I. INTRODUCTION

Conversion of biomass to chemicals or fuels has attracted much attention recently for biomass are potential regenerated natural resources [1]. It is well known that cellulose, hemicellulose and lignin are the three major components of lignocelluloses (one kind of biomass), and their conversion to chemicals or fuels is the basic question to the full application of lignocelluloses. Cellulose is a fascinating biopolymer and the main reinforcing constituent in plant cell walls, and it is a natural linear polysaccharide in which D-glucopyranose rings are connected to the other with a natural linear polysaccharide in which D-glucopyranose glycosidic links [2]. Several more value-added chemicals are the target products for the conversion of cellulose, such as ethanol, ethylene glycol, levulinic acid, sorbitol, furan, isosorbide, and 5-hydroxymethylfurfural (HMF) etc. Among them, HMF has been recognised as a versatile biomass-derived platform compound for the production of fine chemicals, bio-fuels, and polymers currently derived from petroleum [3]. HMF is also a feedstock for the synthesis of γ-valerolactone (GVL), a potential fuel instead of gasoline in near future. Generally, three steps are required for the conversion of cellulose to HMF: (i) depolymerization of cellulose to glucose, (ii) isomerisation of glucose to fructose, (iii) dehydration of fructose to HMF. It is easy to prepare HMF from fructose via dehydration in the presence of liquid or solid acids catalyst, while it is difficult to obtain HMF directly from glucose since the isomerisation of glucose to fructose is not easy for the requirement of base environment [4]. Interestingly, the success conversion of glucose to HMF has been reported recently using ionic liquid as solvent in the presence of CrCl₃ or heteropolyacids catalyst [5]. Those studies revealed that it is possible to prepare HMF directly from cellulose. However, in all the studies ionic liquid was used as the reaction medium. It is well known that ionic liquids are good solvent for cellulose and cellulose is easily depolymerised in ionic liquids in the presence of acid catalyst [6]. Although ionic liquids has been recognized as green solvent, it is still difficult to have a wide application for its relative higher cost [7]. So it is still a challenge to develop new kinds of medium to convert cellulose to HMF efficiently.

The depolymerization of cellulose is one of the key steps in the conversion, and hydrolysis is the most general method. In general, the hydrolysis of cellulose was carried out in the presence of liquid or solid acid catalysts, especially at dissolved state. However, the solvents for cellulose are numbered, and it limits the conversion. Among them, molten ZnCl₂ can dissolve cellulose in molecular level, and it is also reported that cellulose may be quantitatively hydrolyzed to glucose by pre-treatment of cellulose with ZnCl₂ and thereafter hydrolyzing the cellulose with acid [8].

In essence, the key step in conversion of glucose or fructose to HMF is dehydration, and the presence of water should prevent the formation of HMF. Solvents with high boiling point and high solubility for HMF should favor the conversion, and it is one of the reasons why ionic liquids are selected as the suitable solvents. In addition, DMSO may be another candidate solvent for the conversion, and the mixture of acetone/DMSO (70%/30%, mass ration) has been applied to prepare HMF from cassava waste recently [9].
It may be possible to prepare HMF by combining the hydrolysis of cellulose and dehydration of glucose together and result in a simple conversion route. Here, we try to combine the depolymerization of cellulose in acidic ZnCl₂ and consecutive conversion of the as-formed glucose in situ by adding of DMSO to prepare HMF (Scheme 1). The effects of various catalysts, reaction and temperature on the yield of HMF have been studied. The whole process is a one-pot two-steps consecutive reaction at atmosphere pressure.

II. EXPERIMENTS

A. Materials

Analytical grade ZnCl₂·2H₂O, 2,2’-bicinchoninic acid, CrCl₃, MnCl₂, FeCl₃, CoCl₂, NiCl₂, CuCl₂, NaVO₃, ZrOCl₂, CdCl₂, TeCl₄, SnCl₄, aqueous solution of hydrochloric acid, DMSO, glucose, cellobiose, and HMF were purchased from Aladdin Chemical Reagents Company (Shanghai, China), and were used directly without further purification. Microcrystalline cellulose (MCC) with α-cellulose content of more than 99% was provided by Shanghai Chemical Fiber Co. Ltd. (Shanghai, China) with DP of 216. Ultra-pure water (18 MΩ) was produced by a Millipore system (Millipore Q, USA).

B. Fast depolymerization of cellulose

At first, 0.1 g cellulose was mixed homogeneously with 2.0 g ZnCl₂·2H₂O in a 50 mL flask, and it was heated up to 95 °C to the molten state. Next 0.6 mL of 1 mol/L HCl aqueous solution was added droplet in 45 s, and then the mixture was stirred at 95 °C for different times to degrade the cellulose. Some of the sample was separated from the mixture at different times and was cooled down to room temperature for analysis.

The above obtained mixture after cellulose depolymerisation was used directly as the feedstock for the preparation of HMF. In brief, 4 mL DMSO and 1.24 mmol catalyst were added directly into the reaction system at room temperature, and it was heated up to the reaction temperature under reflux condensation for various times. At the end the system was cooled down and diluted by ultrapure water for HPLC measurement.

C. Characteristics

The analyses of glucose and cellobiose were performed by ion chromatography (Dionex ICS-3000, USA) after appropriate dilution with ultra-pure water. A CarboPac PA1 (2 mm×250 mm) analytical column with electrochemical diction was employed. Solution of sodium hydroxide (100 mmol/L) was used as the eluent with a volumetric flow rate of 0.325 mL/min at 30 °C. The amount of each compound in the liquid products was determined using calibration curves obtained by analyzing standard solutions with known concentrations. For HMF analysis, a Shimazu HPLC (LC-20AD, Japan) was used equipped with a SPD-20A UV-VIS Detector. The samples were separated using a reversed-phase C18 column at 283 nm. The column temperature was maintained at 30 °C, and the optimized mobile phase consisted of methanol and water with the volume ratio 15:85. The flow rate was set at 1.0 mL/min. ¹H NMR spectra were measured on a Bruker AC 400 spectrometer. Deuterated chloroform (CDCl₃) containing 0.03% tetramethylsilane (TMS) was used as the solvent.

III. RESULTS AND DISCUSSION

A. Fast depolymerization of cellulose

The dissolving of cellulose in molten concentrated ZnCl₂ aqueous solution is quick, and the depolymerization of cellulose to glucose can be achieved in tens of minutes depending on the concentrations of ZnCl₂ and acid. Here, we found that the depolymerisation of cellulose could be more accelerated when 79% of ZnCl₂ was used in the presence of hydrochloric acid at 95 °C, and the depolymerization could be finished in minutes. The degree of polymerization (DP) of cellulose was measured by the 2,2’-bicinchoninate (BCA) method by measuring the reducing end-groups [10]. As shown in Fig.1, the DP of cellulose decrease quickly at the early one minute from 216 to 2, and the average DP is only 1.27
after 5 min treatment, indicates a quick and efficient depolymerization of cellulose, and the main product are glucose and cellobiose.

It is well known that cellulose can be dissolved into ionic liquids, and can be depolymerized in the presence of acid. However, no so fast depolymerization rate was reported, indicating Zn$^{2+}$ ions would promote the depolymerization. Cao et al. suggested that ZnCl$_2$ worked as both the solvent for cellulose and co-catalyst for cellulose depolymerization in the presence of cellulose [11]. What is the exact role of Zn$^{2+}$ ions here for the fast depolymerization of cellulose? Are there special interactions between the oxygen atoms in repeated units of cellulose to Zn$^{2+}$ ions? Theoretical simulation may provide much more information. Here, the ratio of ZnCl$_2$ to water make it possible to form coordinated complex of Zn(H$_2$O)$_3$Cl$_2$, which still reserves a site to coordinate with one oxygen atom in cellulose, as shown in Fig.2(a). However, which oxygen atoms should be chosen to form coordination with zinc ion? Figure 2(b) shows the structure of cellobiose and the repeated unit of cellulose. Clearly, there are six kinds of oxygens that may interact with zinc ion. Here, density functional theory (DFT) with general gradient-corrected approximations (GGA) such as BLYP was used to predict the possible conformation of the coordinated complex of Zn(H$_2$O)$_3$Cl$_2$ with cellobiose [12]. Table I lists the coordinated energies ($E_{\text{C-OC}}$) of Zn(H$_2$O)$_3$Cl$_2$ with oxygen atoms at different positions, while $E_{\text{total}}$, $E_{\text{left}}$, and $E_{\text{right}}$ stand for the total energy of system and the energy necessary to break the glycosidic bond at left or right positions, respectively. The relationship is: $E_{\text{C-OC}} = E_{\text{left}} + E_{\text{right}} - E_{\text{total}}$. The results reveal that the stability of the glycosidic bond should become weaker efficiently in the presence of Zn(H$_2$O)$_3$Cl$_2$, indicating the stronger interaction of oxygen in cellulose unit with Zn(H$_2$O)$_3$Cl$_2$.

The adsorption of Zn(H$_2$O)$_3$Cl$_2$ molecules on the surface of cellulose was also studied by means of Monte Carlo simulation. The initial structure of crystalline cellulose I$_a$ was taken from X-ray and neutron diffraction experiments [13]. Figure 3 (a) and (b) show the side-view of a four-layer slab of I$_a$ surface of cellulose [14]. The interaction of Zn(H$_2$O)$_3$Cl$_2$ molecules and cellulose was simulated using the Compass force-field, and an Ewald summation was used to calculate the electrostatic interactions. As shown in Fig.3 (c) and (d), the optimal position of zinc atom locates at the position above the cycle of carbon 3, 4, 1', and 5' of cellulose indicated by an arrow, and the distances of Zn atom to the nearby three oxygen atoms of cellulose are 3.885 Å (glycosidic bond), 3.947 Å (pyranoid ring), and 4.382 Å (hydroxyl group), respectively. The result shows clearly that the existence of Zn$^{2+}$ ion should decrease the stability of glycosidic bond, which is the beginning of the depolymerization of the main chain of cellulose. Further studies shown in Fig.3(e) reveal that the distribution of

---

**Figure 1:** DP of cellulose after depolymerization for different time in 79% ZnCl$_2$ under catalysis by hydrochloric acid at 95 °C.

**Figure 2:** Interaction of Zn$^{2+}$ ions with cellulose. (a) Sketch map of Zn(H$_2$O)$_3$Cl$_2$ and cellobiose. (b) Numbered possible oxygen atoms of cellobiose take place interaction with Zn$^{2+}$ ion.

**Table I:** Coordinated energies $E$ of Zn(H$_2$O)$_3$Cl$_2$ with oxygen atoms at different position indicated as in Fig.2(b) (kcal/mol).

<table>
<thead>
<tr>
<th>O atom</th>
<th>$E_{\text{total}}$</th>
<th>$E_{\text{left}}$</th>
<th>$E_{\text{right}}$</th>
<th>$E_{\text{C-OC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>−4482.3</td>
<td>−2133.7</td>
<td>−2252.1</td>
<td>96.5</td>
</tr>
<tr>
<td>1</td>
<td>−5060.5</td>
<td>−2833.9</td>
<td>−2139.2</td>
<td>87.3</td>
</tr>
<tr>
<td>2</td>
<td>−5050.4</td>
<td>−2841.0</td>
<td>−2132.2</td>
<td>77.2</td>
</tr>
<tr>
<td>3</td>
<td>−5066.3</td>
<td>−2946.2</td>
<td>−2035.4</td>
<td>84.7</td>
</tr>
<tr>
<td>4</td>
<td>−5074.1</td>
<td>−2844.9</td>
<td>−2139.9</td>
<td>89.3</td>
</tr>
<tr>
<td>5</td>
<td>−5064.2</td>
<td>−2846.9</td>
<td>−2138.9</td>
<td>78.5</td>
</tr>
<tr>
<td>6</td>
<td>−5066.5</td>
<td>−2850.8</td>
<td>−2137.7</td>
<td>78.0</td>
</tr>
</tbody>
</table>

* Without Zn(H$_2$O)$_3$Cl$_2*
Zn$^{2+}$ ions is not random, and most of them locate at positions near the lines of glycosidic bond with cellobiose as the repeated unit. It reveals that cellulose may be quickly depolymerized into cellobiose at the beginning in the presence of ZnCl$_2$ following a decomposition of cellobiose to glucose.

After depolymerization, cellulose is degraded into small molecules and most of them are water soluble, and the amount of them can be determined by the total organic carbon (TOC) measurement. As shown in Fig. 4, the TOC value increases quickly at the very early stage of the depolymerisation, and arrive at 22 mg/L at 45 s and 44 mg/L at about 100 s, indicating a complete degradation of cellulose into water soluble molecules. These theoretical studies reveal that Zn$^{2+}$ ions interact with the oxygen atom of glucoside, and the presence of hydrochloric acid makes the breaking of the glucoside of stretched cellulose chains by hydrolysis.

The detail content of the depolymerised products was measured by means of ion chromatograms. Figure 5 shows the main products and their relationship with reaction time at different reactive temperature. Clearly, the major product is glucose while trace of cellobiose as by-product. The maximum yield of glucose arrived at 77% when the depolymerisation was carried out at 95 °C for 120 s, indicating an efficient conversion of cellulose to glucose in a very short time. In addition, the depolymerisation has a strong relationship with reaction temperature, and it was depolymerized more slowly at 85 °C than that at 95 °C. However, the yield also arrived at about 74% after reaction for 180 s. In addition, the yield of cellobiose is below 10% at the beginning of depolymerisation and near zero at 180 s, indicating the conversion of cellulose to cellobiose may be the first step followed by the conversion of cellobiose to glucose continuously for glucose formation.

**FIG. 3** Distribution of Zn(H$_2$O)$_3$Cl$_2$ molecules on the top L$_a$ (100) surface of cellulose. (a) Side-view and (b) top-view of a four-layer slab of L$_a$ surface of cellulose, (c) side-view and (d) top-view of single Zn$^{2+}$ ion (indicated by arrow) on the L$_a$ (100) surface of cellulose, (e) distribution of Zn$^{2+}$ ions on the surface of cellulose.

**FIG. 4** TOC of the aqueous solution of cellulose after it was depolymerized for different time in 79% ZnCl$_2$ under the catalysis by hydrochloric acid at 95 °C.

**FIG. 5** Yield of glucose and cellobiose formed by the hydrolysis of cellulose in molten ZnCl$_2$ in the presence of hydrochloric acid at 85 or 95 °C.
After the depolymerization of cellulose, glucose was obtained, and was used directly as the feedstock for the HMF conversion. The reaction was carried out in DMSO in the presence/absence of catalysts. It has been reported that DMSO itself could also work as catalyst to convert D-fructose to HMF under heating at 150 °C [15]. Recently, Shotipruk et al. reported that glucose can also be dehydrated in the mixture of DMSO/acetone/water to form HMF and fructose in the absence of any other catalysts [9]. It had been reported that Cr$^{3+}$ ion is an efficient catalyst to dehydrate glucose or fructose to HMF in ionic liquid [5], and here CrCl$_3$ was used as catalyst for the conversion of the as-formed glucose in DMSO. The effect of reaction temperature on the yield of HMF has also been studied by carrying out the conversions at 110, 120, and 130 °C, respectively. As shown in Fig.6, the higher reaction temperatures can efficiently shorten the reaction time. At 130 °C, the yield of HMF increased with reaction time and the maximum yield was 42.0% at 90 min, while it arrived at 42.6% at 240 min for 120 °C. However, for reaction at 110 °C the conversion was slow and the yield arrived at 43.2% just at 480 min. It reveals that reaction temperature is a key factor and higher reaction temperature is helpful for the quick conversion. HMF can be extracted by using MIBK as organic phase, and then the catalyst can be reused.

For comparison, pure glucose, the mixture of glucose and ZnCl$_2$, and the as-formed glucose obtained from fast degradation of cellulose in ZnCl$_2$/HCl were used as feedstock for the dehydration in DMSO at 125 °C. As shown in Fig.6, the major product is HMF. For pure glucose, the yield is 28.8%, indicating the existing of Zn$^{2+}$ ions in the mixture may be helpful for the HMF conversion. The reason and detail should be studied in the near future. The above results reveal that the as-formed products from cellulose fast degradation can be converted into HMF in DMSO in the absence of any other catalysts. As shown in Fig.7, the maximum yield of HMF arrived at 53%, indicating an efficient of Cr$^{3+}$ ion in the system.

Different catalysts, such as MnCl$_2$, FeCl$_3$, CoCl$_2$, NiCl$_2$, CuCl$_2$, NaVO$_3$, ZrOCl$_2$, CdCl$_2$, TeCl$_3$, and SnCl$_4$, have also been used to convert the as-formed glucose to HMF in DMSO. As shown in Fig.8, most of them showed catalytic activation for the HMF conversion. However, the best catalyst is still CrCl$_3$ with a HMF yield of 53%, while it is 42% for MnCl$_2$ and 37% for TeCl$_3$. The yields of HMF are above 30% for Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$, and V$^{5+}$ catalysts. For Cu$^{2+}$ and Zr$^{4+}$, the yields of HMF are low and about 10%.
IV. CONCLUSION

An efficient method to prepare HMF from cellulose has been established, which combined the fast depolymerization of cellulose to glucose and the conversion of the as-formed glucose to HMF. The fast depolymerization of cellulose was carried out in molten ZnCl$_2$ in the presence of hydrochloric acid at 85 or 95 °C, and the yield of glucose was 77% in 120 s. Then the as-formed glucose was directly used as feedstock without purification by adding some DMSO and catalyst into the system, and the reaction was carried out continually at 110–130 °C for different time, and different catalysts were also studied. The results reveal that CrCl$_3$ is the optimal catalyst and the maximum yield of HMF is 53%. The method is simple and the conversion of cellulose to HMF is efficient. It provides a new route to convert biomass-based cellulose to value-added chemicals or fuels in near future.

V. ACKNOWLEDGEMENTS

This work is supported by the National High Technology Research and Development Program (No.2012AA051803) and the National Basic Research Program of China (No.2011CB921403).

[14] (a) V. Černý, J. Optimization Theory Appl. 45, 41 (1985);