stable, as can be reused in the next experiment.

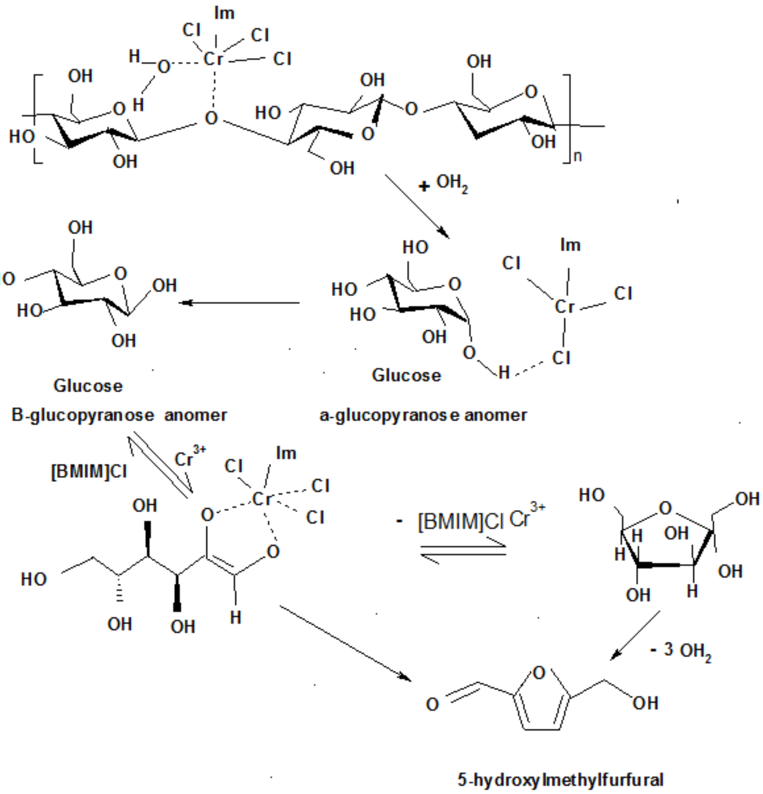
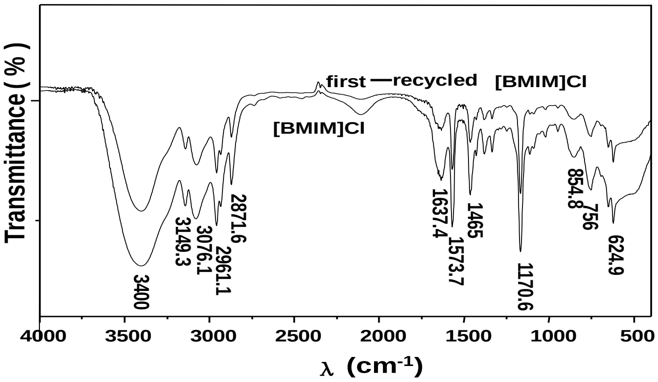
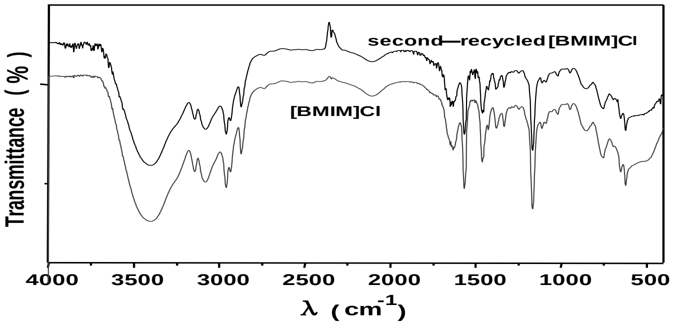


Fig. 3. The mechanism of conversion of cellulose to HMF in [BMIM]Cl with CrCl$_3$



a)



b)

Fig. 4. IR spectrum of a) first recycled [BMIM]Cl and b) second recycled [BMIM]Cl

As shown in Fig. 4, the primary and secondary recovery of [BMIM]Cl were consistent with the characteristic absorption peaks of pure [BMIM]Cl sample, and showed that the recovered [BMIM]Cl did not change structurally. In this work, the primary recovery rate of [BMIM]Cl was as high as 70.9%, the secondary recovery rate of [BMIM]Cl was 45%, and the tertiary recovery of [BMIM]Cl was virtually devoid of [BMIM]Cl because of the loss caused by the recovery process.

Recovery of ionic liquids for the preparation of 5-HMF

The recovered ionic liquid did not change structurally. To make full use of the amount of $CrCl_3$, 5-HMF, and a large amount of glucose in the reaction solution, microcrystalline cellulose was added directly into the reaction solution from which 5-HMF had been extracted. The appropriate reaction conditions were temperature - 130 °C and reaction time - 3 h. The final yield of 5-HMF was 64.7% through the primary [BMIM]Cl recovery, and the yield of 5-HMF was 39.6% by using the secondary [BMIM]Cl recovery. The yield of 5-HMF was too low by using the secondary [BMIM]Cl recovery because the char-type compounds in the reaction solution has increased. This increase in char content resulted in the increase in the viscosity of the system, which restricted the movement of the ions in [BMIM]Cl.

The recovery of [BMIM]Cl was partial, as the high reaction temperature generated material, which was generated charred material in the reaction liquid, even though the properties of recovery of the ionic liquid did not change structurally. Thus, the [BMIM]Cl could not be recycled at this stage. In addition, certain loss occurs in the later filtration and washing process, and the final [BMIM]Cl recovery rate was only 45%. Moreover, virtually no [BMIM]Cl surplus remained after three reactions (two recoveries). We should attempt to reduce the generation of humin materials during the future research.

Comparison of the Biphasic System with the Homogeneous System

Effects of biphasic and homogeneous systems on cellulose dissolution

We investigated the dissolution of cellulose using [BMIM]Cl or a 1:4.4 mixture of [BMIM]Cl:methylbenzene under the reaction conditions: microcrystalline cellulose:ionic liquid - 1:10 (mass ratio); $CrCl_3$ content - 6.8 mol.%; temperature - 100 °C; reaction time - 2 h; and with stirring for dissolving. The measured XRD spectra of cellulose after dissolution were as shown in Fig. 5. Figure 5a shows the XRD spectra of microcrystalline cellulose, and Fig. 5b shows the XRD spectra of microcrystalline cellulose dissolved by [BMIM]Cl.

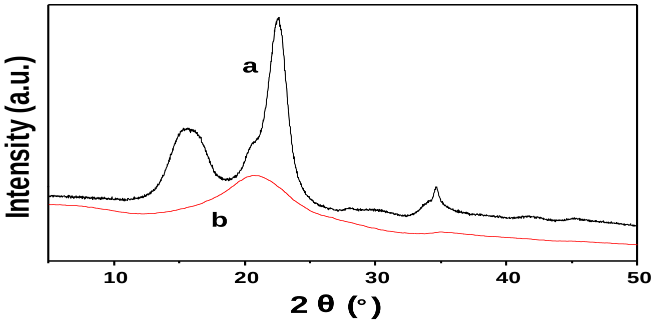


Fig. 5. XRD spectra of microcrystalline cellulose and cellulose dissolved in [BMIM]Cl

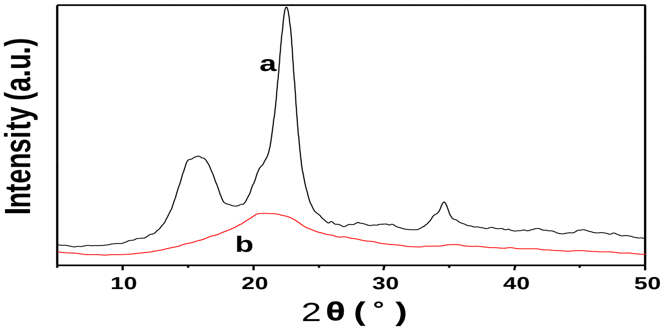


Fig. 6. XRD spectra of microcrystalline cellulose and cellulose dissolved in a mixture of [BMIM]Cl and methylbenzene

Figure 6a shows the XRD spectra of microcrystalline cellulose, and 6b shows the XRD spectra of microcrystalline cellulose dissolved in a mixture of [BMIM]Cl and methylbenzene.

Figures 5 and 6 show that the crystals of microcrystalline cellulose were all transformed from type I cellulose into type II cellulose after the dissolution in [BMIM]Cl or in a mixture of [BMIM]Cl and toluene, illustrating that both solvents are able to degrade the crystals of microcrystalline cellulose and eventually dissolve cellulose. In addition, as can be seen from these figures, the diffraction peak of microcrystalline cellulose intensity was low, and the peak was also relatively wide after the dissolution in [BMIM]Cl and toluene in comparison with that after the dissolution in [BMIM]Cl. The results show that the degree of reduction of the microcrystalline cellulose crystals was higher from the coefficient of [BMIM]Cl and toluene, with better solubility effect. The addition of toluene could separate 5-HMF from ionic liquid phase to organic phase as the reaction was continued. More thorough reaction indicates more product formation.

Advantages and disadvantages of the biphasic system and the homogeneous systems.

This work primarily investigated the preparation of glucose and 5-HMF in a biphasic system with microcrystalline cellulose as a raw material. To explore the feasibility of the biphasic system, we studied the preparation of glucose and 5-HMF in a monophasic or homogeneous system. The advantages and disadvantages of the biphasic system and the homogeneous system were explored.

Table 2. Comparison between One-Phase and Biphasic Systems

	Homogeneous system	Biphasic system
Reaction temperature (°C)	160	130
Reaction time (h)	1	3
Operability	Complex	Simple
Repeated use of [BMIM]Cl	Reused at one time	Reused twice
Product yield (%)	Glucose: 31%; 5-HMF: 61%	Glucose: 27%; 5-HMF: 55%

Reaction time

The reaction temperature was not excessively high because of the limitations of the boiling point of organic extraction agent in the biphasic system, resulting in a slow rate of transformation of cellulose, and hence the reaction time was relatively long.

Meanwhile, the reaction temperature in homogenous phase was not limited, and the reaction time could be shortened at high temperature.

Reaction temperature

The biphasic system showed a relatively low reaction temperature, fewer by-products, and less decomposition of the target product. The reaction temperature in the one-phase system should be improved to prevent the decomposition of the target product caused by the long reaction time.

Operability

The product was extracted in real time with the reaction in biphasic system, which not only prevented the decomposition of the product but also reduced the operation steps. Additional extraction steps were necessary to isolate the target product in the one-phase system after the reaction.

Repeated use of [BMIM]Cl

Reuse times of [BMIM]Cl in the biphasic system were higher than that in the one-phase system because the color of the reaction liquid after primary recovery was lighter, as less black material was produced, and recycling consumption of [BMIM]Cl was relatively small in the biphasic system. In the one-phase system, because of the presence of numerous byproducts, the reaction medium appeared black at high temperature. In the recovery process, part of [BMIM]Cl was surrounded by dark material, making the recycling difficult and resulting in considerable decrease in the recovery yield of [BMIM]Cl in comparison with the biphasic system.

Product yield

Compared with the one-phase system, the reaction temperature of the biphasic system was lower. The conversion rate of cellulose was relatively small in this case, and the yield of 5-HMF was about 6% lower than that of the one-phase system. However, as the recovery and recycling frequency of the ionic liquid in the biphasic system was considerably higher than that of the one-phase system. The overall, the yields of products in the one-phase system were higher than that of the biphasic system.

To sum up, the biphasic system is more suitable for the preparation of glucose and 5-HMF by the degradation of cellulose in comparison with the one-phase system.

CONCLUSIONS

1. Among acetone, ethyl acetate, methyl isobutyl ketone, toluene, and methanol, toluene, methyl isobutyl ketone and ethyl acetate showed better 5-HMF extraction efficiency. Toluene was selected as the extractant in the biphasic system synthesizing all kinds of factors.
2. The yield of 5-HMF reached the maximum value when the reaction temperature and time were 130 °C and 3 h, respectively. At this time, the yields of glucose and 5-HMF were 27% and 55%, respectively.
3. The structure of recovered [BMIM]Cl was consistent with the structure of pure [BMIM]Cl sample after primary and secondary recoveries, showing that [BMIM]Cl

could be recycled and used twice in the cellulose degradation reaction. In this work, the primary recovery rate of [BMIM]Cl was as high as 70.9%, and the yield of 5-HMF was 64.7%. The second recovery rate of [BMIM]Cl was 45%. The yield of 5-HMF was 39.6%, after the second [BMIM]Cl recycling.

4. Comparison of the one-phase system and the biphasic system in terms of energy consumption, operability, repeated use of [BMIM]Cl, and product yields, indicated that the biphasic system is more suitable in the degradation of cellulose for the preparation of glucose and 5-HMF.

ACKNOWLEDGMENTS

This work was financially supported by the Qingdao Municipal Science and Technology Plan Project (12-1-4-3-(28)-jch), the open fund of State Key Laboratory of Pulp and Paper Engineering of China (201474), and the Science and Technology Major Project (Emerging Industries) of Shandong Province (2015ZDXX0403B03).

REFERENCES CITED

Binder, J. B., and Raines, R. T. (2009). "Simple chemical transformation of lignocellulosic biomass into furans for fuels and chemicals," *Journal of the American Chemical* Society 131(5), 1979-1985. DOI: 10.1021/ja808537j

Feridoun, S. A., and Hiroyuki, Y. (2010). "Conversion of Japanese red pine wood (*Pinus densiflora*) into valuable chemicals under subcritical water conditions," *Carbohydrate Research* 345(1), 124-131. DOI: 10.1016/j.carres.2009.10.006

Goncalves, C., Rodriguez-Jasso, R. M., Gomes, N., Teixeira, J. A., and Belo, I. (2010). "Adaptation of dinitrosalicylic acid method to microtiter plates," *Analytical Methods* 2(12), 2046-2048. DOI: 10.1039/c0ay00525h

Han, H., Y. (2014). "The preparation of 5-HMF from microcrystalline cellulose in ionic liquid and kinetics study," *China, Qingdao University of Science and Technology*

Hattori, K., Cuculo, J. A., and Hudson, S. M. (2002). "New solvents for cellulose: Hydrazine/thiocyanate salt system," *Journal of Polymer Science Part A: Polymer Chemistry* 40(4), 601-611. DOI: 10.1002/pola.10135

Holladay, J. E., White, J. F., Bozell, J. J., and Johnson, D. (2007). "Top value-added chemicals from biomass-volume II–Results of screening for potential candidates from biorefinery lignin," Report prepared by members of NREL, PNNL and University of Tennessee (http://www.osti.gov/scitech/biblio/921839) accessed on February 3, 2016.

Hou, X. L. (2011). "One biphasic system method for the production of hydroxyl methyl furfural," China Patent #101941957.

Kim, J. H., Na, J. G., Yang, J. W., and Chang, Y. K. (2013). "Separation of galactose, 5-hydroxymethylfurfural and levulinic acid in acid hydrolysate of agarose by nanofiltration and electrodialysis," *Bioresource Technology* 140, 64-72. DOI: 10.1016/j.biortech.2013.04.068

Seddon, K. R., Stark, A., and Torres, M. J. (2000). "Influence of chloride, water, and organic solvents on the physical properties of ionic liquids," *Pure and Applied Chemistry* 72(12), 2275-2287. DOI: 10.1351/pac200072122275

Pagàn-Torres, Y. J., Wang, T., Gallo, J. M. R., Shanks, B. H., and Dumesic, J. A. (2012). "Production of 5-hydroxymethylfurfural from glucose using a combination of Lewis and Brønsted acid catalysts in water in a biphasic reactor with an alkylphenol solvent," *ACS Catalysis* 2(6), 930-934. DOI: 10.1021/cs300192z

Ragauskas, A. J., Williams, C. K., Davison, B. H., Britovsek, G., Cairney, J., Eckert, C. A., Frederick, W. J., Hallett, J. P., Leak, D. J., Liotta, C. L., *et al.* (2006). "The path forward for biofuels and biomaterials," *Science* 311(5760), 484-489. DOI: 10.1126/science.1114736

Reich, G. (2005). "Near-infrared spectroscopy and imaging: Basic principles and pharmaceutical application," *Advanced Drug Delivery Reviews* 57(8), 1109-1143. DOI: 10.1016/j.addr.2005.01.020

Shen, Y., Sun, J. K., Yi, Y. X., Li, M. F., Wang, B., Xu, F., and Sun, R. C. (2014). "$InCl_3$-catalyzed conversion of carbohydrates into 5-hydroxymethylfurfural in biphasic system," *Bioresource Technology* 172, 457-460. DOI: 10.1016/j.biortech.2014.09.077

Shimizu, K. I., Uozumi, R., and Satsuma, A. 2009). "Enhanced production of hydroxymethylfurfural from fructose with solid acid catalysts by simple water removal method," *Catalysis Communications* 10(14), 1849-1853. DOI: 10.1016/j.catcom.2009.06.012

Shuit, S. H., Tan, K. T., Lee, K. T., and Kamaruddin, A. H. (2009). "Oil palm biomass as a sustainable energy source: A Malaysian case study," *Energy* 34(9), 1225-1235. DOI: 10.1016/j.energy.2009.05.008

Sun, J. K., Yuan, X. D., Shen, Y., Yi, Y. X., Wang, B., Xu, F., and Sun, R. C. (2015). "Conversion of bamboo fiber into 5-hydroxymethylfurfural catalyzed by sulfamic acid with microwave assistance in biphasic system," *Industrial Crops and Products* 70, 266-271. DOI: 10.1016/j.indcrop.2015.03.044

Teixeira, R. S. S., Silva, A. S. D., Ferreira-Leitão, V. S., and Bon, E. P. D. S. (2012). "Amino acids interference on the quantification of reducing sugars by the 3,5-dinitrosalicylic acid assay mislead carbohydrase activity measurements," *Carbohydrate Research* 363(23), 33-37. DOI: 10.1016/j.carres.2012.09.024

Zhang, H., Li, S. X., Xu, L., Sun, J. H., and Li, J. X. (2016). "Kinetic study of the decomposition of cellulose to 5-hydroxymethylfurfural in ionic liquid," *BioResources* 11(2), 4268-4280. DOI: 10.15376/biores.11.2.4268-4280

Zhou, L. L., He, Y. M., Ma, Z. W., Liang, R. J., Wu, T. H., and Wu, Y. (2015) . "One-step degradation of cellulose to 5-hydroxymethylfurfural in ionic liquid under mild conditions," *Carbohydrate Polymers* 117, 694-700. DOI: 10.1016/j.carbpol.2014.10.062

Article submitted: February 15, 2016; Peer review completed: March 31, 2016; Revised version received: April 11, 2016; Accepted: April 12, 2016; Published: April 26, 2016.
DOI: 10.15376/biores.11.2.5190-5203