Kinetic Study of the Decomposition of Cellulose to 5-Hydroxymethylfurfural in Ionic Liquid

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The kinetics of cellulose decomposition in ionic liquid was investigated using microcrystalline cellulose as a raw material. Curve fitting of cellulose degradation kinetic data was carried out by MATLAB. Experimental results demonstrated that the cellulose decomposition rate constant, k_1, was less than the constant for glucose decomposition to 5-hydroxymethylfurfural (5-HMF), k_2, in the ionic liquid system, gaining a larger gap with increasing temperature. Results indicated that cellulose degradation is a slow reaction compared with glucose decomposition, which controls the speed of the overall reaction steps. $CrCl_3$ increased the rate constant of cellulose and glucose degradation to almost the same degree, thus achieving simultaneous conversion of cellulose, glucose, and 5-HMF. Compared with other reaction systems, the ionic liquid system considerably reduced activation energy. Regression analysis of kinetic data indicated that the catalytic decomposition reactions of cellulose, glucose, and 5-HMF are all first-order reactions.

Keywords: Cellulose; Ionic liquid; 5-HMF; Decomposition; Kinetics

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INTRODUCTION

Our high dependence on the supply of diminishing fossil fuel reserves has raised great concerns with respect to its environmental, political, and economic consequences. Thus, utilization of renewable biomass as an alternative resource has become increasingly important (Shuit *et al.* 2009; Yan *et al.* 2014). Cellulose, as the most abundant renewable biomass resource worldwide, has not been efficiently utilized and is of low value at present. Taking advantage of cellulose to prepare 5-HMF is one approach for the effective conversion of biomass resources (Liu *et al.* 2012). There are many kinds of raw materials for the production of 5-HMF (Ståhlberg *et al.* 2011; Zhang *et al.* 2011; Yan *et al.* 2014). With multiple functional groups within the molecule, 5-HMF can be used to prepare diverse chemicals of high value (Yan *et al.* 2014) through hydrogenation, halogenation, esterification, and other chemical reactions. For example, the selective oxidation of 5-HMF produces 2,5-furandicarboxylic acid, which is used for the preparation of insecticides, fungicides, and pesticides (Smay 1985; Siewping *et al.* 2014). 2,5-Dimethylfuran, a high-efficiency clean fuel, can also be obtained by the selective reduction of 5-HMF. 5-HMF is widely used, but the direct preparation of 5-HMF from cellulose industrial product has yet to be achieved because of the low yield of traditional preparation methods and the difficulty of separating and extracting the compound.

In recent years, ionic liquids have gained widespread attention because of their lower vapor pressure and good thermal stability (Dupont *et al.* 2003). Ionic liquids have been used to prepare biomass catalytic degradation reactions of 5-HMF. As an aid for cellulose pyrolysis to prepare 5-HMF, ionic liquids obtain a relatively high yield and suppress many side reactions (Kim *et al*. 2011). However, there are few reports on the kinetics of this reaction. The present study used $CrCl_3$ as a catalyst and established a kinetic model of microcrystalline cellulose degradation in ionic liquid. The kinetic constants and activation energy of the catalytic degradation of cellulose, glucose, and 5-HMF were investigated, obtaining the relationships between the three reactions, for the first time. A theoretical reference is provided by this work for improving the yield of products of catalytic cellulose degradation in ionic liquids. The degradation reaction of cellulose is very complicated, so it is important to provide a basis for reducing the prevalence of side effects.

EXPERIMENTAL

Materials

Microcrystalline cellulose and glucose (biochemical reagent) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 3,5-Dinitrosalicylic acid, sodium tartrate, phenol, sodium hydroxide, and sodium sulfite were of analytical grade and acquired from Shanghai Pu Chen Biotechnology Co., Ltd. (Shanghai, China). 5-HMF (>99%) was obtained from Sigma Reagent Company (Beijing, China). 1-Butyl-3-methylimidazolium chloride (referred to as [BMIM]Cl) (>99%) was purchased from Shanghai Cheng Jie Chemical Co. Shanghai, China). All materials were used without further purification.

Methods

The reaction conditions were as follows: temperature, 140 °C to 170 °C; amount of $CrCl_3$, 0.5% to 2%; and mass ratio of 1-butyl-3-methyl-imidazolium chloride and microcrystalline cellulose, 5:1 to 15:1. A given amount of 1-butyl-3-methylimidazolium chloride was added to the flask. While the oil bath was heated to the setting temperature, the stirrer was turned on after ionic liquids were melted, and small amounts of microcrystalline cellulose and $CrCl_3$ catalyst were gradually added in sequence. The system was timed after the additions were completed. At certain instances, a quantitative reaction solution was obtained. The reaction was then quenched with cold water by diluting to multiple settings; the measured value of absorbance was ensured to fall between 0.2 and 0.8. The supernatant was obtained after centrifugal separation (4000 rpm, 1 min) to determine glucose content and 5-HMF product. A standard solution of different concentrations of glucose and pure product of 5-HMF were prepared. To obtain pure HMF from a reaction mixture the following procedure has been given by Middendorp (1919) and Haworth and Jones (1944): filtration of humin, neutralization with $CaCO_3$, addition of $Pb(OAC)_2$ and filtration, extraction of the filtrate with EtOAc, drying the extract with Na_2S0_4 evaporation of EtOAc, and high vacuum distillation of the dark brown syrup obtained (Kuster 1990). The products were quantitatively analyzed using a TU-1810 UV-Vis spectrophotometer (Beijing Puxi, Beijing, China). Glucose content was determined *via* the DNS method (Zhu *et al*. 2005), and the measurement wavelength was 540 nm. The measurement wavelength of 5-HMF was 284 nm. The standard curve and regression equation were plotted. The standard curve is shown in Fig. 1. The cellulose degradation kinetic data was analyzed by MATLAB (MathWorks, Natick, MA, USA).

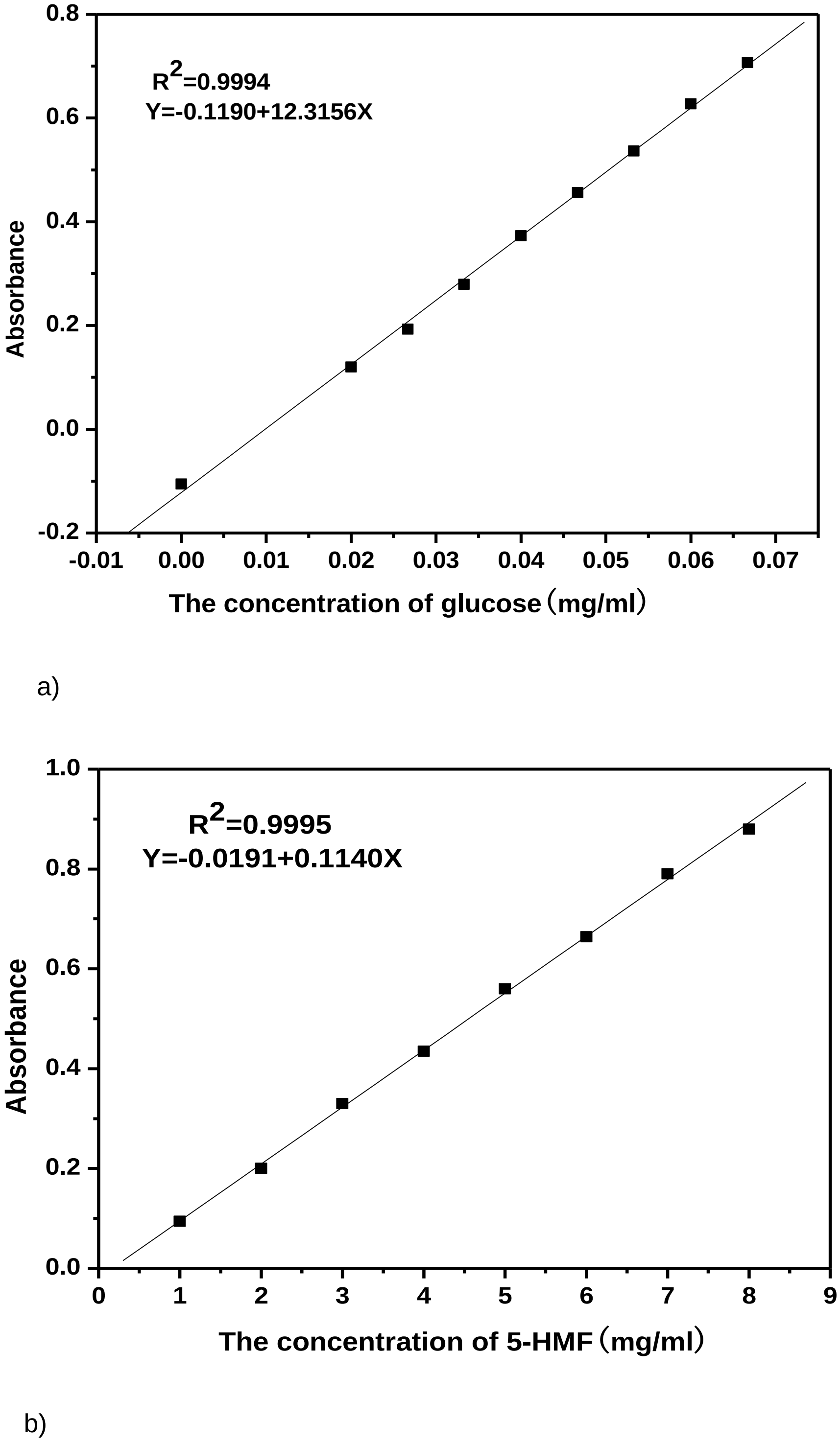
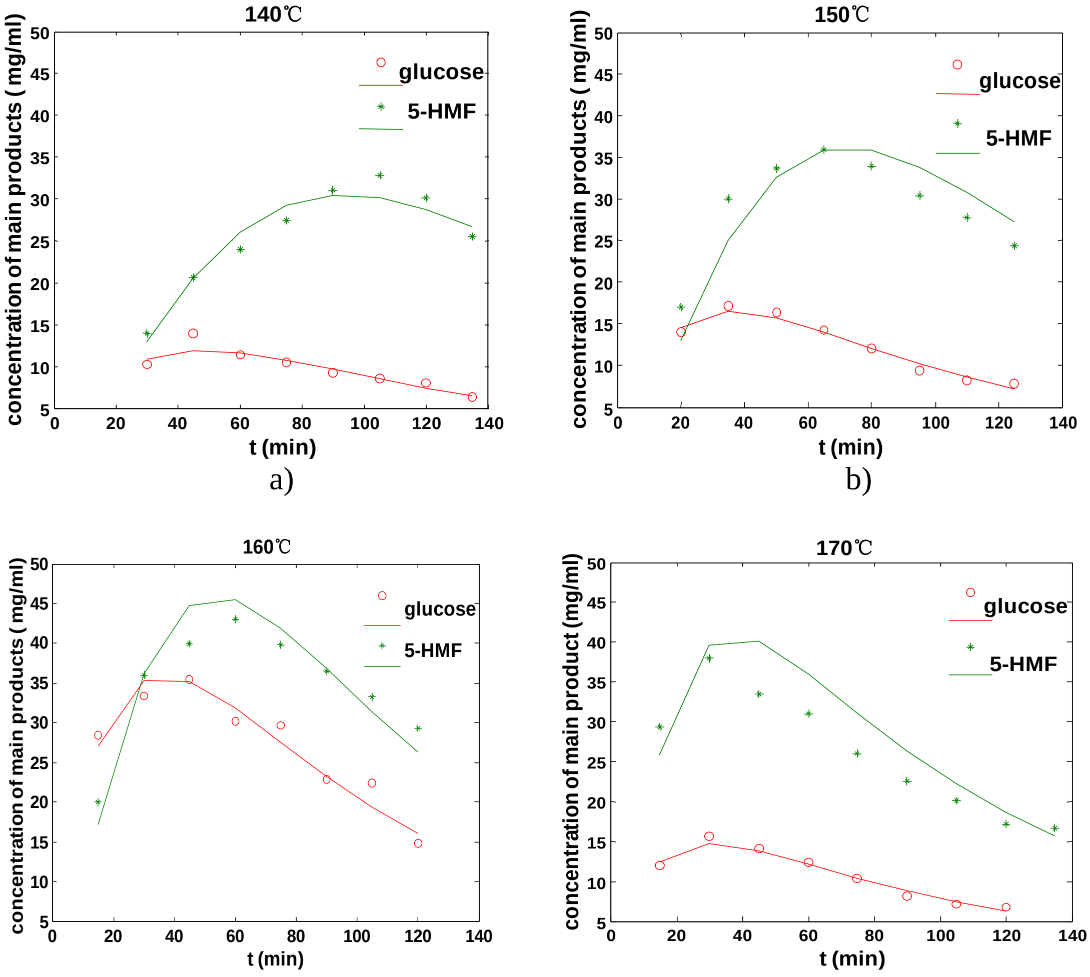


Fig. 1. Calibration curves of (a) of glucose content and (b) of 5-HMF content

RESULTS AND DISCUSSION

Effect of Temperature and Time on the Yield of Glucose and HMF

Reaction temperature and time influence the rate of cellulose degradation, and increasing the reaction temperature to accelerate the reaction rate is one of the most effective approaches. Shortening the reaction time improves the reaction efficiency and reduces side reactions, thereby reducing the difficulty of product extraction and purification. The changes in reducing sugar concentration and 5-HMF concentration at different temperatures and reaction times were fitted to kinetic model curves (Fig. 2).



a) b)

c) d)

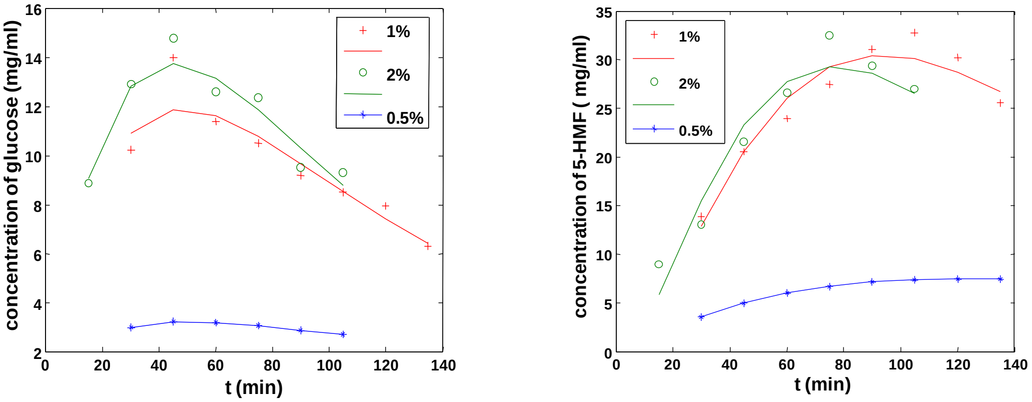
Fig. 2. Effect of temperature and reaction time on yield at (a) 140 °C, (b) 150 °C, (c) 160 °C, and (d) 170 °C

The glucose maximum concentration increased with increasing temperature. Higher temperature required a shorter reaction time to reach the maximum concentration at 160 °C. With the extension of time and with temperature increasing over 160 °C, HMF is easily recombined with glucose, and this effect may have contributed a lot to the decreased yield of HMF. The shortest time occurred when the temperature rose to 170 °C, but the highest concentration of products showed varying degrees of decline, where a drastic decline in the concentration of glucose production occurred. When the temperature was extremely high, cellulose degradation was more complex, causing a decrease in the selectivity and yield of glucose. The decline of the highest concentration of 5-HMF may be related to a sharp rise in the rate of 5-HMF degradation constant k_4. The optimum reaction temperature of 160 °C was considered.

With extended reaction times, glucose and 5-HMF—the intermediate products of the continuous reaction—decreased after the first increase. With a short reaction time, the cellulose was not completely dissolved using the ionic liquid, resulting in a lower yield of products. In contrast, an excessively long reaction time led to poly 5-HMF, which reduced the yield. The reaction time in this study was 60 min.

Catalyst Effect on Glucose and Yield of HMF

The yield of 5-HMF and sugar was low at 140 °C. The low rate of cellulose conversion is conducive to the study of catalytic effect. Therefore, the effect of catalysts on glucose and 5-HMF was studied at 140 °C.



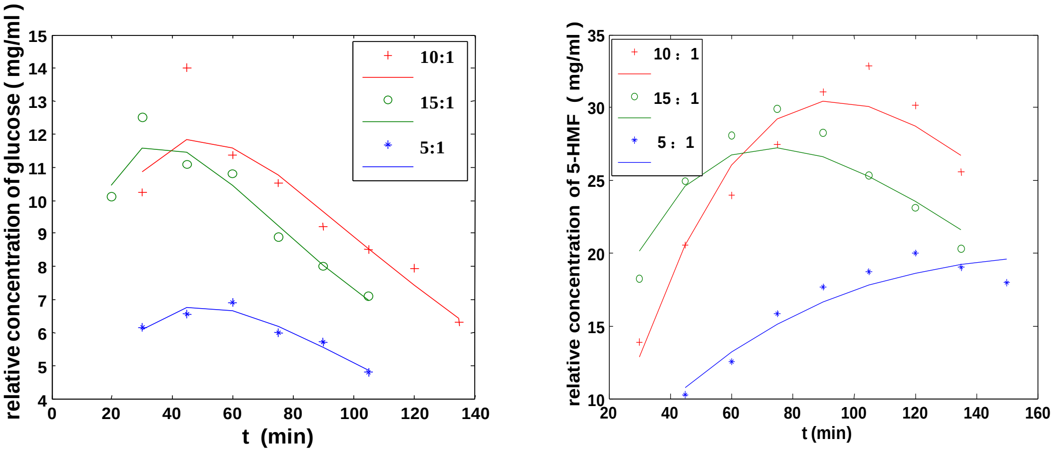
a) b)

Fig. 3. Effect of catalyst on (a) glucose yield and (b) 5-HMF yield

Figure 3 shows that the concentrations of glucose and 5-HMF were very low and changes were very small, almost in a linear state, when the amount of $CrCl_3$ was 0.5%; therefore the lines for the kinetic model for 0.5% catalyst completely overlap. Results indicated that product yields were very little affected over time when the amount of $CrCl_3$ was 0.5%. These results suggest that $CrCl_3$ noticeably improved the yield of glucose and 5-HMF because $CrCl_3$, a Lewis acid, can improve the acidity of the cellulose degradation system to promote cellulose degradation. In addition, Cr, a transition metal, possesses numerous empty orbitals. The lone pair electrons in oxygen of cellulose hydroxyl enter into the unoccupied orbitals in metal ions, and the intermediate state complex is formed (May 1967), changing the reaction mechanism and reducing the reaction energy barrier by coordination function in the formation. Cl^-, as a strong hydrogen acceptor, can damage the hydrogen bonds in cellulose molecular chains that are formed between the O—H…Cl and is converted to the hydrogen bond O—H…Cl, thereby promoting cellulose degradation (Zhuang *et al*. 2006). However, when excessive $CrCl_3$ is added, 5-HMF is conversely decreased because excess $CrCl_3$ leads to a decrease in the pH of the reaction system. Under acidic conditions, 5-HMF reacts with water molecules and is degraded, generating levulinic acid and other substances. Therefore, 0.1% catalyst was selected in this study.

Amount of Ionic Liquid Effects on Glucose and HMF Yield

In the mechanism of ionic liquid [BMIM]Cl catalysis, cellulose degradation occurs as follows. Cl− attacks the proton H in hydroxyl groups on cellulose, and [BMIM]+ is combined with the O in hydroxyl groups, destroying the interaction between the two intra-molecular and intermolecular hydrogen bonds of cellulose to form new hydrogen bonds to dissolve cellulose in the ionic liquid (Wang *et al.* 2011). With the addition of a catalyst, [BMIM]Cl in combination with $CrCl_3$ generates [BMIM] $CrCl_4$. [BMIM] $CrCl_4$ can promote the reaction of enolate glucose, achieving the transformation from glucose to fructose; this transformation increases the degradation rate and glucose conversion (Binder and Raines 2009). The experimental data in Fig. 4 show that a larger ratio of the ionic liquid and cellulose translated to a shorter time for glucose and 5-HMF to reach maximum concentration. However, when this ratio reached 15:1, the 5-HMF concentration showed a downward trend. Therefore, a ratio of 10:1 was selected for ionic liquids to cellulose in this work.



a) b)

Fig. 4. Effect of ionic liquid dosage on (a) glucose yield or (b) 5-HMF yield

Cellulose Degradation Kinetic Model and Parameter Calculation

Degradation kinetic model

Cellulose degradation is a relatively complicated process, and a large number of unknown intermediates are generated in degradation. This paper investigated the effect of ionic liquid on glucose and 5-HMF yield for ease of calculating kinetic parameters of glucose degradation and related cellulose degradation. In this work certain minor products were disregarded, and the simplified model of cellulose degradation was as follows:

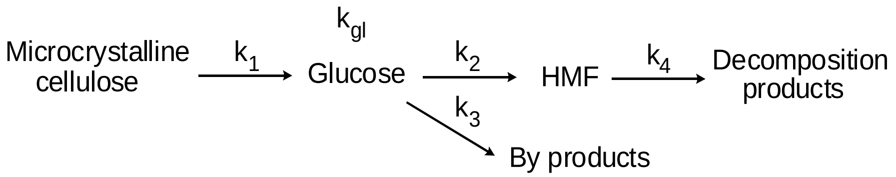


Fig. 5. Kinetic model of cellulose hydrolysis. k_1 is the degradation rate constant of cellulose; k_4 and k_l are the degradation rate constant of 5-HMF and glucose that contain k_2 (the generation rate constant of 5-HMF) and k_3, respectively.

In the degradation of macromolecular substances, while the degradation reaction mechanism is complex, most of the component reactions can be treated as zero order, first order, and pseudo-first order reactions. It is easy to guess that the degradation reaction of cellulose is a first order reaction from the reaction characteristics of the three. And according to the literature (Bradbury *et al.* 1979; Girisuta *et al.* 2007; Zhuang *et al.* 2009; Lee and Wu 2012; Zhang *et al.* 2012), while also assuming that the catalytic degradation of cellulose, glucose, and 5-HMF are first-order reactions, the reaction rate equations are as follows,

$$\frac{-\mathrm{d}C_{c}}{\mathrm{d}t} = k_{1}C_{c} \tag{1}$$

$$\frac{\mathrm{d}C_{gl}}{\mathrm{d}t} = k_{1}C_{c} - k_{gl}C_{gl} \tag{2}$$

$$\frac{\mathrm{d}C_{5-HMF}}{\mathrm{d}t} = k_{2}C_{gl} - k_{4}C_{5-HMF} \tag{3}$$

$$C_{gl} = \frac{k_{1}C_{co}}{k_{gl} - k_{1}}\left(e^{-k_{1}t} - e^{-k_{gl}t}\right) \tag{4}$$

$$C_{5-HMF} = k_{1}k_{2}C_{co}\left[\frac{e^{-k_{1}t}}{\left(k_{gl}-k_{1}\right)\left(k_{4}-k_{1}\right)} - \frac{e^{-k_{gl}t}}{\left(k_{gl}-k_{1}\right)\left(k_{4}-k_{gl}\right)} + \frac{e^{-k_{4}t}}{\left(k_{4}-k_{gl}\right)\left(k_{4}-k_{1}\right)}\right] \tag{5}$$

where C_c, C_{gl}, $C_{5\text{-HMF}}$, and C_{co} are the concentrations of cellulose, glucose, 5-HMF, and the initial concentration of cellulose, respectively (mg/mL).

MATLAB fitting was obtained by applying Eqs. 4 and 5 to the experimental data under different reaction conditions for cellulose degradation. The cellulose degradation rate constant, k_1, the rate of glucose degradation to 5-HMF generated constant, k_2, the degradation rate of glucose, k_{gl}, and the rate of degradation of 5-HMF constant, k_4, under different conditions were obtained using MATLAB fitting. The activation energy of the degradation of cellulose, glucose, and 5-HMF were obtained according to Arrhenius SA equations (Li *et al*. 2009).

Kinetic parameter estimates

As shown in Fig. 2, by fitting a high degree curve using experimental values and the resulting simulation values, the model agreed with the actual process of cellulose degradation, previously assuming that several reactions are first-order reactions. The relevant kinetic parameters of the model are shown in Tables 1, 2, and 3.

Table 1. Kinetic Rate Constants at Different Temperatures

T (°C)	k_1 (min^{-1})	k_2 (min^{-1})	k_4 (min^{-1})
140	0.0357	0.1471	0.0251
150	0.0532	0.2060	0.0324
160	0.0811	0.2827	0.0416
170	0.0712	0.2597	0.1746

Table 2. Kinetic Rate Constants at Different Dosages of Catalyst

Dosage (%)	k_1 (min^{-1})	k_2 (min^{-1})	k_4 (min^{-1})
0.5	0.0138	0.0478	0.0101
1	0.0357	0.1471	0.0251
2	0.0324	0.1706	0.0477

Table 3. Kinetic Rate Constants at Different Dosages of Ionic Liquid

[BMIM]Cl : cellulose/mass ratio	k_1 (min^{-1})	k_2 (min^{-1})	k_4 (min^{-1})
5:1	0.0093	0.0316	0.0067
10:1	0.0357	0.1471	0.0251
15:1	0.0610	0. 2028	0.0304

Table 1 shows the degradation rate constants of cellulose. The generation rate constants of 5-HMF increased with increasing temperature, $k_1 < k_2$. As the temperature rose, the gap between the ionic liquid and the glucose degradation became greater. Cellulose degradation is a slow reaction, and the increase in reaction rate should focus on improving fiber pigment degradation rate. Table 1 also shows that k_4 underwent a large increase at 170 °C, which is consistent with the above speculation, indicating that the 5-HMF began to degrade rapidly at 170 °C. Compared with k_1 and k_2, the 5-HMF degradation rate constant, k_4, was a large value. Most studies have focused on improving the efficiency of 5-HMF generation. Studies on reducing 5-HMF degradation are scarce and need considerable attention.

$CrCl_3$ increases the rate constants of cellulose and glucose degradation to almost the same degree, as well as achieves cellulose → glucose → 5-HMF at the same time (Table 2). An efficient, selective catalyst should catalyze the degradation of cellulose into glucose to increase the slow reaction rate. This subject requires more in-depth study. Table 3 shows that, in comparison with the catalyst, the ionic liquid can more efficiently increase the rate of cellulose and glucose degradation. The rate constant of 5-HMF degradation is also relatively small compared with $CrCl_3$. [BMIM]Cl is neutral and can effectively inhibit the occurrence of side effects of 5-HMF.

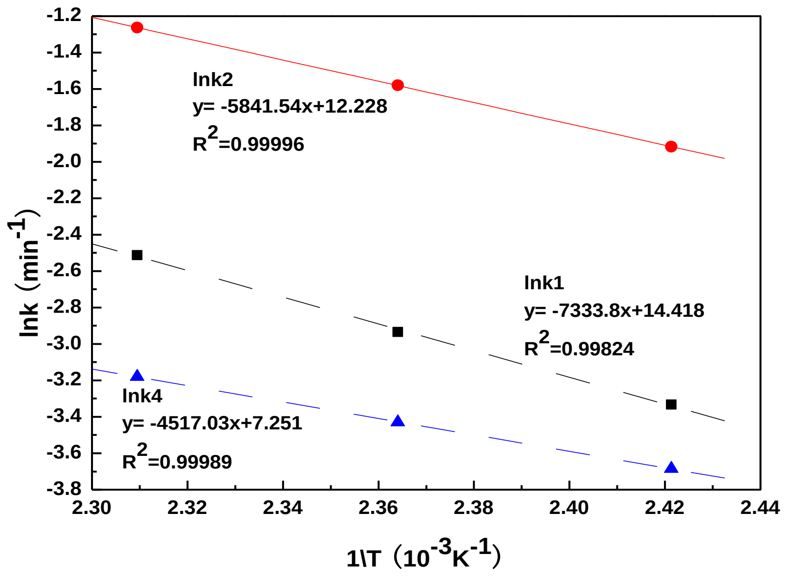


Fig. 6. Arrhenius plot of ln*k* and 1/*T* for cellulose hydrolysis with ionic liquid

The pre-exponential factors k_{i0} and active energies E_{ai} of the hydrolysis model were obtained from the plots of ln*k* versus 1/*T*, using the least squares method (Fig. 6). The results are presented in Table 4. Figure 6 is drawn according to Table 1. One point is ignored of each straight line in Fig. 6 in which the temperature is 170 °C. This is because when the temperature reaches 170 °C, cellulose degradation is more complex, and the reaction is no longer a first-order reaction, and its k_i could not fit into the plot.

According to Arrhenius SA equations, the reaction rate constants for nonlinear regressions were used to obtain the activation energy of each step (Table 4).

Table 4. Related Reaction Activation Energy

E_{a1} (KJ/mol)	E_{a2} (KJ/mol)	E_{a4} (KJ/mol)
61.04	48.56	37.57

Note: E_{a1} is the activation energy of cellulose hydrolysis, E_{a2} is the activation energy of degradation of glucose to 5-HMF, and E_{a3} is the activation energy of degradation of 5-HMF.

Table 4 shows the order $E_{a1} > E_{a2} > E_{a4}$. According to Arrhenius, an increased temperature makes it more likely that the activation energy for a reaction will be surpassed. Thus, increasing temperature will be conducive to cellulose degradation. Throughout the continuous reaction, the degradation of 5-HMF activation energy was the smallest, and the reaction energy barrier was low. Therefore, the degradation rate was also fast.

Comparison with other reaction systems

To increase the rate of formation and yield of 5-HMF, the degradation kinetics of cellulose were compared in different systems. Pang *et al*. (2007) studied the mechanism and kinetics of cellulose degradation in the preparation of 5-HMF subcritical water/carbon dioxide system. They experimentally derived glucose degradation from cellulose degradation, and the apparent activation energies were 113.32 and 104.74 KJ/mol. Chang *et al.* (2009) investigated the degradation kinetics of cellulose under high temperature and dilute acid conditions. The activation energy of cellulose degradation was 88.29 KJ/mol, whereas that of glucose degradation was 56.84 KJ/mol. By contrast, in the present work it was found that the experimental activation energy of cellulose degradation was relatively small. Thus, the ionic liquid catalyst system reduces the activation energy of the reaction, increasing the reaction rate.

CONCLUSIONS

1. In the ionic liquid [EMIM]Cl system, the optimal reaction conditions were as follows: reaction temperature, 160 °C; reaction time, 60 min; amount of catalyst, 1%; and amount of cellulose, 10%.
2. The degradation rate constant, k_2, of glucose was greater than the cellulose degradation rate constant, k_1, and higher temperature indicates greater gap. Cellulose degradation was a slow reaction with respect to glucose degradation, and the reaction rate was controlled throughout a series of steps.
3. $CrCl_3$ was almost the same level to increase cellulose and glucose degradation rates to a constant value. Compared with $CrCl_3$, ionic liquid can more efficiently increase the rate of cellulose and glucose degradation. The 5-HMF degradation rate constant was also relatively small.
4. Cellulose degradation activation energy (E_{a1}) was greater than the glucose degradation activation of 5-HMF (E_{a2}). The activation energy for glucose degradation on 5-HMF (E_{a2}) was greater than that for the degradation on 5-HMF (E_{a4}). High temperature favored cellulose degradation. Compared with other reaction systems, the ionic liquid reduced the activation energy of the continuous reaction and increased the reaction rate.

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