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Highly efficient conversion of microcrystalline cellulose to 5-hydroxymethyl furfural in a homogeneous reaction system

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Abstract

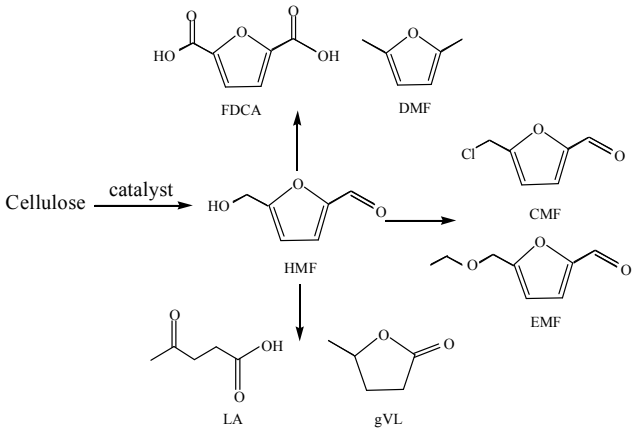
The development of novel methods to obtain biofuels and chemicals from biomass has been an immediate issue in both academic and industrial communities. The present work introduces a new route to synthesize 5-hydroxymethyl furfural (5-HMF) in a one-vessel system through a tandem pathway involving decrystallization, depolymerization and conversion of microcrystalline cellulose (MCC) in a molten hydrates solution. 71.62 wt% $ZnCl_2$ aqueous solution was employed as the reaction media and methylisobutylketone (MIBK) as the extracting solvent in the reaction system. A yield of 80.6 mol% of 5-HMF was obtained at 150 °C with the HCl concentration of 0.2 mol/L in the solution for 40 min. Aqueous phase can be reused without significant loss of catalytic activity.

1. Introduction

In view of the irreversible consumption of fossil fuels and the serious concerns with global climate, lignocellulosic biomass, as the renewable and sustainable resources, has received significant attentions.[1] So far, efforts have been devoted to chemical and biological conversion of lignocellulosic biomass into biofuels and chemicals.[2]

Among a variety of biomass-derived chemicals, 5-hydroxymethylfurfural (5-HMF) has been regarded as an important platform chemical which can be the substitute for petroleum-based building blocks in making polymers or other materials and biofuels.[3]

As presented in Scheme 1, the subsequent transformation of 5-HMF into a multitude of high-value added bio-based chemicals, such as 2, 5-dimethyl furan (DMF),[4] 2, 5-furan dicarboxylic acid (FDCA),[5] 5-chloromethylfurfural (CMF),[6] 5-ethoxymethylfurfural (EMF),[7] levulinic acid (LA)[8] and γ-valerolactone (gVL)[9] has been explored using 5-HMF as a starting substrate.



Scheme 1. 5-HMF production and its use for making many value added chemicals.

There are emerging interests in producing 5-HMF from biomass-based sugars and polysaccharides at present. Although high yield of 5-HMF from pure fructose[10] and glucose[11] can be obtained, large scale and sustainable production of 5-HMF requires cellulosic biomass as the feedstock. But it is still challenging to efficiently convert cellulose into 5-HMF because of the firm crystal structure. Dissolution and depolymerization of cellulose could be the good choice to solve the problem. It is well known that ionic liquids, DMF, and dimethyl sulfoxide (DMSO) are promising solvents in dissolving cellulose and have been used as a reaction media in the production of 5-HMF.[13] Despite its effectiveness toward 5-HMF production, ionic liquids is too expensive to be used in commercial scale.[14] DMSO and DMF also have to face the similar challenges for the costliness in the separation of 5-HMF from the solvent due to their high boiling point. Therefore, further studies are still necessary to develop new green systems for the conversion of natural cellulose into 5-HMF.

Zinc chloride hydrate has been considered a low-toxic and inexpensive solvent compared with ionic liquids in the dissolution of cellulose. Lv et al.[15] reported 68 wt% $ZnCl_2$ aqueous solution could dissolve cotton cellulose to prepare homogenous solution. Lu and Shen[16] found that $ZnCl_2 \cdot 4H_2O$ (65.43 wt%) could be used as swelling agent for

bacteria cellulose while $ZnCl_2 \cdot 3H_2O$ (71.62 wt% $ZnCl_2$) can efficiently dissolve bacteria cellulose with a maximal concentration of 5.5 wt% in the solution. This inexpensive solvent not only exhibits good solubility for celluloses, but also can promote the conversion of glucose, fructose, maltose, sucrose, cellulose and starch.[12] Recently, attentions have been paid on zinc chloride hydrate as a reaction media in the conversion of lignocellulosic materials. Wang et al.[17] found that 21.9 % of 5-HMF yield could be obtained from $GlcNH_2$ in 67 wt% $ZnCl_2$ aqueous solution at 120 ^oC without co-catalyst. Deng et al.[12] produced 40 % of 5-HMF from carbohydrate using a two-phase system in concentrated aqueous $ZnCl_2$ solution.

In this work, an efficient conversion process for the production of 5-HMF from cellulose in 71.62wt% $ZnCl_2$ aqueous solution with a low-boiling point solvent methylisobutyl-ketone (MIBK) as organic phase was investigated, the effect of HCl concentration, reaction time, temperature and the reusing of aqueous phase on conversion was discussed.

2. Experimental section

2.1 Materials

Analytical grade $ZnCl_2$, MIBK, MCC (DP=162), cotton fiber (DP=1024), HCl (36.5 %), glucose, fructose and 5-HMF were purchased from Beijing ZKKA Biotechnology Co., Ltd. (Beijing, China) and used without further purification. Deionized water was used for all reactions.

2.2 The dissolution of cellulose

The dissolving process was observed under a polarizing microscope (Leica DMLP; Leica Microsystems, Wetzlar, Germany) equipped with a hot plate at 70 ^oC. Cotton fiber was used in the observation. The dissolution experiment of MCC was conducted by charging 0.2 g of MCC into 5 mL of 71.62 wt% $ZnCl_2$ aqueous solution in a 20 mL glass reaction bottle at 90 ^oC.

2.3 Conversion of MCC into 5-HMF

Reactions in homogeneous reaction system were conducted in a 20 mL autoclave lined with teflon and heated in a temperature-controlled oil bath equipped with an

electronically controlled magnetic stirrer (Zhengzhou Great Wall Scientific Industry and Trade Co., LTD). MCC solution (0.2 g) in 71.62 wt% $ZnCl_2$ (9.8 g, 5mL) was prepared at 90 °C and then hydrochloric acid was charged into autoclave to the preset concentrations. The mixture was saturated with 0.5 g of NaCl. 10 mL of MIBK was used as an extraction solvent. The mixture was heated to the preset temperature and stirred at 1200 rpm. After reactions, the autoclave was immediately cooled to room temperature in the water bath.

2.3 Analytical methods

The reaction sample was diluted with the eluent used for HPLC, then the solid products, if present, were separated by centrifugation and filtration. Sugars in aqueous layers were analyzed with an Agilent Technologies HPLC system equipped with an Aminex HPX-87H column (Biorad) and a refractive index (RI) detector, and 0.005 M H_2SO_4 as mobile phase with flowing rate of 0.5 mL/min. Products in organic layers were analyzed by HPLC equipped with a QuikSep UV-100D detector and an Inertsil ODS-C18 column at 298 K, using methanol-water (40:60) as eluents. The rate of conversion, yield, and selectivity of the products were calculated as follows:

$$\text{Conversion of MCC}\ (\%) = \frac{m_{cellulose,t=0} - m_{cellulose,t=t}}{m_{cellulose,t=0}} \times 100\%$$

$$\text{Yield of 5-HMF (mol \%)} = \frac{m_{HMF}/126}{m_{cellulose,t=0}/162} \times 100\%;$$

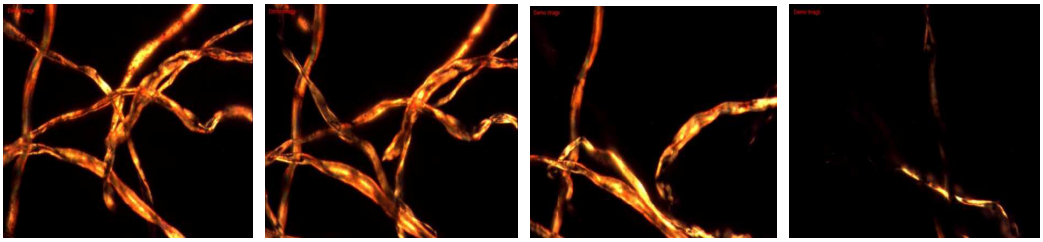
$$\text{Selectivity of 5-HMF (mol \%)} = \frac{m_{HMF}/126}{(m_{cellulose,t=0} - m_{cellulose,t=t})/162} \times 100\%;$$

3. Results and Discussion

3.1 The solubility of cellulose in $ZnCl_2$ aqueous.

To make the dissolving process easy to be observed, cotton fiber was employed. The pictures for the dissolving process in 71.62 wt% $ZnCl_2$ was recorded with a polarization microscope at 70 ^oC. As shown in Figure 1, we can clearly see the whole cellulose fiber before the dissolution strating because the crystalized cellulose fiber can reflect the polarized light beam. After a while, for example, 35 s and 75 s, fractures

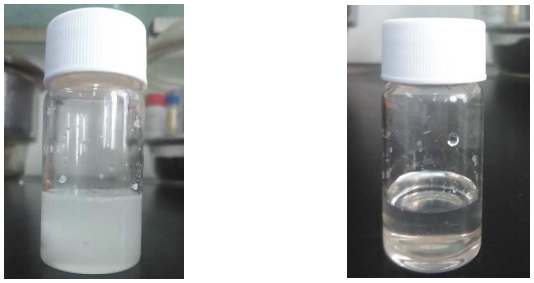
could be found owing to its decrystallization. Gradually, the light fade away, which signified the complete dissolving of crystalized cellulose fiber. This process finished in couple of minutes for cotton fiber. Therefore, we have the reason to believe that MCC will also behave the same way for the dissolution.



(a) 0 s (b) 35 s (c) 75 s (d) 100 s

Figure 1. The dissolution of cotton fiber in 71.62 wt% $ZnCl_2$ aqueous solution.

The dissolution process of MCC in 71.62 wt% $ZnCl_2$ was observed at 90 ^oC and shown in Figure 2. The MCC suspension at 25 ^oC (Figure 2 a) was turned into a transparent and viscous liquid solution in the solvent system (Figure 2 b). This is correlated well with the results in the literature.[18] This indicates that 71.62 wt% $ZnCl_2$ is an effective solvent for cellulose, which will make the reaction system homogeneous.

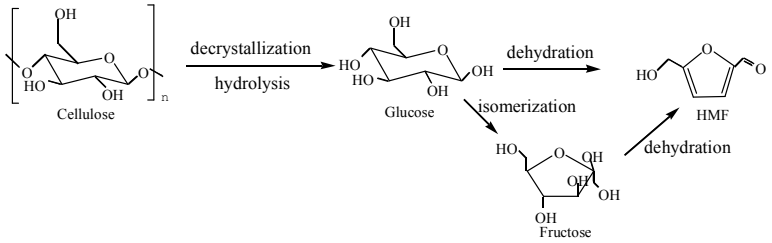


a. MCC in 71.62 wt% $ZnCl_2$ at 25 ^oC b. MCC in 71.62 wt% $ZnCl_2$ at 90 ^oC in 5 minutes

Figure 2. The dissolution of MCC in 71.62 wt% $ZnCl_2$ aqueous solution

3.2 Conversion of MCC into 5-HMF

It is generally accepted that three steps are required for the conversion of cellulose to 5-HMF: (1) decrystallization and hydrolysis of cellulose to glucose; (2) isomerization of glucose to fructose; (3) dehydration of fructose to 5-HMF (Scheme 2).[19] 5-HMF was produced in a single step starting from MCC solution in $ZnCl_2$ aqueous solution. The effect of reaction conditions on conversion was explored by varying concentration of $ZnCl_2$, HCl concentration, reaction time and temperature.



Scheme 2. Schematic representation of cellulose conversion into 5-HMF with acid catalysts.

As shown in Figure 3，with the increase of the concentration of $ZnCl_2$ solution from 0 wt% to 71.62 wt%, 5-HMF yield increased. We found that, without $ZnCl_2$ in the system，only 31.3 mol% of 5-HMF was yielded and trace amount of fructose was found. This suggested the synthesis of 5-HMF mainly followed the mechanism directly from glucose, which was suggested in the report.[20] $ZnCl_2$, as a Lewis acid catalyst, can catalyze the isomerization of aldoses (glucose) to ketose (fructose), which made acidic dehydration catalyzed reactions more efficient for the production of 5-HMF.[21] For example, the yield of 5-HMF increased from 31.3 mol% to 43.1 mol% with 0 wt% and 10 wt% $ZnCl_2$ respectively at 150 ^oC in 60 min in this biphasic reaction system. 5-HMF yield of 80.6 mol% could be obtained at 150 °C in just 40 min with 71.62 wt% $ZnCl_2$ in the reaction system by using MIBK as extracting solvent, which was higher than that reported 53 % in ionic liquids.[22] This suggests that the production of HMF mainly follows the mechanism of acidic dehydration of fructose. It can be seen in Figure 3 D that the production of fructose in the system with high concentration is much more than that with low concentration, which offered the support for the expectation. In this homogenous reaction system with high concentrated $ZnCl_2$ solutions, the formation of the coordination between Zn^{2+} and hydroxyl groups in cellulose chains promoted the dissolution of MCC, isomerization of hydrolyzed glucose into fructose, and conversion to 5-HMF through acidic catalyzed dehydration.

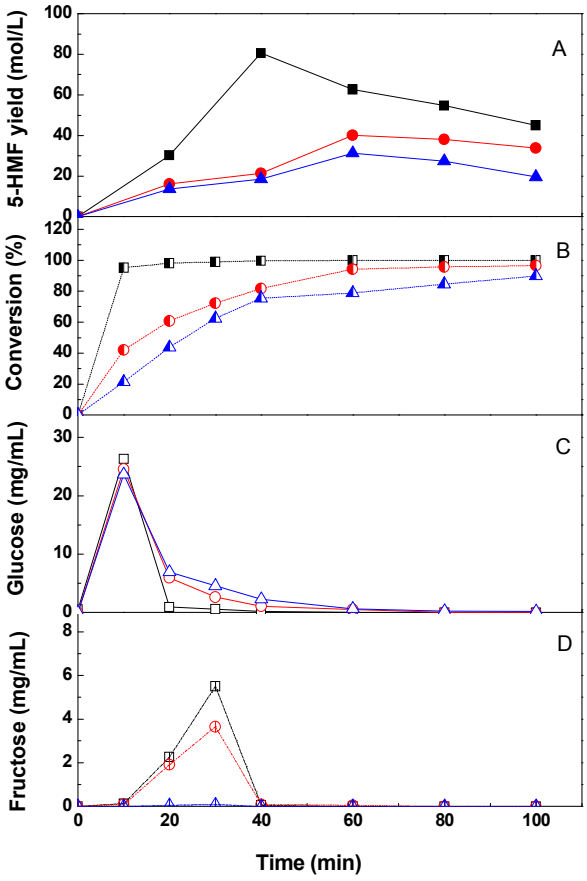


Figure 3. Conversion of MCC into 5-HMF in $ZnCl_2$ solution. Reaction conditions: MCC, 0.2 g; $ZnCl_2$, 5 mL (71.62 wt%, 9.8 g; 10 wt%, 5.49 g; 0 wt%, 5 g); MIBK, 10 mL; NaCl, 0.5 g; HCl concentration, 0.2 mol/L; 150 °C. $ZnCl_2$ concentration: A:■ 71.62 wt%, 10 wt%, 0 wt%; B: ◧ 71.62 wt%, 10 wt%, 0 wt%; C: □ 71.62 wt%, 10 wt%, 0 wt%; D: ⊞ 71.62 wt%, 10 wt%, 0 wt%.

In this system, the Brønsted acid offered hydrogen ions which catalyzed both the hydrolysis of MCC into glucose monomer and the conversion to 5-HMF.[20] The effect of the HCl concentration on the conversion of 5-HMF was investigated and the results were shown in Table 1. It indicated that the concentration of hydrochloric acid played an important role in the conversion. Without HCl in the conversion system, only 28.5 mol% of 5-HMF yield was obtained after 40 min at 150 °C, while it increased to 80.6 mol% with 0.2 mol/L of HCl concentration. However, excess use of HCl would deteriorate the conversion. For example, the 5-HMF yield of 28.6 mol% was obtained under 1 mol/L of HCl concentration in the aqueous phase even if the MCC was completely conversed (100%). This suggested that high concentration of hydrogen ions will promote the further decomposition of the 5-HMF, which will increase the formation

of humins and the production of levulinic and formic acids.[23]

Table 1. Conversion of MCC to 5-HMF in biphasic system with various hydrochloric acid concentrations.

Entry	HCl loading (mol/L)	Yield (mol%)	Conversion (%)	Selectivity (mol%)
1	0	28.5	71.7	39.7
2	0.03	35.6	78.9	45.1
3	0.1	64.5	83.9	76.8
4	0.2	80.6	99.6	81.0
5	0.3	55.4	100	55.4
6	1	28.6	100	28.6

Reaction conditions: MCC, 0.2 g; $ZnCl_2$, 71.62 wt%, 9.8 g (5 mL); MIBK, 10 mL; NaCl, 0.5 g; 150 ℃; 40 min.

The effect of reaction temperature on 5-HMF selectivity and MCC conversion was investigated in this homogenous reaction system (Figure 4). 5-HMF selectivity of 54 mol% was observed at 140 °C after 40 min. 5-HMF selectivity of 81 mol% was obtained when the reaction mixture was heated to 150 °C. Over elevated temperature would result in the rehydration of 5-HMF to form levulinic acid and formic acid and accelerate the production of humins.[23]

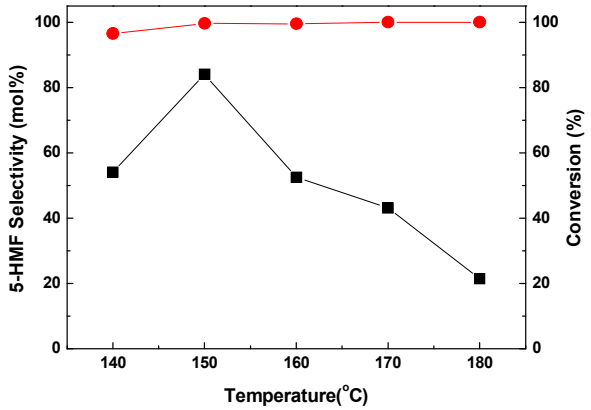


Figure 4. Synthesis of 5-HMF from MCC at different reaction temperature. Reaction conditions: MCC, 0.2 g; $ZnCl_2$, 71.62 wt%, 9.8 g (5 mL); MIBK, 10 mL; NaCl, 0.5 g; HCl concentration, 0.2 mol/L; 40 min. –■–5-HMF selectivity; Conversion.

The effect of reaction time on the conversion was investigated under the optimized reaction temperature. As shown in Figure 3, the yield of 5-HMF increased remarkably from 30.3 mol% to 80.6 mol% upon increasing the reaction time from 20 min to 40 min.

Afterward, 5-HMF yield decreased gradually. This suggested that 5-HMF is an unstable product and subjected to the further conversion into other products. Based on the overall yield of conversion, the reaction time should be limited to about 40 min.

To elucidate the effect of recycling of $ZnCl_2$ aqueous solution on the conversion in this biphasic reaction system, four consecutive runs were carried out. First, the organic layer containing the produced 5-HMF was removed. Then the aqueous phase were centrifuged to separate humins before being reused. After that, 0.2 g of MCC was charged into the recycled aqueous phase and the dissolution of MCC was performed at 90 ^{o}C and 5 min on a hot plate. Finally the fresh MIBK (10 mL) was charged into the autoclave. The steps afterward followed the method and conditions previously described. The results were shown in Figure 5. It can be seen that the system with recycled aqueous phase performed very well in the conversion with almost the same conversion rate among the four runs. The system maintained a high selectivity for the conversion with only slight decrease from 81 mol% to 76.2 mol% (eg. 4.8 mol%), which is supposed to be caused by the coordination of some amount of zinc cation with unseparated products in the aqueous phase.

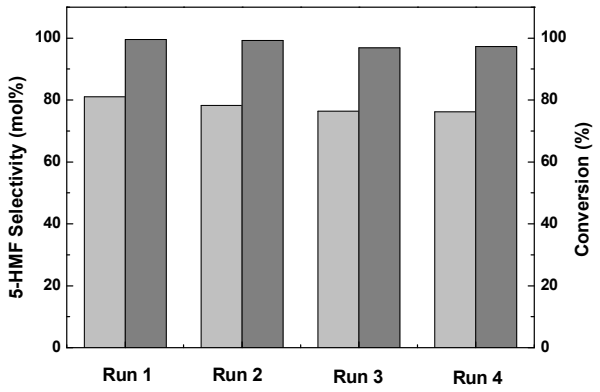


Figure 5. Conversion and selectivity for production of 5-HMF from MCC in consecutive runs using the same acidic aqueous solution in homogeneous reaction system. Reaction conditions: MCC, 0.2 g; $ZnCl_2$, 71.62 wt%, 9.8 g (5 mL); MIBK, 10 mL; NaCl, 0.5 g; HCl concentration, 0.2 mol/L; 40 min. 5-HMF selectivity; Conversion.

4. Conclusion

The synthesis of 5-HMF from MCC was performed in a reaction system with MIBK as the extraction solvent and 71.62 wt% $ZnCl_2$ as the aqueous phase. This system

showed a high conversion efficiency. The 5-HMF selectivity of 81 mol% from MCC was obtained at 150 ^{o}C for 40 min with concentration of 0.2 mol/L HCl in the aqueous phase. The aqueous phase also displayed a good reusability for the conversion. The results suggested that this method can be used as a facile and efficient system for the one step conversion of bio-based cellulose into 5-HMF.

Acknowledgements

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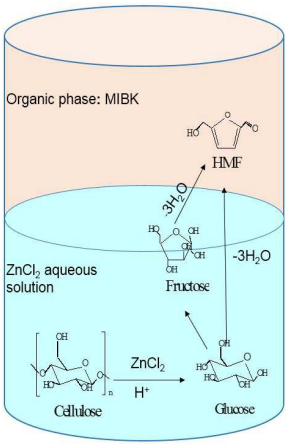

A homogenous reaction system with zinc chloride hydrate was explored for the synthesis of 5-HMF from MCC.