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One-pot synthesis of 5-hydroxymethylfurfural directly from cottonseed hull biomass using chromium (III) chloride in ionic liquid

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Abstract−We studied the direct synthesis of 5-hydroxymethylfurfural (5-HMF) from cottonseed hull biomass under acid condition in one-pot. The influence of HCl dosage, reaction temperature and time, $CrCl_3 \cdot 6H_2O$ amount, and cottonseed hull loading on the yield of 5-HMF was investigated. As a result, a 5-HMF yield up to 51% was obtained using 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) catalyzed with chromium (III) chloride at 130 °C for 2 h. The [Bmim]Cl/$CrCl_3 \cdot 6H_2O$/HCl system was found to have high activity and selectivity for the dehydration of cellulose into 5-hydroxymethylfurfural. This work provides a low cost, environment-friendly and energy-efficient process to directly convert raw biomass into bio-fuels and chemicals.

Keywords: Cottonseed Hull, 5-Hydroxymethylfurfural, Furfural, Chromium (III) Chloride, [BMIM]Cl

INTRODUCTION

The global energy crisis and environmental issues have been major concerns. Biomass, the only renewable carbon source in the world, has attracted increasing attention for its importance to environmental protection and the utilization of energy against the depletion of fossil fuel [1-3]. Some recent studies have demonstrated that biomass-derived carbohydrates such as fructose, glucose, sucrose, and cellulose can be used for the production of various carbon-derived compounds [4-6]. 5-Hydroxymethylfurfural (5-HMF), one of the platform chemicals from biomass, has received much attention as an interesting platform molecule in biomass conversion. It can be converted into a broad range of ne chemicals, polymeric materials and biofuels [7,8]. In recent years, the dehydration of sugars to 5-HMF has become a hot topic. Zhao et al. have reported a signicant HMF yield of nearly 70% from glucose by using chromium (II) chloride ($CrCl_2$) in 1-ethyl-3-methylimidazoliumchloride ([EMIM]Cl) at 100 °C for 3 hours [9]. Jadhav et al. discovered that zeolite could catalyze glucose into HMF with a yield of 45% in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), and that if the solvent was replaced with non-toxic tetrabutylammonium chloride (TBAC), the yield of HMF was more than 55% [10].

Cellulose is the oldest and the most abundant polysaccharide in nature; it is composed of D-glucose monomers linked by *β*-1,4-glycosidic bonds [11]. Thus it can be hydrolyzed to glucose which can be further translated into 5-HMF. Several studies have been devoted during recent years to producing 5-HMF from cellulose. Wang et al. studied the production of HMF from cellulose in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) using $CrCl_3$/LiCl as a catalyst and achieved a 5-HMF yield of 62% under microwave irradiation [12]. More recently, a high 5-HMF yield up to 51% was obtained from cellulose, which was catalyzed by $ZrCl_4$ in [BMIM]Cl under microwave at 400 watts for 3.5 min [13]. Most of the biomass contains luxuriant cellulose, such as agricultural residues and forest waste [14]. If raw biomass could be directly used for HMF production, it would be a promising approach to reducing the cost of 5-HMF production.

China is now the largest cotton producer and consumer in the

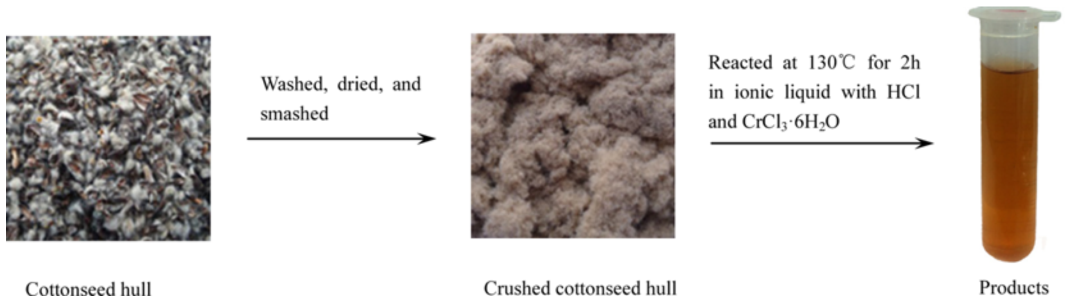

Fig. 1. Direct synthesis of 5-hydroxymethylfurfural from cottonseed hull biomass in one-pot.

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world. In 2012, China's cotton production was over 7.2 million tons. As one of the important by-products of cotton productions [15], cottonseed hull is currently used as a substrate for mushroom cultivation and roughage in animal feed [16-18]. In that cottonseed hull has a higher content of cellulose and lower price, it is a perfect raw biomass to produce 5-HMF under acid condition (Fig. 1). In particular, the use of the cottonseed hull in chemical syntheses can be conducive to the efficient utilization of biomass energy and sustainable development.

According to previous report, a low-toxicity catalyst, chromium (III) chloride ($CrCl_3 \cdot 6H_2O$), has been used in the conversion of glucose and cellulose into 5-HMF in ionic liquid and has achieved gratifying results [7,12,19]. We have developed an efficient method for the direct conversion of cottonseed hull to 5-HMF with $CrCl_3 \cdot 6H_2O$/HCl as catalyst and [BMIM]Cl as the reaction solvent. The effects of HCl dosage, reaction temperature, reaction time, feedstock concentration, and catalyst loading were investigated for process optimization. What's more, to the best of our knowledge, there has been no study on the direct synthesis of 5-HMF from cottonseed hull biomass.

MATERIALS AND METHODS

1. Materials

Cottonseed hull was purchased from CHENGUANG BIOTECH GROUP CO., LTD. (Hebei, China). 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) is synthesized according to previous report [20]. $CrCl_3 \cdot 6H_2O$ (≥99%) was obtained from Tianjin Guangfu Chemical Fine Chemical Research Institute (Tianjin, China). Hydrochloric acid (37%) was supplied by Beijing Chemicals Co. Ltd. (Beijing, China). All other reagents of this experiment were purchased from the local dealers and used without further purication.

2. Sample Preparation and General Reaction Procedures

First, cottonseed hull was washed three times with pure water and dried in a vacuum drying oven at 80 °C for 48 h. The dried cottonseed hull was then smashed by using a high speed pulverizer, and the samples were screened to obtain crushed cottonseed hull with a tapping sieve equipped with a 20-mesh.

The reactions were performed in an oil bath. Cottonseed hull (100 mg), 1-Butyl-3-methylimidazole chloride (2 g), and the desired amount of hydrochloric acid were added into a round-bottom flask (50 ml) at 80 °C with magnetic stirring. With the hydrolysis of cellulose and hemicellulose, the cottonseed hull completely dissolved in ionic liquid 10 min later. The temperature of the thermostatic oil bath increased to the desired reaction temperature after about 30 minutes of heating and stirring. A given mass of $CrCl_3 \cdot 6H_2O$ was added to this solution. The reaction mixture was stirred magnetically at 500 rpm. At the end of reaction, the reaction system was cooled to room temperature with cool water. 10 ml distilled water was added to the reactor and the aqueous solution was centrifuged at 10,000 rpm for 5 min, and a supernatant fluid was formed.

3. Analysis of 5-HMF and Furfural

Reaction samples containing 5-HMF and furfural were determined by HPLC (Shimadzu LC-20AT) with an ultraviolet detector at 284 nm and a reversed-phase C18 column (4.6×150 mm) at 35 °C. The mobile phase was methanol/water (20/80, v/v) at a ow rate of 0.7 ml/min. Each sample was filtered with a microporous membrane (0.45 μm) before being measured by HPLC to prevent the blocking of the column.

Table 1. The main compositions content of cottonseed hull

Main compositions	Quality content (%)
Hemicellulose	20
Cellulose	45
Lignin	23
Water and Ash	12

The yield of 5-HMF and furfural was calculated by Eq. (1) and Eq. (2).

5-HMF yield (mol%)

$$=\frac{\text{moles of 5-HMF}}{\text{moles of glucose unit of cellulose and hemicellulose}}\times 100\% \quad (1)$$

Furfural yield (mol%)

$$=\frac{\text{moles of furfural}}{\text{moles of pentose unit of hemicellulose}}\times 100\% \quad (2)$$

RESULTS AND DISCUSSION

1. The Main Composition of Cottonseed Hull

Cottonseed hull, which contains a high amount of cellulose and hemicellulose, can be an excellent raw biomaterial for chemical production because cellulose and hemicellulose are good feed materials in the synthesis of 5-HMF and furfural, respectively. Thus, we first analyzed the composition content of cottonseed hull. The main composition content of cottonseed hull was analyzed according to Ververis [21] and the results are given in Table 1.

2. The Effect of HCl Dosage

There are two main steps in the production of furfural and 5-HMF from cottonseed hull; cellulose and hemicellulose were hydrolyzed into their six and ve carbon sugar monomers, and then the sugars were converted into furanic compounds. The hydrolysis step was a key to the conversion of cottonseed hull cellulose into 5-HMF and it was supported by HPLC analysis (Fig. 2). Therefore, in the present study, we used HCl to accelerate the hydrolysis of cellulose and hemicellulose of cottonseed hull into monosaccharide. The effect of HCl dosage on the yield of 5-HMFwas investigated in [Bmim]Cl at 130 °C for 2 h. As shown in Fig. 3, in the absence of hydrochloric acid, nearly none of 5-HMF yield was produced. When an amount of 10%-20% (relative to cottonseed hull) hydrochloric acid was added, the yield of HMF increased with the increase of hydrochloric acid loading, and when 20% hydrochloric acid was applied, the yield of 5-HMF achieves a maximum of 51%. However, if the amount of HCl continued to increase, its yield began to decline. When hydrochloric acid was added to 25%, the yield of HMF decreased to 33%. This phenomenon might be caused by the decomposition of 5-HMF to levulinic acid and formic acid being accelerated at high concentration of H^+ [22]. Furthermore, when 20% HCl was added, the amount of water in hydrochloric acid was already enough for the hydrolysis reaction of cellulose in theory; thus superfluous water of hydrochloric acid would inhibit the dissolution and transformation of cellulose [23]. The yield of furfural had similar tendency, but its yield was significantly lower than 5-HMF. This result might be that $CrCl_3 \cdot 6H_2O$ is not an ideal catalyst for the conversion of hemicellulose

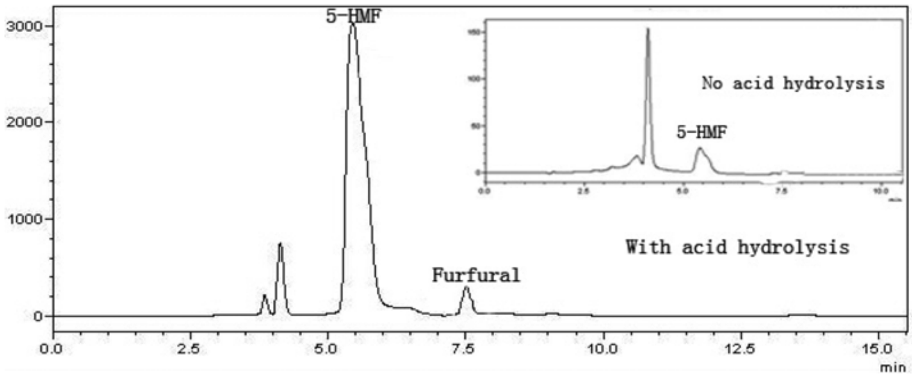

Fig. 2. HPLC analysis of 5-HMF and furfural.

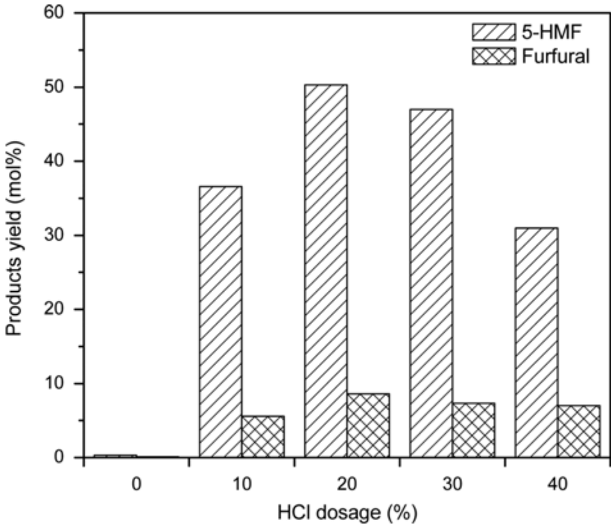

Fig. 3. Effect of hydrochloric acid dosage on the yield of 5-HMF and furfural. Reaction condition: Cottonseed hull, 100 mg; [Bmim]Cl, 2.0 g; $CrCl_3 \cdot 6H_2O$, 25 mg; 130 ºC for 2 h.

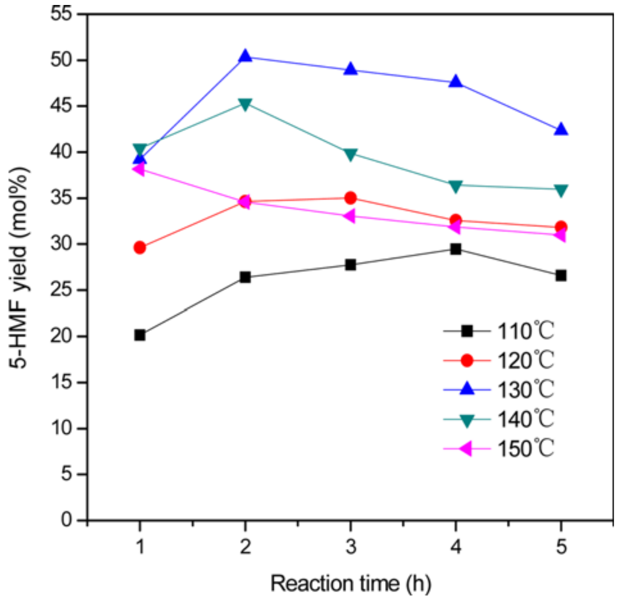

Fig. 4. Effect of reaction temperature and time on the yield of 5-HMF. Reaction condition: Cottonseed hull, 100 mg; [Bmim]Cl, 2.0 g; $CrCl_3 \cdot 6H_2O$, 25 mg; Hydrochloric acid, 20%.

into furfural [24]. In addition, the self-polymerization and cross-polymerization of furfural at a high temperature under acid condition also can reduce the yield of furfural [25,26]. To obtain the optimal conditions for the conversion of cottonseed hull to 5-HMF, 20% HCl was selected for subsequent study.

3. The Effect of Reaction Temperature and Time

The reaction temperature and time are important influential factors for the preparation of 5-HMF from cottonseed hull such as kinetics, selectivity, and the activity of catalyst [23]. In this paper, the reaction was carried out from 110 ºC to 150 ºC for different reaction times. As illustrated in Fig. 4, only 20% of 5-HMF was achieved at 110 ºC for 1 h. The gradual increase in 5-HMF yield was observed with the increase of reaction temperature. At a reaction temperature of 140 ºC, the 5-HMF yield of 40% was obtained in 1 h. The increasing 5-HMF yield with increasing reaction temperature is due to the fact that a higher temperature can reduce the viscosity of ionic liquid that is helpful to the dissolution of sugars [27] What's more, a higher temperature can accelerate the formation of 5-HMF. However, further increase of the temperature will lead to the decrease of 5-HMF yield. This totally agrees with the results of other reports [28,29]. When the reaction temperature was 150 ºC, the yield of 5-HMF was reduced as the reaction continued, which could lie in the fact that excessive temperature was advantageous to the decomposition and self-polymerization of 5-HMF [30]. At different reaction temperatures (except 150 ºC), the yield of 5-HMF rose with the increase of time at first. But when the yield reached maximum value, further increase of time would result in the decline of 5-HMF yield. It could be clearly seen that the maximum value 51% of 5-HMF yield was obtained at 130 ºC for 2 h.

4. The Effect of $CrCl_3 \cdot 6H_2O$ Amount

The inuence of catalyst amount with respect to cottonseed hull cellulose conversion into 5-HMF over $CrCl_3 \cdot 6H_2O$ in [BMIM]Cl was investigated and the results are shown in Fig. 5. The amount of $CrCl_3 \cdot 6H_2O$ varied from 0 to 32 mg. In absence of $CrCl_3 \cdot 6H_2O$, the yield of 5-HMF and furfural was 17% and 6%, indicating that HCl can catalyze cottonseed hull into 5-HMF and furfural with low activity and selectivity. As shown in Fig. 5, adding 5 mg $CrCl_3 \cdot 6H_2O$ into the reaction system led to a marked increase in 5-HMF yield at 130 ºC for 2 h. For instance, the 5-HMF yield could reach 51% when the dosage of $CrCl_3 \cdot 6H_2O$ was added to 25 mg. As the usage

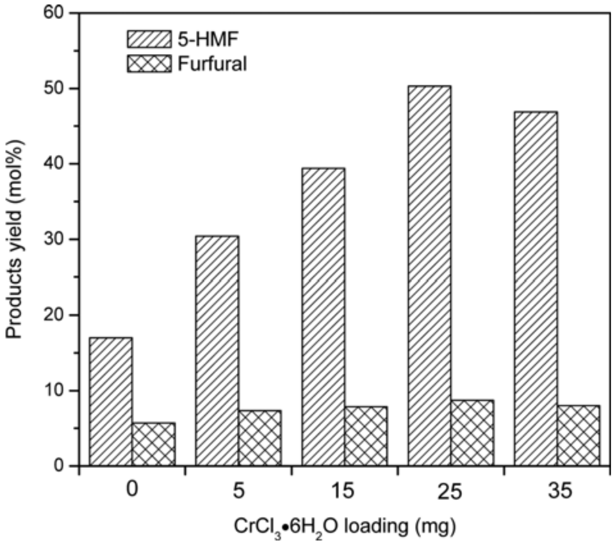

Fig. 5. Influence of catalyst dosage on the conversion of cottonseed hull into 5-HMF and furfural. Reaction condition: Cottonseed hull, 100 mg; [Bmim]Cl, 2.0 g; Hydrochloric acid, 20% 130 °C for 2 h.

of catalyst increased, the yield of 5-HMF decreased. When the amount of $CrCl_3 \cdot 6H_2O$ rose to 35 mg, the yield of 5-HMF decreased to 47%. This decrease was attributed to the fact that excessive catalyst can accelerate the rehydration of 5-HMF to levulinic acid and formic acid [31]. In addition, too much water of $CrCl_3 \cdot 6H_2O$ also inhibited the dissolution and transformation of cellulose. Hence, we selected 25 mg of $CrCl_3 \cdot 6H_2O$ as the optimal catalyst loading in the following experiments. As shown in Fig. 5, the yield of furfural had a slight change with the increase of $CrCl_3 \cdot 6H_2O$.

5. The Effect of Cottonseed Hull Loading on 5-HMF

The amount of initial biomaterial is one of the important factors for the industrialized application of 5-HMF. In this work, we studied the influence of cottonseed hull added, including 0.05 g, 0.1 g, 0.15 g, and 0.2 g, on 5-HMF yield. It can be seen that (Table 2) the yield of 5-HMF was affected by different initial cottonseed hull added. When the amount of cottonseed hull was 0.05 or 0.1 g, the yield of 5-HMF increased with the increase of cottonseed hull concentrations. However, when the concentration of cottonseed hull was over 0.15 g, the yield decreased obviously. This result might be because of the self-polymerization of glucose and 5-HMF, and cross-polymerization between glucose and 5-HMF [32].

Table 2. Effect of cottonseed hull loading on 5-HMF yield

Entry	Cottonseed hull/[Bmin]Cl (g/g)	5-HMF yield (mol%)
1	0.05/2	49
2	0.10/2	51
3	0.15/2	42
4	0.20/2	38

Reaction condition: [Bmim]Cl, 2.0 g; $CrCl_3 \cdot 6H_2O$, 25 mg; Hydrochloric acid, 20%; 130 °C for 2 h

6. The Pathway for Direct Conversion of Cottonseed Hull into 5-HMF

The hypothesized pathway for direct conversion of cottonseed hull into 5-HMF is given in Fig. 6. The 1,4-glycosidic bond of cellulose in cottonseed hull was broken with H^+ to form the β-glucose. The β-glucose was then isomerized into fructopyranose as Zhao et al. reported [9]; and β-glucose was first transformed to an enol intermediate with a complex compound of $CrCl_3 \cdot 6H_2O$ and [Bmim]Cl. Subsequently, D-fructose was generated though the enol intermediate discharged the complex compound and finally fructose was converted into 5-HMF by losing three water molecules.

CONCLUSION

This paper presents an efficient route for converting cottonseed

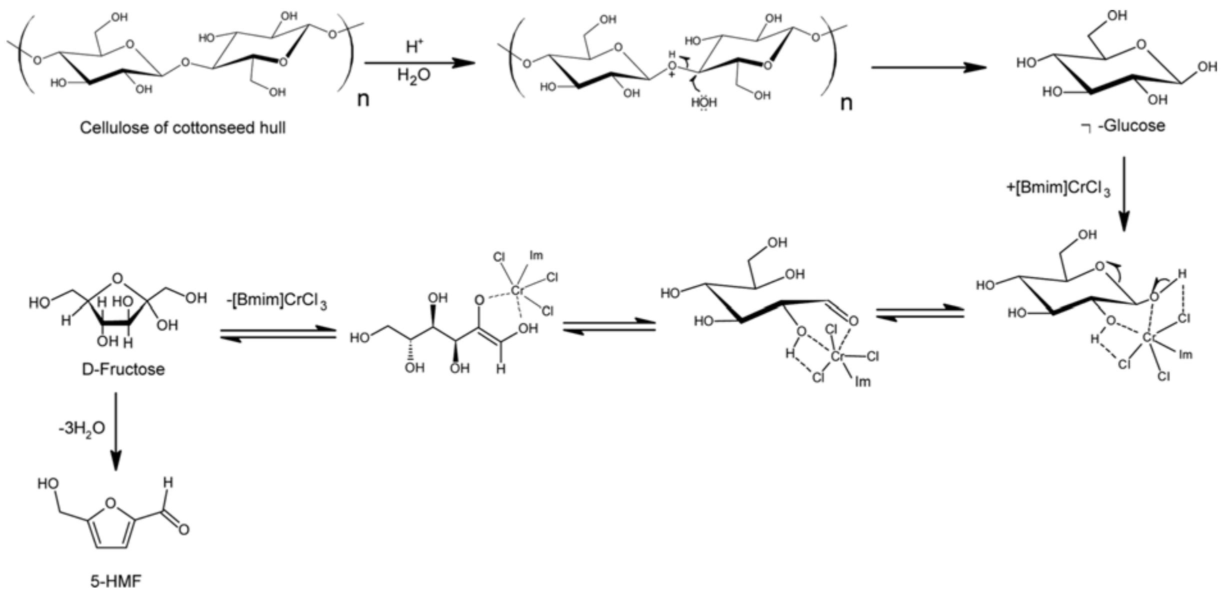

Fig. 6. The pathway of direct conversion of cottonseed hull biomass into 5-HMF.

hull biomass, a cheap agricultural by-product, into 5-HMF in one-pot for the fist time and proposes a pathway for the conversion of cottonseed hull into 5-HMF. After all conditions were investigated, a 5-HMF yield up to 51% was obtained using 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) catalyzed with chromium (III) chloride and hydrochloric acid at 130 ºC for 2 h. As is demonstrated in this work, $[Bmim]Cl/CrCl_3 \cdot 6H_2O/HCl$ is an excellent reaction system in synthesizing 5-HMF from cottonseed hull biomass. The most significant aspect in our work is providing a cheaper and environmentally friendly process for direct transformation of raw biomass into chemicals.

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