One-vessel Synthesis of 5-Hydroxymethylfurfural in Concentrated Zinc Chloride Solution from Lignocellulosic Materials

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The synthesis of bio-based chemicals, such as 5-hydroxymethylfurfural (HMF) and its derivatives, from cellulosic biomass resources has been attempted for years. However, the harsh reaction condition, toxicity of the catalysts applied, and low efficiency of the conversion process have deterred its industrial implementation. Herein, the authors investigated the degradation and conversion of cellulose into HMF in a concentrated zinc chloride solution. The effects of reaction conditions and co-catalysts on the conversion were evaluated. A 69.5% HMF yield from cellulose was obtained in the condition of 1 h and 150 °C using 0.2 mol·L^{-1} of HCl without co-catalyst during the conversion. Moreover, the $ZnCl_2$ aqueous solution displayed good reusability. Finally, a simplified kinetic model of the conversion of cellulose to HMF in a concentrated zinc chloride solution was developed, and the reaction kinetics were investigated.

INTRODUCTION

The conversion of sustainable lignocellulosic materials to fuels and chemicals has been gaining significant attention in recent years due to the diminishing availability of fossil resources and an increasing global demand for energy. The chemical 5-hydroxymethylfurfural (HMF) and its derivatives are valuable building blocks obtainable from biomass for many products such as plastics, pharmaceuticals, fine chemicals, and green solvents (Buntara *et al.* 2011; Rosatella *et al.* 2011; Liu *et al.* 2012; Choudhary *et al.* 2013).

Many studies have been conducted on the production of HMF from mono/poly-saccharides using Brønsted/Lewis acids as catalyst in a homogeneous/heterogeneous system with a high-boiling-point reaction media (Zakrzewska *et al.* 2011; Dutta *et al.* 2014; Mondal *et al.* 2015; Sun *et al.* 2015) such as dimethylsulfoxide (DMSO) (Jia *et al.* 2014), N,N-dimethylformamide (DMF) (Simmie and Würmel 2013), N,N-dimethylacetamide (DMA) (Binder and Raines 2009), and ionic liquids. Nevertheless, the processes reported are not yet economically satisfying for their commercial application due to operating costs (Saha and Abu-Omar 2014). Compared with a high-boiling point organic solvent, water is a convenient solvent for the synthesis of HMF from carbohydrates. However, aqueous systems suffer from low production yield and poor selectivity in their conversion due to the further degradation and condensation of HMF in the heterogeneous mixture of cellulose

and catalysts (De Souza 2011). Special attention has been given to finding an economical and efficient way of biomass conversion (Jiang *et al.* 2012; Lai *et al.* 2013; Thombal and Jadhav 2014). Ionic liquids as solvents in catalyzed biomass conversions (Peng and Ren 2011; Guo *et al.* 2012) were reported as promising systems for the conversion of cellulose, glucose (Zakrzewska *et al.* 2011), and fructose (Binder and Raines 2009) to HMF due to their low vapor pressure, good thermal stability, and a range of tunable hydrophobicity. However, they are expensive and difficult to recycle and purify (Gallezot 2012; Van Putten *et al.* 2013). A binary aqueous/organic system for the conversion of sugars to HMF was reported to avoid the cost and complexity in the conversion and improve the efficiency, in which organic solvents were used as the extraction phase to remove the products from the aqueous phase (Pagán-Torres *et al.* 2012).

A one-vessel synthesis of HMF directly from cellulose can simplify the conversion process and reduce the operation costs (Hu *et al.* 2012). Deng *et al.* (2012) obtained 40% of HMF from the conversion of carbohydrate in zinc chloride solution, and the effect of the incomplete coordination zinc ion on the conversion of carbohydrates was discussed. Recently, the conversion of cellulose into HMF in one-vessel using 71.62 wt.% $ZnCl_2$ aqueous solution has been reexamined (Zhang *et al.* 2016). It was found that this inexpensive system exhibited a very good solubility for cellulose and excellent conversion efficiency with methyl isobutyl ketone as the extraction solvent. In this case, 80.6 mol% of HMF was achieved at 150 °C and 40 min.

Inspired by these results, the conversion of cellulose was investigated in this work with n-butanol, a low boiling point solvent, as the extraction solvent. In the present study, various co-catalysts were considered, including $CrCl_3$, $SnCl_4$, $AlCl_3$, and $FeCl_3$ in the catalytic conversion of the cellulose component. The effects of HCl concentration, reaction temperature, reaction time, and the substrate concentration on the conversion were studied. In this work, the conversion of wheat straw, eucalyptus wood, pine wood, and sugar cane bagasse into valuable platform chemicals was also investigated using the biomass–$ZnCl_2$ solution system. The flow chart of the experiment is shown in Fig. 1.
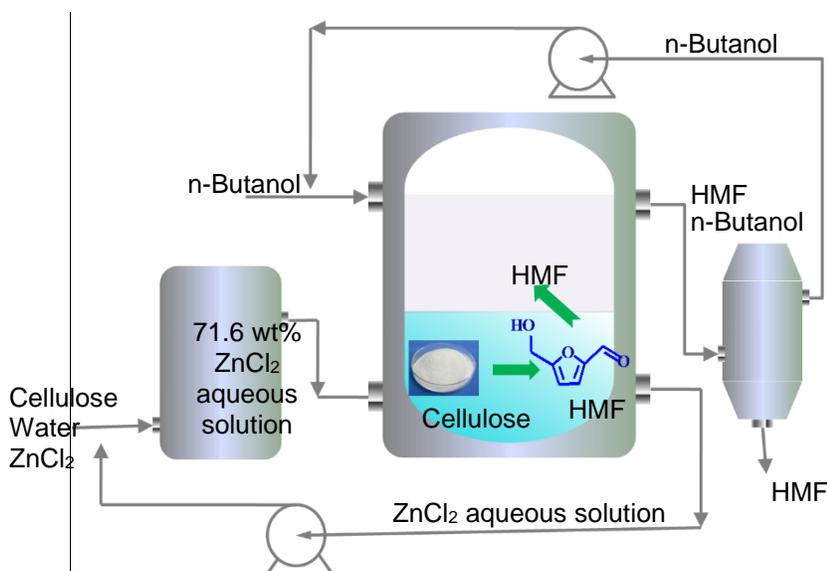

Fig. 1. Diagram of the homogenous conversion of cellulose into HMF; aqueous layer: cellulose solution in 71.6 wt.% $ZnCl_2$ aqueous solution; Organic layer: n-butanol

EXPERIMENTAL

Materials

Zinc chloride, aluminum chloride, stannic chloride, ferric chloride, chromium chloride, n-butanol, hydrochloric acid (aq. 37%), microcrystalline cellulose, glucose, fructose, and chemicals for calibration, such as HMF, were purchased from Beijing ZKKA Biotechnology Co., Ltd. (Beijing, China) and used without further purification. The water used in the experiments was deionized in the lab. Wheat straw was collected from the Hebei Province, China. Eucalyptus wood, pine wood, and sugar cane bagasse was harvested in Guangxi, China. Their chemical composition was determined according to the NREL Laboratory Analytical Procedures (Sluiter *et al.* 2008).

General reaction procedure

The conversions were performed in a 20-mL autoclave lined with Teflon and heated in an oil bath on a hot plate (Zhengzhou Great Wall Scientific Industry and Trade Co., Ltd., Zhengzhou, China). First, biomass substrates (0.2 g) and 71.6 wt.% $ZnCl_2$ aqueous solution (5 mL) were added to the autoclave with stirring at 85 °C for 5 min. Then, NaCl (0.65 g), hydrochloric acid (0.1 mL), and n-butanol (10 mL) with and without co-catalyst (1 mmol) were charged into the reaction mixture, and heated to 150 °C. After the reaction, the reactor was immediately cooled down to room temperature with cold water.

Methods

For high-performance liquid chromatography (HPLC), the samples were filtered with a 0.22 μm syringe filter prior to analysis. The HMF was analyzed by HPLC (H&E Co., Ltd, Beijing, China) fit with a QuikSep UV-100D detector (H&E Co., Ltd, Beijing, China) and an Inertsil ODS-C18 column (Shimadzu Crop., Japan) at 282 nm and the mobile phase was methanol-water (30:70 in volume) at a flow rate of 0.5 mL·min⁻¹. Sugars were analyzed using a Waters 2695 HPLC system (Milford, USA) with an Aminex HPX-87P column (Biorad, Hercules, CA) and a refractive index (RI) detector (Waters, Milford, USA), and deionized water as eluent at 85 °C with 0.6 mL·min⁻¹. The HMF yield, Y_{HMF}, and the biomass conversion, C_i, were calculated as follows:

$$Y_{HMF} \ (\%) = \frac{m_{HMF}}{m_{i,cellulose} \times 0.778} \times 100 \ \%$$

$$C_i \ (\%) = \frac{m_{i,cellulose,t=0} - m_{i,cellulose,t=t}}{m_{i,cellulose,t=0}} \times 100 \ \%$$

where $m_{i,cellulose}$ is the molar amount of cellulose of lignocellulosic materials.

RESULTS AND DISCUSSION

Cellulose Conversion to HMF in Different Conditions

The conversions were performed under different reaction temperatures, time, acid concentrations, and substrate concentrations to optimize the reaction conditions.

The effects of reaction temperature and time on the conversion of cellulose to HMF were examined in the homogenous system, and the results are shown in Fig. 2. As shown, the conversion of cellulose increased with increased reaction temperature. However, the

yield of HMF did not behave the same. The yield of HMF was approximately 25% at 130 °C. When the temperature was increased from 130 °C to 150 °C, the yield of HMF increased to 69.5%, which signified that high temperatures favored the conversion. This may have resulted from both the efficient conversion and from the quick mass transfer of HMF in the aqueous phase to the organic phase, thus causing an increase of the yield of product. However, higher temperature may deteriorate the HMF yield, as 52.5% at most of HMF was obtained at 170 °C. As for the reaction time, prolongation of the reaction did not improve the yield of HMF at higher temperatures. In fact, HMF has been reported to be easily condensed with sugars to form humins or rehydrated to form levulinic acid and formic acid at high temperatures (Dee and Bell 2011), which resulted in the decrease of conversion selectivity. Therefore, 150 °C and 60 min were set in the subsequent experiments.
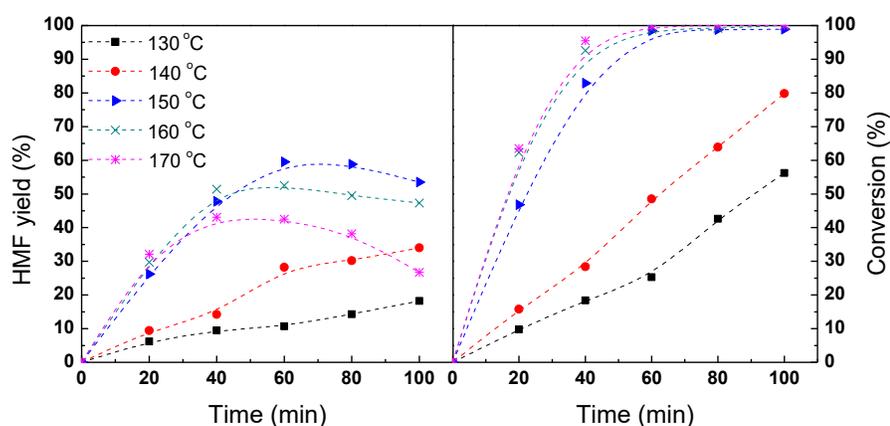

Fig. 2. Conversion of cellulose into HMF at different temperature and time; reaction conditions: cellulose (40 g·L⁻¹), n-butanol (10 mL), NaCl (0.65 g), and HCl (0.2 mol·L⁻¹)

The effect of hydrochloric acid concentration in the conversion system was examined, and the results are shown in Fig. 3. As shown, the product yield improved with the increase of hydrochloric acid concentration. Both the HMF yield and cellulose conversion were achieved in a high level at the concentration of 0.2 mol·L⁻¹. The increased acid concentration resulted in the low HMF yield due to the further decomposition of HMF.
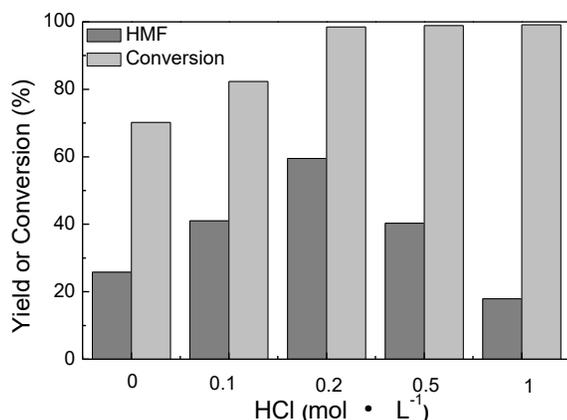

Fig. 3. Conversion of cellulose into HMF at different acid concentrations; reaction conditions: cellulose (40 g·L⁻¹), n-butanol (10 mL), NaCl (0.65 g), 150 °C, for 1 h

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The higher substrate concentration is more ideal for commercialized processes when the energy consumption and efficiency is considered (Peng *et al.* 2010). The influence of substrate concentration on the HMF yield in the conversion system was investigated in the condition of $0.2 \ mol \cdot L^{-1}$ HCl and 150 °C, and the results are shown in Fig. 4. It was shown that the HMF yield and cellulose conversion were at a high level when the concentration of the substrate increased from $20 \ g \cdot L^{-1}$ to $40 \ g \cdot L^{-1}$. However, when the substrate concentration increased from $40 \ g \cdot L^{-1}$ to $120 \ g \cdot L^{-1}$, the yield of HMF and cellulose conversion decreased markedly from 69% to 42.3%, and 98.7% to 80.2% respectively at 60 min. This was due to the low efficiency in product extraction and the reactions having occurred in a concentrated system. Therefore, $40 \ g \cdot L^{-1}$ was used in the following experiments.
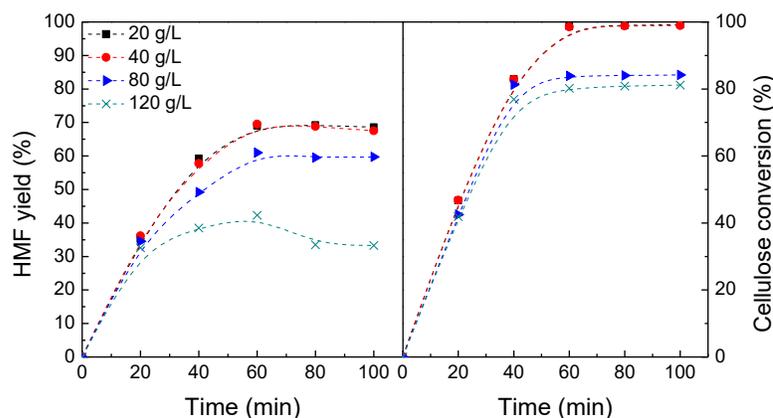

Fig. 4. Cellulose conversion results with different substrate concentrations; reaction conditions: n-butanol (10 mL), NaCl (0.65 g), HCl ($0.2 \ mol \cdot L^{-1}$), and 150 °C

Cellulose Conversion Using Different Co-catalysts

To find whether the addition of a co-catalyst would result in an extra effect, 4 co-catalysts ($AlCl_3$, $SnCl_4$, $FeCl_3$, and $CrCl_3$) were used in the conversion process. The optimized reaction conditions from the previous experiment (with a HCl concentration of $0.2 \ mol \cdot L^{-1}$ at 150 °C for 60 min) were employed. The HMF yields of the conversion of cellulose with co-catalysts are listed in Table 1. It has been reported that $AlCl_3$, $SnCl_4$, $FeCl_3$, and $CrCl_3$, have good catalytic activity in the cellulose conversion to HMF (Peng *et al.* 2010; Pagán-Torres *et al.* 2012). However, when $AlCl_3$, $SnCl_4$, $FeCl_3$, and $CrCl_3$ were employed as co-catalysts, the results were not as good (Table 1). For $AlCl_3$, HMF decreased to 63.1%, which was against the previous study's findings (Wang *et al.* 2013). Moderate HMF yields of 62.5% and 62.0% were obtained at cellulose conversions of 95.7% and 96.8% for the addition of $CrCl_3$ and $SnCl_4$, respectively, to the aqueous layer. The addition of $FeCl_3$ to the aqueous layer led to an HMF yield of 56.3% with 86.2% of cellulose conversed. Therefore, the homogenous reaction system using 71.6 wt.% $ZnCl_2$ solution without co-catalyst was employed for this experiment.

It should be noted that the HMF yield (69.5%) was higher than 51.4% in the ionic liquids [Bmim]Cl from cellulose with $ZrCl_4$ (Liu *et al.* 2013). Moreover, compared with ionic liquids, 71.6 wt.% $ZnCl_2$ aqueous solution is a much cheaper, less toxic cellulose solvent (Deng *et al.* 2012) that is easy to handle in downstream operations.

Table 1. Conversion of Cellulose in 71.6 wt.% ZnCl$_2$ Aqueous Solution at 150 °C with Co-catalyst

Entry	Co-catalyst	HMF Yield (%)	Cellulose Conversion (%)
1	Control	69.5	98.5
2	CrCl$_3$	62.5	95.7
3	SnCl$_4$	62.0	96.8
4	FeCl$_3$	56.3	86.2
5	AlCl$_3$	63.1	98.8

Conditions: cellulose (40 g·L^{-1}), n-butanol (10 mL), NaCl (0.65 g), HCl (0.2 mol·L^{-1}), co-catalysts (1 mmol), 150 °C, for 1 h

Conversion of Lignocellulosic Materials to HMF

From the results described, 150 °C, 0.2 mol·L^{-1} of HCl concentration, and 71.6 wt.% ZnCl$_2$ aqueous solution without co-catalyst were employed in the conversion of lignocellulosic materials, *i.e.* wheat straw, eucalyptus wood, pine wood, and sugar cane bagasse. The direct preparation of HMF from these less-expensive and widely-available biomasses was essential for expanding substrate selection and the reduction of production cost.
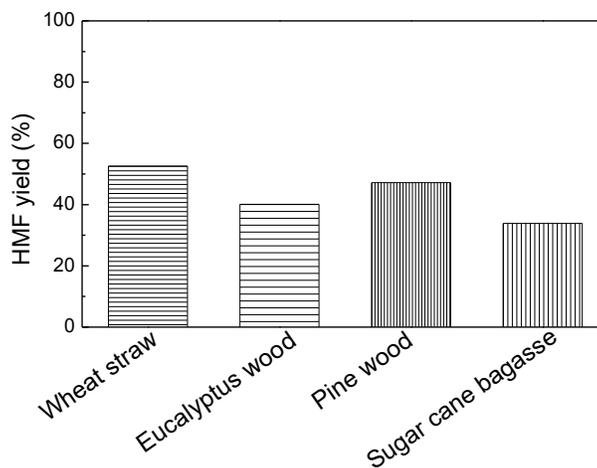

Fig. 5. Conversion of different lignocellulosic materials into HMF in 71.6 wt.% ZnCl$_2$ aqueous solution; reaction conditions: starting materials (40 g·L^{-1}), n-butanol (10 mL), NaCl (0.65 g), HCl (0.2 mol·L^{-1}), 150 °C, for 1 h

The yields of HMF from different substrates with a concentration of 40 g·L^{-1} in 71.6 wt.% ZnCl$_2$ aqueous solution are shown in Fig. 5. As shown, wheat straw gave the best result (52.6%) compared to the yields of other lignocellulosic materials. The use of pine wood and eucalyptus wood as the starting materials gave HMF yields of 47.2% and 40.1%, respectively, which was higher than the yield from sugar cane bagasse at the same conditions. It was possible to explain the observed difference based on the structure and contents of the composition in the lignocellulosic materials used in this work (Tamaki and Mazza 2010).

Reuse of ZnCl$_2$ Aqueous Solution

Due to the costs and toxicities associated with the ZnCl$_2$ aqueous phase, it was highly appropriate to determine if it could be reused. If so, the conversion of cellulose to

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HMF could be implemented in a semi-continuous process with the aqueous phase as a closed loop as shown in Fig. 1. To assess the aqueous media reusability efficiency, sequential experiments were performed with 40 g·L^{-1} of cellulose in ZnCl$_2$ aqueous phase at 150 °C for 60 min. After the reaction, the n-butanol phase was removed, and the aqueous phase was centrifuged to be used for three additional rounds of cellulose conversion. As shown in Fig. 6, the HMF yield monotonically declined from 69.5% in the fresh sample to approximately 50% by the end of the fourth reaction cycle. The reason for the decrement in the yield of HMF after four consecutive runs may be caused by the soluble by-products remained in aqueous phase, which could not be simply removed by centrifugation. This may deteriorate the solubility of cellulose in the ZnCl2 aqueous solution and hence the conversion efficiency afterward.
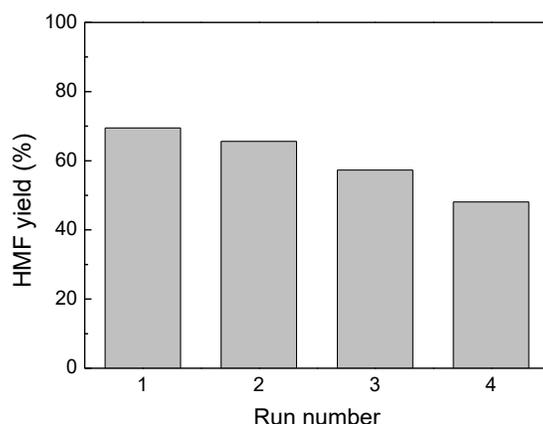

Fig. 6. Conversion of cellulose into HMF from inconsecutive runs with the ZnCl$_2$ aqueous solution; reaction conditions were cellulose (40 g·L^{-1}), n-butanol (10 mL), NaCl (0.65 g), HCl (0.2 mol·L^{-1}), 150 °C, and 40 min

Kinetic Study of Cellulose to HMF

A kinetic model of cellulose hydrolysis as a consecutive first-order reaction with the acidic catalysts is widely accepted: (i) hydrolysis of cellulose to glucose, (ii) isomerization of glucose to fructose (iii) dehydration of fructose to HMF (Binder and Raines 2009). In the present experiments, the main products detected in the biphasic system were glucose and HMF.

The fructose concentration for all experimental conditions was very low. The reason for this could be that the fructose was unstable at present condition and was converted to HMF very quickly when it was formed (Girisuta *et al.* 2006).

Based on a previous report, the decomposition of HMF into levulinic acid and other decomposed products under this moderate condition (150 °C) was considered negligible (Bahari *et al.* 2014). Therefore, the cellulose reaction process in this system was expressed as,

$$\text{cellulose} \xrightarrow{k_1} \text{glucose} \xrightarrow{k_2} \text{HMF}$$
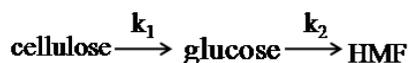
where k_1 and k_2 are the reaction rate constants for the hydrolysis and further degradation steps, respectively (Jiang *et al.* 2011).
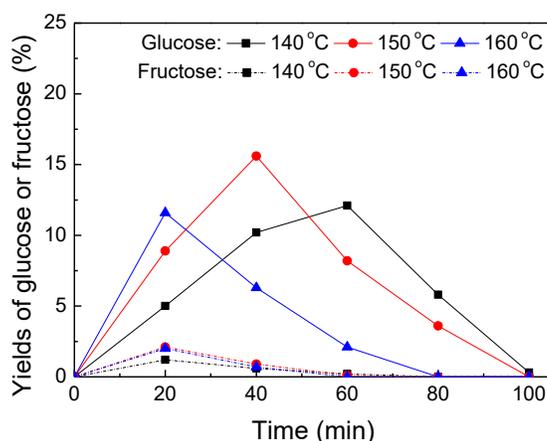
Fig. 7. Yields of glucose and fructose at 140 ^{o}C,150 ^{o}C and 160 ^{o}C with the reaction time; reaction conditions: cellulose (40 g·L^{-1}), n-butanol (10 mL), NaCl (0.65 g), HCl (0.2 mol·L^{-1})

Experimental rate data of the cellulose conversion and yield of HMF at 140 °C, 150 °C, and 160 °C employed in the formulation of the reaction model are depicted in Fig. 2, and the yields of glucose and fructose are displayed in Fig. 7. The reaction rate equations are as follows,

$$\frac{\mathrm{d}C_c}{\mathrm{d}t} = -k_1 C_c \tag{2}$$

$$\frac{\mathrm{d}C_g}{\mathrm{d}t} = k_1 C_c - k_2 C_g \tag{3}$$

$$\frac{\mathrm{d}C_H}{\mathrm{d}t} = k_2 C_g \tag{4}$$

where C_c, C_g, and C_H are the concentrations of cellulose, glucose, and HMF in g/L, respectively.

The reaction rate constants for cellulose conversion into HMF were obtained using a MATLAB fitting. A least-squares algorithm was adopted to minimize the error between the experimental and predicted data, and then subsequent evaluation of reaction rate constants was conducted through curve fitting. The activation energies of the degradation of cellulose and glucose were calculated using the Arrhenius equation,

$$k = Ae^{-E_a/RT} \tag{5}$$

The simulated reaction rate constants are listed in Table 2, and the Arrhenius plots for the cellulose hydrolysis and glucose degradation are shown in Fig. 8. The rate constant of the hydrolysis of cellulose increased with temperature increase as well as with the generation of HMF, which implied that a relatively high temperature might be necessary for practical application. Therefore, increased temperature would be conducive to cellulose conversion.

The activation energies of 126.4 kJ·mol^{-1} and 102.6 kJ·mol^{-1} were calculated for both the hydrolysis and the degradation steps, respectively. The estimated kinetic data for cellulose conversion to HMF in this biphasic reaction system provides a reasonable estimation that is in fair agreement with those reported in previous literature (Jiang *et al.* 2011; Atanda *et al.* 2016).

Table 2. Reaction Rate Constants for Cellulose and Glucose Conversion to HMF at Different Temperatures

Rate Constant (min^{-1})	Temperature (K)		
	413	423	433
k_1	1.39×10^{-2}	5.35×10^{-2}	7.78×10^{-2}
k_2	4.81×10^{-3}	9.87×10^{-3}	1.91×10^{-2}
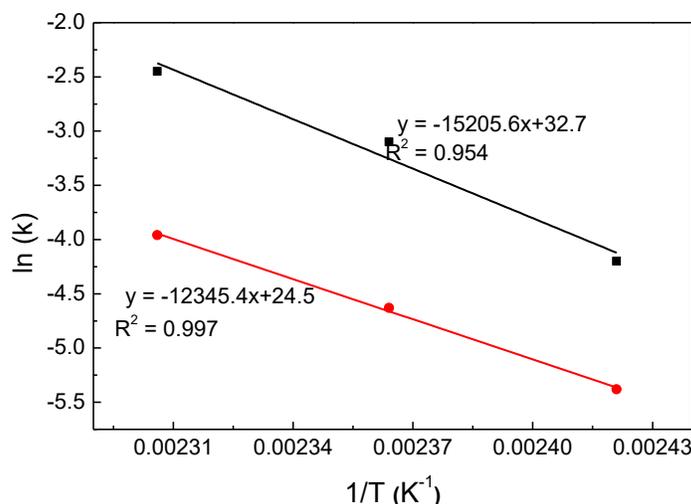
Fig. 8. Arrhenius plot of cellulose conversion to HMF: (■) cellulose hydrolysis to glucose, (●) glucose dehydration to HMF.

CONCLUSIONS

Cellulose was easily converted to 5-hydroxymethylfurfural in the system with n-butanol as the extraction solvent and 71.6 wt.% $ZnCl_2$ as the aqueous phase. A 69.5% yield of HMF was obtained under the conditions of 150 °C for 60 min and 0.2 mol·L^{-1} of HCl concentration as the catalyst. No further conversion effects were found for the four co-catalysts used in this system. A simple kinetic model was used to estimate the kinetic parameters for the tandem hydrolysis–dehydration reaction. The activation energy of cellulose hydrolysis process was 126.4 kJ·mol^{-1}, and the energy required for the product formation was 102.6 kJ·mol^{-1}.

ACKNOWLEDGEMENTS

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