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Cellulosic conversion in ionic liquids (ILs): Effects of H₂O/cellulose molar ratios, temperatures, times, and different ILs on the production of monosaccharides and 5-hydroxymethylfurfural (HMF)

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ABSTRACT

The effects of several critical factors including H₂O/cellulose molar ratios, dissolution temperatures (T_{dis}), dissolution times (t_{dis}), reaction temperatures (T_{rxn}), reaction times (t_{rxn}), and types of ionic liquids (IL) were investigated for cellulosic conversion. We optimized the reaction conditions as: H₂O/cellulose = 10/1, T_{dis} = 120 °C, t_{dis} = 0.5 h, T_{rxn} = 120 °C, t_{rxn} = 3 h for 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl)-based system, and the maximum yield of 5-hydroxymethylfurfural (HMF) up to 21% could be achieved without adding extra catalysts. Another pyridinium-typed IL, [Epyr]Cl, was also used in the cellulosic conversion, and the results showed a high selectivity toward monosaccharides. The information obtained in this study will benefit many biofuel-related applications.

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1. Introduction

The usage of fossil fuel causes serious problems of energy crisis and global warming. To solve these problems, so far much attention has been paid on the development of renewable energies such as solar or wind energy. Biofuels produced from biomass is one of the potential alternatives. First-generation biofuel (i.e., biodiesel) produced from corn and soybean oil has proved the possibility of biomass-to-biofuel; however, the use of edible agriculture as sources will cause another problems such as food deficiency [1]. Therefore, second-generation biofuel generated from nonedible lignocellulosic biomass has attracted more attention so far.

Lignocellulosic (or so-called wood-based) biomass consists of three major components: cellulose (41%), hemicellulose (28%), and lignin (27%) [2]. Generally, cellulose and hemicellulose can be used to produce bioethanol, and ligin offers a broad spectrum of conversion (thermal cracking, fast pyrolysis, and complete gasification) to achieve valuable chemicals and transportation fuels [3]. So far, a great deal of effort has been put toward the degradation of cellulose with enzymes [4], mineral acids [5], bases [6], and supercritical water [7]. Enzymatic hydrolysis of cellulose is effective, but the system is sensitive to contaminants originating from other biomass

* Corresponding author. E-mail address: kevinwu@ntu.edu.tw (K.C.-W. Wu). components. Furthermore, pretreatment of cellulose (e.g., ammonia or steam treatments in a high-pressure process or mechanical milling) is typically required to increase the accessible area of cellulose for a reasonable rate of enzymatic hydrolysis [8]. Mineral acids have been extensively investigated to catalyze hydrolysis at a variety of acid concentrations and temperatures. Only a rather high temperature (180–230 °C) has been used in order to obtain an acceptable rate of cellulose hydrolysis. Furthermore, degradation of the resulting glucose becomes an issue at such high temperatures [9].

Recently, ionic liquids (ILs) have attracted a lot of attention and have been utilized as solvents for the degradation of the lignocellulosic biomass [10–14]. The importance of ionic liquid in cellulose dissolution has been emphasized in several reviews [15–17]. Ionic liquids are kinds of the novel green solvents. They are organic salts with relatively low melting point. In other words, ionic liquids usually appear as crystal in normal conditions; however, they can be molten and dissociated into two ionic parts at relatively higher temperatures (usually less than 100 °C). In contrast to other crystalline salts (ex: NaCl), the attractive characteristic of ILs is that they can transform into liquid phase.

The first report on the dissolution of cellulose in an IL was back to 1934[18]; however, the utilization of ILs in the lignocellulose-tobiofuel conversion just started from 2000 due to the energy crisis. Numerous papers have been published on the control of the viscosity and polarity of ionic liquids by varying their ionic structures [16,17]. The main focus of these papers was the solubility of the

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synthesized ILs toward different carbohydrates such as glucose, sucrose, amylose, cellulose, and so on. In 2002, Rogers and coworkers reported that cellulose could be dissolved in ionic liquids at 100 °C [10]. The solubility of cellulose in ionic liquids results from its anions. It can disrupt the hydrogen bonds between polysaccharide chains of cellulose and then to dissolve cellulose [19]. This discovery started a new pathway to deal with cellulose in low temperature and ambient atmosphere.

In 2007, Zhao et al. discovered CrCl₂ in [EMIM]Cl (1-ethyl-3methylimidazolium chloride; an imidazolium type ionic liquid) can efficiently catalyze glucose to HMF [20]. HMF is a promised platform chemical because it can further transform to a widely used biofuel called 2,5-dimethylfuran (DMF) [21] and other useful materials [22]. Since then, many efforts have worked on the production of HMF from cellulose or glucose in the ionic liquid systems. Binder and Raines combined HCl, CrCl₂ or CrCl₃, DMA/LiCl and [EMIM]Cl to convert cellulose to HMF [13]; Zhang and co-workers used CrCl₂/CuCl₂ as catalysts in [EMIM]Cl [14]; Han and co-workers also discovered SnCl₄ in [EMIM]BF₄ can convert glucose to HMF with a high yield [23]; Riisager and co-workers discussed HMF produced from lanthanide-containing ionic liquid systems [24]; Chidambaram and Bell discovered that 12-molybdophosphoric acid in [EMIM]Cl/acetonitril or [BMIM]Cl/acetonitril can selectively convert glucose to HMF [25]. Although there have been many researches focused on the addition of various kinds of catalysts in ionic liquid systems, very few papers discussed the effects of reaction conditions such as dissolution temperatures and times of ILs, reaction temperatures and times, and the amounts of water on the conversion efficiency in ionic liquids without additional catalysts [26]. In fact, in the above-mentioned papers, HMF still could be produced when using ILs only (no other additives) although the yields were very low. This indicates that ILs in these systems serve not only as solvent but also as catalyst. We suggest that the low HMF yield was because the reaction conditions for HMF production in these cases were not optimized. For example, Zhao et al. has shown that the yield of HMF converted from fructose was greatly affected by the reaction temperature in an [EMIM]Cl only system [20]. Very recently, Binder and Raines discussed the sequence and timing of the addition of water into the cellulosic conversion and showed that an optimal sequence and timing strongly affected the conversion efficiency [27].

Consequently, we believed that the optimization of reaction conditions is a very important and fundamental work in the initial stage of cellulosic conversion using ILs as both solvent and catalyst. Herein we studied the effects of several critical factors: H₂O/cellulose ratios, dissolution temperatures of ILs, dissolution times of ILs, reaction times, reaction temperatures, and two kinds of ILs (including [EMIM]Cl and [Epyr]Cl) on the production of glucose and HMF directly from cellulose. We aimed to set up the most efficient reaction conditions for cellulosic conversion in ILs without additional catalysts.

2. Experimental

2.1. Chemicals

Cellulose (powder, CA. 20 µm) was purchased from Sigma. 1-Ethyl-3-methylimidazolium chloride ([EMIM]Cl, 98%) and 1-Butyl-3-methylimidazolium ([BMIM]Cl, \geq 95%) were supplied by Aldrich. 1-Ethylpyridinium chloride ([Epyr]Cl, 98%) was obtained from Acrose. Glucose (Sigma), fructose(Sigma), HMF(Alfa Aesar), arabinose (Fluka), cellobiose (Sigma), xylose (Sigma), sucrose (Sigma), mannose (Sigma), galactose (Sigma–Aldrich), sorbitol (Sigma–Aldrich), mannitol (Sigma–Aldrich), 1,6-anhydro- β -glucopyranose (Alfa Aesar), formic acid (Sigma), furfural (J.T. Baker), furfural alcohol (Aldrich), levulinic acid (Aldrich) were purchased with a HPLC analysis standard.

2.2. Method

In a typical experiment, we first heated ILs at 90°C to melt them for easy operation. 150 mg IL was loaded into vials $(15 \text{ mm} \times 45 \text{ mm})$ with a small stirring bar, and vials were closed by tops rapidly. Then the vials were heated to the dissolution temperatures (T_{dis}) using oil bath with stirring. For the experiments of dissolution temperatures, T_{dis} were controlled as 90, 100, 120, and 140 °C. After the temperature got equilibrium, 15 mg cellulose was rapidly added into the vials, and the vials were heated for various times (defined as dissolution time t_{dis}). For the experiments of dissolution times, t_{dis} were set as 0, 0.5, 1, 3, and 6 h. After dissolution of cellulose in ILs, H₂O was rapidly added into each vial. The amounts of H₂O (H₂O/cellulose ratio in molar) were 4.17 (2.5), 8.33 (5), 12.50 (7.5), 16.67 (10), 20.83 (12.5), 25.00 (15), 29.17 (17.5), and 33.33 (20) μ L. After addition of H₂O, the vials were moved to an oil bath which was preheated to a reaction temperature (T_{rxn}). For the experiments of reaction temperatures, T_{rxn} were controlled as 80, 100, 120, and 140 °C. The reaction times (t_{rxn}) were 0.5, 3, 6, and 24 h. After reaction, an exceeded amount of Na₂HPO₄ buffer (10 mM, 2 mL, pH 7.2) was added into the vials to quench the reaction, and the vials were then shaken by a shaker (VTX-30002) for at least 1 min followed by sonication with a ultrasonic cleaner (DELTA) for least 5 min to ensure all products dissolved in buffer. The solid residue precipitated in the bottom of each vial was then removed by syringe filter (Nylon $25 \text{ mm} \times 0.45 \mu \text{m}$). The filtered liquid was collected, and the products in the liquid were analyzed by HPLC.

HPLC analysis was performed on EC2000 equipped with RI 2000 Refractive Index Detector and a Shodex Asahipak GS-220 HQ column and a Shodex Asahipak NH2P-50 4E precolumn. During the analysis process, the temperature of the column remained at 50 °C; the mobile phase was 10 mM Na₂HPO₄ buffer (pH 7.2) at a flow rate of 0.6 mL/min. The volumn for each injection was 20 μ L. The HPLC peak of HMF standard, the calibration curve of HMF, and the calculation of the HMF yield are shown in Supporting Information. X-ray diffraction (XRD) was carried out on a Rigaku diffractometer with Cu K α irradiation.

The structure of the final product was also analyzed by ¹H and ¹³C NMR spectroscopy (400 MHz, CDCl₃) in order to confirm it is 5-hydroxymethylfurfural (HMF). ¹H NMR peaks at δ (ppm): 4.49 (s, 2 H), 6.35 (d, *J*=3.4 Hz, 1 H), 7.06 (d, *J*=3.4 Hz, 1 H), 9.32 (s, 1 H). ¹³C NMR peaks at δ (ppm): 176.907, 151.315, 109.427, 109.427, 162.099, and 56.141. The original NMR spectra of HMF standard, [EMIM]Cl, and our product are also shown in Supporting Information.

3. Results and discussion

3.1. Effects of H₂O/cellulose molar ratios

The conversion processes of cellulose to HMF are summarized in Fig. 1. The amount of water is a critical issue because water acts both as a reactant (for producing monosaccharides) and an inhibitor (for producing HMF) in the overall cellulosic conversion. Therefore, we firstly studied the effect of the amount of water on the production of monosaccharides and HMF. In the hydrolysis step of cellulose to monosaccharides, increasing the amount of water should increase the yield of monosaccharides according to the Le Chatelier's principle. Our results indeed showed that the total amounts of monosaccharides and HMF increased when the H₂O/cellulose molar ratios increased and the maximum yield of 25% was obtained when the ratio was 10 (Fig. 2). However, it is



Fig. 1. The processes and critical factors for production of HMF from cellulosic conversion.

interesting to note that when the ratios were over 10 the amount of monosaccharides still increased but the amount of HMF decreased, resulting the similar total yields in the range of 22-26%. Because the conversion of fructose to HMF is a dehydration process, too much water would inhibit the production of HMF. Therefore, we decided the optimal H₂O/cellulose molar ratio to be 10.

3.2. Effects of dissolution temperature (T_{dis}) and dissolution time (t_{dis})

Remsing et al. have reported that cellulose can be dissolved into ILs because the chloride ions in IL can go into the interspace of 1,4-linked β -D-glucose units and disrupt intermolecular hydrogen bonds between the units [19]. However, as cellulose was mixed with ILs, the viscosity of the mixture usually increases. The highly viscous environment leads to a low rate of molecular transport (i.e., chloride ions move very slow) so the efficiency of dissolution is usually very low. Although one can reduce the viscosity of IL/cellulose mixture by adding water, it may contrariously affect the dissolution efficiency [10]. Therefore, raising temperatures is an alternative strategy to reduce the viscosity of IL/cellulose mixture and can also accelerate the speed of molecular transfer, enhancing the dissolution temperature and time period is therefore a very significant issue.

We studied the effects of dissolution temperatures and times on the cellulosic conversion and aimed to find an optimal dissolution temperature and time. As shown in Fig. 3a, the maximum yield (including maximum monosaccharides and HMF) was found at $T_{dis} = 120$ °C. As described above, high temperatures are helpful for reducing the viscosity of IL. However, we found that when $T_{dis} = 140$ °C the yield of monosaccharides decrease while the yield



Fig. 2. Monosaccharides and HMF yields vs. H₂O/cellulose molar ratios. Other condition were fixed as follows: [EMIM]Cl 0.17 g, cellulose 0.015 g, dissolution temperature 100 °C, dissolution time 0.5 h, reaction temperature 120 °C, reaction time 3 h. Yields are based on HPLC analysis and are relative to the mol of glucose unit in the cellulose.

of HMF remained similar. We supposed that cellulose would further decompose (the final products are still unclear at the present stage) when the T_{dis} was closed to its melting point (around 150 °C).

Next, we examined the effect of dissolution time (t_{dis}) on the conversion efficiency. As shown in Fig. 3b, the lowest yield was obtained at the condition without any dissolution ($t_{dis} = 0$). When the t_{dis} increased to 0.5 h, the yield of monosaccharides increased while the yield of HMF was similar, resulting an increasing total yield (from 30% increased to 45%). The results indicated that dissolution of cellulose in IL indeed help depolymerization of cellulose to generate monosaccharides. Since longer dissolution periods only caused a slight increase of total yield, we chose 0.5 h as the optimal t_{dis} from the viewpoint of economy.

Although it seemed that the dissolution time has little effect on the final conversion rate for the case of [EMIM]Cl, we found that the t_{dis} is a critical issue for other ILS. For example, when [BMIM]Cl was used as a solvent, the yield of monosaccharides raised from 11% to



Fig. 3. (a) Monosaccharides and HMF yield vs. dissolution temperature and (b) Monosaccharides and HMF yield vs. dissolution time. Other conditions were fixed as follows: cellulose 0.015 g, H₂O/cellulose molar ratio 10/1, $T_{\rm rxn}$ 120 °C, $t_{\rm rxn}$ 3 h. Yields are based on HPLC analysis and are relative to mol of glucose unit in the cellulose.



Fig. 4. XRD patterns of cellulose with (blue line) and without (red line) dissolution pretreatments. In the dissolution pretreatment, cellulose were heated at 120 °C for 0.5 h in [EMIM]Cl. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

36% as the $t_{\rm dis}$ increased from 0.5 h to 3 h, respectively. The longer dissolution period is necessary for the case of [BMIM]Cl because cellulose needs more time to dissolve in the [BMIM]Cl that exhibiting a longer alkyl chain.

To check the efficiency of cellulosic dissolution by IL pretreatment, we examined the crystalline structure of cellulose before and after cellulosic dissolution with XRD. As shown in Fig. 4, the crystalline peak of the cellulose at $2\theta = 22^{\circ}$ disappeared after IL pretreatment (i.e., dissolution at $120 \,^{\circ}$ C for 0.5 h in [EMIM]Cl). It proved that the crystalline structure was destroyed by chloride ion of [EMIM]Cl.

3.3. Effects of reaction temperature (T_{rxn}) and reaction time (t_{rxn})

Reaction temperature influences many factors in the IL-based cellulosic conversion such as kinetics, selectivity, K_w , and the activity of catalysts. For example, siliceous MCM-41 showed activity toward pyrolysis of lignocellulosic biomass in high temperature (up to 550 °C) [28]. Chen and co-workers have reported that temperature influenced the K_w (i.e., the concentration of H⁺ and OH⁻), and the p K_w values varied at different temperatures (298 K and 373 K) in the [EMIM]Cl/H₂O system [26]. Therefore, finding an optimal reaction temperature and time is highly demanded.

Fig. 5a shows the effect of reaction temperature (T_{rxn}) on the production of monosaccharides and HMF. As T_{rxn} was increased to $120 \,^{\circ}$ C, the total yield increased to 42.8%, about five times higher than that at $80 \,^{\circ}$ C (the total yield was 7.8%). We supposed that higher T_{rxn} would increase [H⁺] from H₂O and help the hydrolysis of cellulose to glucose. Similar with the condition of $T_{dis} > 120 \degree C$, when $T_{\rm rxn}$ was increased from 120 °C to 140 °C, the total yield decreased from 42.8% to 22.2% but the HMF yield kept almost the same. We suggested that it was because of some side reactions such as formation of insoluble humines and soluble polymers [22,29,30] (kinds of decomposition product of fructose) that prefer to occur when the temperature was closed to the melting point of monosaccharides. In contrast to monosaccharides, the HMF yield increased from 0.54% to 17% as the $T_{\rm rxn}$ increased from 80 °C to 140 °C, respectively. In addition, the selectively of HMF (defined as HMF yield/monosaccharides yield) also increased from 6.9% to 39.8%, as shown in Fig. 5a. The enhanced selectivity toward HMF also proved that higher [H⁺] and [OH⁻] resulted from increasing temperature could efficiently catalyze the isomerization of glucose and the dehydration reaction of fructose.

Next, we study the effect of reaction times t_{rxn} on the conversion efficiency, and the results are depicted in Fig. 5b. As t_{rxn} increased,



Fig. 5. (a) Monosaccharides and HMF yield vs. reaction temperature and (b) Monosaccharides and HMF yield vs. reaction time. Other conditions were controlled as follows: [EMIM]Cl 0.15 g, cellulose 0.015 g, H₂O/cellulose molar ratio 10/1, $T_{\rm dis}$ 120 °C, $t_{\rm dis}$ 0.5 h. Yields are based on HPLC analysis and are relative to mol of glucose unit in the cellulose.

we found that the monosaccharides yield decreased while HMF yield increased and reached at maximum at $t_{rxn} = 6$ h and then decreased. It is reasonable that the increase of HMF within the first 6 h was resulted from the decrease of monosaccharides (i.e., isomerization and dehydration reaction). However, HMF yield also decreased when the $t_{rxn} > 6$ h. We supposed that this was due to the decomposition of HMF to other byproducts. We examined the possible byproducts such as formic acid and levulinic acid but could not detect them. Several papers have also reported the decomposition of HMF to some unidentified products [22,29,30]. Conclusively, we suggest the optimal reaction temperature is 120 °C and reaction time to be 3 h in [EMIM]Cl/H₂O systems. This optimal condition can obtain the highest total yield of 45.9% (24.9% for monosaccharides and 21.0% for HMF).

3.4. Effects of the types of IL

We study the effects of different ILs including imidazoliumtyped ILs and pyridinium-typed ILs on the cellulosic conversion. The positively charged cations such as imidazolium or pyridinium contain alkyl substituent to make the cations hydrophobic and the anions more nucleophilic. Imidazolium-typed ILs have been widely studied and used for biomass dissolution [10,15,17]. On the contrary, the efficiency of pyridinium-typed ILs on cellulosic conversion still remains unclear. Different ILs may alter the efficiency of cellulosic dissolution, efficiency of conversion, and selectivity of final products; therefore, finding out an appropriate IL that can dissolve cellulose quickly and catalyze further reactions effectively has been strongly demanded. In this study, two types of ILs ([EMIM]Cl (imidazolium type) and [Epyr]Cl (pyridinium type)), were used. All reaction conditions are the same (i.e., H₂O/cellulose molar ratio = 10, T_{dis} = 120 °C, t_{dis} = 0.5 h, T_{rxn} = 120 °C, and t_{rxn} = 3 h).



Fig. 6. Monosaccharides and HMF yields vs. different types of ILs. Other condition were fixed as follows: ILs 0.15 g, cellulose 0.015 g, H₂O/cellulose molar ratio 10/1, dissolution temperature 120 °C, dissolution time 0.5 h, reaction temperature 120 °C, reaction time 3 h. Yields are based on HPLC analysis and are relative to mol of glucose unit in the cellulose.

As shown in Fig. 6, the total yield from [EMIM]Cl (43%) was higher than that of [Epyr]Cl (35%). The yield of monosaccharides and HMF was 24% and 19%, respectively, for the [EMIM]Cl case and was 32% and 3%, respectively, for the [Epyr]Cl case. [Epyr]Cl apparently had a better selectivity toward the production of monosaccharides than [EMIM]Cl. Although the reason for such a high specificity toward monosaccharide is still unclear, to the best of our knowledge, this superior selectivity in the [Epyr]Clbased system has never been reported so far. A further combination of [Epyr]Cl and [EMIM]Cl may join the advantages of each IL and produce HMF with high selectivity and efficiency.

4. Conclusion

We have demonstrated that high yields of monosaccharides and HMF (24.9% and 21%, respectively) could be produced directly from cellulosic conversion using ionic liquids as both a solvent and a catalyst after optimization of the reaction conditions. We have studied the effects of the following parameters and decided the optimal conditions: H₂O/cellulose molar ratio = 10, dissolution temperature ($T_{\rm dis}$) = 120 °C, dissolution time ($t_{\rm dis}$) = 0.5 h, reaction temperature ($T_{\rm rxn}$) = 120 °C, and reaction time ($t_{\rm rxn}$) = 3 h for [EMIM]Cl-based system. The information we obtained here would be helpful for further studies on the cellulosic conversion with the addition of solid catalysts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2011.03.020

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