Metal Chlorides as Effective Catalysts for the One-Pot Conversion of Lignocellulose into 5-Chloromethylfurfural (5-CMF)

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5-chloromethylfurfural (5-CMF) was produced from carbohydrates and lignocelluloses under the catalysis of Lewis acids. The millimole scale-up synthesis of 5-CMF from carbohydrates was successfully performed using metal chlorides or mixed metal chlorides as a catalyst in a heterogeneous system. The process involved the heating of the feedstock in a biphasic hydrochloric acid/organic solvent reactor over several hours. The process was later applied to raw biomass, which gave 5-CMF yields comparable to that of carbohydrates, based on the hexose content. It was found that mixed catalysts consisting of $CrCl_3$ and $ZnCl_2$ played an effective role in the transformation. The 5-CMF can be directly obtained in nearly 80% yield from the fructose under the mixed catalysts heterogeneous system. Bamboo pulp, eucalyptus pulp, and bagasse pulp were also directly converted into 5-CMF under this system at the yield of 32.7%, 36.2%, and 50.1%, respectively.

Keywords: 5-Chloromethylfurfural; Lignocelluloses; Heterogeneous system

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INTRODUCTION

Throughout the development of human society, energy sources such as oil and coal have been exploited in almost an unsustainable way, which has now resulted in diminishing reserves of fossil fuels and global warming by CO_2 emission (Ragauskas *et al.* 2006; Stephanopoulos 2007). This urgent situation has strongly prompted scientists around the world to try replacing the fossil-based resources with renewable ones in recent years (Chheda *et al.* 2007a; Corma *et al.* 2011). Theoretically speaking, plentiful biomass has the potential to be applied as renewable sources for fuels. Indeed, in some countries such as the United States, bioethanol produced from corn is already used as a transportation fuel. However, this way of using crop-based feedstock has been very fiercely argued among experts worldwide, since it could worsen the food shortage problem (Kim *et al.* 2011). In order to overcome this dispute, scientists have begun to focus on the lignocellulosic biomass, which is generally regarded as a promising carbon source due to its abundance in nature (Zhang and Zhao 2010). Until now, studies have mainly focused on the efficient conversion of lignocelluloses into 5-hydroxymethylfurfural (5-HMF) because of its excellent performance as renewable chemical platforms for the production of fuels and some high value-added chemical intermediates (Chheda *et al.* 2007b; Rosatella *et al.* 2011; Hu *et al.* 2012; Zhang *et al.* 2012; Sung *et al.* 2013; Saha and Abu-Omar 2014). However, at the present stage, the depolymerization step of celluloses into glucose still remains a costly and energy-intensive process, which has greatly slowed the utilization of biomass.

5-chloromethylfurfural (5-CMF) is another template compound bearing some similarities to 5-hydroxymethylfurfural, which, as mentioned before, has great value as an intermediate of biofuel. According to related reports in the past few years, 5-CMF can be obtained by straightforward dehydration of fructose, glucose, cellulose, and corn stover (Mascal and Nikitin 2008, 2009; Bredihhin *et al.* 2013). The cited authors also found that the lignocellulosic biomass could be converted into 5-CMF in recordable yield by using metal chloride as a metal catalyst. In the subsequent studies, Mark and his coworkers targeted some reaction parameters for optimization, which further improved the performance of this reaction. However, research work is still not adequate, compared to that of 5-HMF.

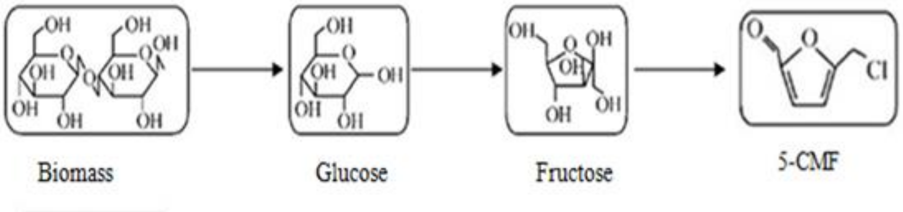

Fig. 1. Transformation of lignocellulosic biomass into 5-CMF

Hence, inspired by some other researchers' work (Kim *et al.* 2011; Dutta *et al.* 2012; Bredihhin *et al.* 2013), the idea of using metal chlorides to produce 5-CMF from biomass was generated, which would be a one pot reaction without continuous extraction. In this manuscript, the effects of various reaction parameters on the 5-CMF yield were respectively investigated. Furthermore, some efforts to utilize different lignocellulose as starting material for the direct synthesis of 5-CMF by means of metal chlorides catalysis conversion were tried.

EXPERIMENTAL

Materials

All the chemicals used in this experiment, including all inorganic salts, carbohydrates, organic solvents, and hydrochloric acid (HCl), were obtained from Sigma-Aldrich Corp. (USA) in reagent grades. Lignocellulosic raw materials used in this experiment were provided by pulp mills in Guangdong Province (China) and ground into powder after being air-dried.

Methods

Typically, batch experiments were carried out in a 150-mL thick-walled glass reactor (sealed), which was heated in a temperature-controlled oil bath. The temperature of all experiments was set in the range of 25 to 45 °C. Powdered lignocellulosic raw materials of 5 mmol were added into the reaction chamber containing chloroform (added according to the $ZnCl_2$ /HCl solution and organic solvent ratio (v/v)). The organic solvent was heated with continuous mechanical stirring, and then aqueous concentrated hydrochloric acid containing $ZnCl_2$ was added (5 mL). Metal catalysts were dissolved with concentrated hydrochloric acid without extra water and formed an aqueous solution (25 mol%). After 5 to 15 h, the reactor was removed, and the reaction was stopped in an iced bath. After the organic solvent extraction (1,2-dichloro-methane, 15 mL), phase separation, and dewatering (anhydrous sodium sulfate), the mass of the products were measured. Finally, the yield of 5-CMF was calculated, and sample product analyses were performed by means of gas chromatography/mass spectrometry (GC-MS, Agilent 5973, USA) and ^{1}H-NMR (Varian INOVA500, USA) to insure that the targeted product was obtained.

The yield of 5-CMF is defined as follows,

$$Y = M_1 / M_2 \times 100\% \qquad (1)$$

where Y is the yield of 5-CMF, M_1 the moles of product, and M_2 the moles of lignocellulosic raw materials, based on sugar content.

RESULTS AND DISCUSSION

In this work, hydrochloric acid (HCl) was chosen as an acidic reagent because of its advantages compared to other acids, since it is a stable, stronger acid. Because it can change its concentration easily through evaporation, a sealed container is used. Besides, it is also believed that the Cl^- can form H-bonds with the -OH groups of cellulose, disrupting its extensive network of hydrogen bonds, which would accelerate the cellulose hydrolysis process (Dutta *et al.* 2012). The choice of the solvent is also significant because an organic not only can remove the product from the reaction area in time, but it also can have an effect on the subsequent separation step. In previous related work, chloroform showed an excellent selectivity for extracting CMF from the acidic aqueous phase (Gao *et al.* 2013). Considering that, chloroform was considered as the best solvent. Zinc chloride was supposed to help promote the dehydration of fructofuranose to CMF, and easily dissolved in hydrochloric acid, so it was chosen as the catalyst in most of the reactions.

The experiment was initiated by optimizing the reaction parameters for the conversion of carbohydrates into 5-CMF. The synthesis reactions were initially applied to some monosaccharides such as glucose and fructose and carried out according to the procedures mentioned above. The results are shown in Tables 1, 2, and 3.

Table 1. Effect of $ZnCl_2$ /HCl Solution and Organic Solvent Ratio (v/v) on the Yields of CMF

Materials	Ratio	Temperature (°C)	Time (h)	Yield (mol%)
Glucose	1:2	45	10	7.9
	1:3	45	10	11.2
	1:4	45	10	6.8
	1:5	45	10	6.1
Fructose	1:2	45	10	41.1
	1:3	45	10	52.5
	1:4	45	10	51.6
	1:5	45	10	43.1
	Materials amount, 5 mmol carbohydrate; ratio, $ZnCl_2$/HCl solution to organic solvent; organic solvent, chloroform; catalyst, $ZnCl_2$			

From Table 1, it can be seen that at the ratio of 1:3, with the catalyst $ZnCl_2$ for 10 h, glucose gave a highest yield of 11.2% at 45 °C, whereas fructose gave a 52.5% yield. Clearly, the yield of glucose was far lower than that of fructose, which exactly corresponds to previous research regarding 5-HMF (Rosatella *et al.* 2011), which showed that glucose was harder to be transformed into furfurals. Therefore, the formation of 5-CMF would normally be expected to follow the mechanism shown as Fig. 1: the glucose is isomerized into fructose by the acid-catalyzed enolization, and then the isomerized fructose undergoes several dehydrations to give an intermediate, which has a very reactive alcohol that reacts with HCl to form 5-CMF.

Table 2. Effect of Reaction Temperature on the Yields of CMF

Materials	Ratio	Temperature (°C)	Time (h)	Yield (mol%)
Glucose	1:3	25	10	4.5
	1:3	35	10	9.6
	1:3	45	10	11.2
	1:3	55	10	3.2
Fructose	1:3	25	10	39.8
	1:3	35	10	49.8
	1:3	45	10	52.5
	1:3	55	10	49.5
	Materials amount, 5 mmol carbohydrate; ratio, $ZnCl_2$/HCl solution to organic solvent; organic solvent, chloroform; catalyst, $ZnCl_2$			

Temperature also had a great effect on the yield of 5-CMF. As the temperatures was raised from 25 to 55 °C, the yields of 5-CMF were increased, with whatever kinds of raw material were applied. And at the temperature of 45 °C, both the glucose and fructose yielded the most amounts of 5-CMF. Since fructose dehydration is endothermic, the reaction rate was accelerated with the rise of temperature. However, when the temperature was higher than 45 °C, the yield was reduced, due to the carbonation of raw material, and targeted products could also be further condensed into by-products. It is worth mentioning that carbonation of raw material in this reaction is a serious problem that could largely lower the yield of 5-CMF. Therefore, temperature control is significant at the beginning of the reaction.

Table 3. Effect of Reaction Time on the Yields of CMF

Materials	Ratio	Temperature (°C)	Time (h)	Yield (mol%)
Glucose	1:3	45	5	4.0
	1:3	45	10	11.2
	1:3	45	15	10.7
	1:3	45	20	6.3
Fructose	1:3	45	5	41.1
	1:3	45	10	52.5
	1:3	45	15	50.5
	1:3	45	20	49.8
	Materials amount, 5 mmol carbohydrate; ratio, $ZnCl_2$/HCl solution to organic solvent; organic solvent, chloroform; catalyst, $ZnCl_2$			

In addition, the influence of time was investigated. With the extension of time after 10 h, no obviously higher product yields were observed. Therefore, the time of 10 h was judged to be suitable for the synthesis of 5-CMF, as shorter or longer periods provided inferior performance. The explanation for this may be that a shorter reaction time is not enough to complete the 5-CMF synthesis reaction, while in the cases of excess time, targeted product 5-CMF could be further turned into by-products such as levulinic acid; other side effects might occur, according to the research of Mascal and Nikitin (2008).

Additional metal chlorides were employed based on the recent results about the hydrolytic efficiency of cellulose into glucose (Zhao *et al.* 2007; Hu *et al.* 2012). Besides, Bali *et al.* (2012) studied the Cr catalysts conversion of glucose and fructose to 5-HMF in ionic liquid solvents, and unprecedentedly high yields were reported. They also claimed in their manuscript that Cr(III) should be the active species, rather than Cr(II), which had previously been implicated and subsequently assumed by others. Therefore, in the later research, $CrCl_3$ was also chosen as the catalyst, as well as $ZnCl_2$. It can be seen from Table 4 that $CrCl_3$ was a better catalyst than $ZnCl_2$ under the conditions employed.

Table 4. Influence of Catalyst on the Yield

Entry	Materials	Catalyst $ZnCl_2$ Yield (mol%)	Catalyst $CrCl_3$Yield (mol%)
1	Glucose	11.2	13.9
2	Fructose	52.5	61.6
3	Sucrose	51.5	71.7
4	Cellulose	4.40	5.5
Materials amount, 5 mmol carbohydrate; Ratio, 1:3; Organic solvent, chloroform; Temperature, 45 °C; Time, 10 h			

Based on the results, it can be concluded that, under the conditions of a ratio of 1:3, temperature at 45 °C, and time of 10 h, the best performance can be achieved. Thus, one can apply these for further transformations of biomass raw materials to 5-CMF. In the attempt to investigate the direct transformation of biomass into 5-CMF, the metal chloride $CrCl_3$ or $ZnCl_2$ was respectively used as catalyst with biomass as raw material.

The sugar content of the involved biomass raw materials (bagasse, bamboo pulp, eucalyptus wood) was detected by ion chromatography. The average molecular weight of bagasse, bamboo pulp, and eucalyptus wood was calculated as 170.37 g/mol, 173.44 g/mol, and169.44 g/mol, respectively. Single metal chloride catalyzed transformations of biomass raw materials to 5-CMF were carried out at 45 °C for 10 h. Results are shown in Fig. 2.

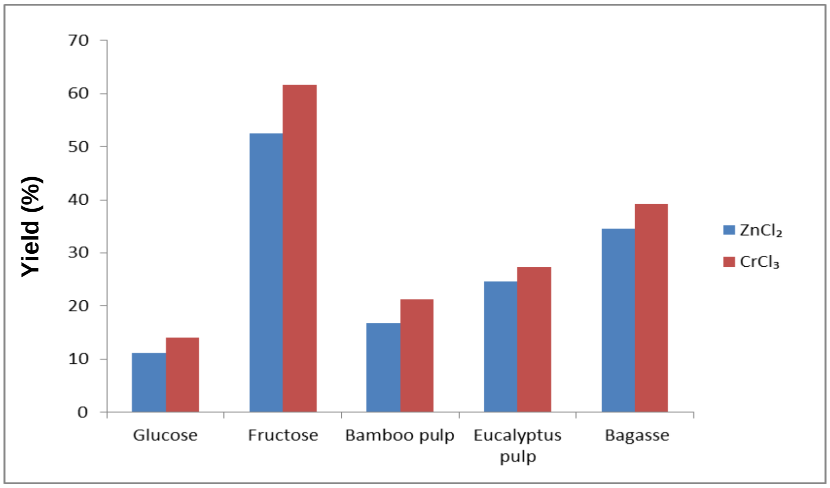

Fig. 2. Metal chlorides catalyzed transformations. Ratio, 1:3; organic solvent, chloroform; temperature, 45 °C; time, 10 h

The method employed in this work is easily applied to biomass. In most cases, by using $CrCl_3$, relatively good yields of 5-CMF were obtained at 45 °C for 10 h (red bars in Fig. 2), giving a yield from 13.95% (glucose) to 61.59% (fructose). Biomass catalyzed with $CrCl_3$ can also afford a good yield, with the bagasse, bamboo pulp, and eucalyptus pulp yielding 39.14%, 21.3%, and 27.32%, respectively. Although these results cannot match those former studies, they are positive to some extent. Meanwhile, a similar or less amount of 5-CMF was obtained with $ZnCl_2$, corresponding to the above conclusion that $CrCl_3$ is a better catalyst than $ZnCl_2$.

Therefore, it can be seen that the direct transformation of raw materials into 5-CMF with single metal chloride was unable to afford a good yield. This result probably can be attributed to the low efficiency of biomass depolymerizaton or isomerization of glucose. Hence, some measures must be taken to enhance this progress, and in this research, a combination of the two metal chlorides was applied. The reactions were carried out at 45 °C for 10 h, respectively. The results are shown in Fig. 3.

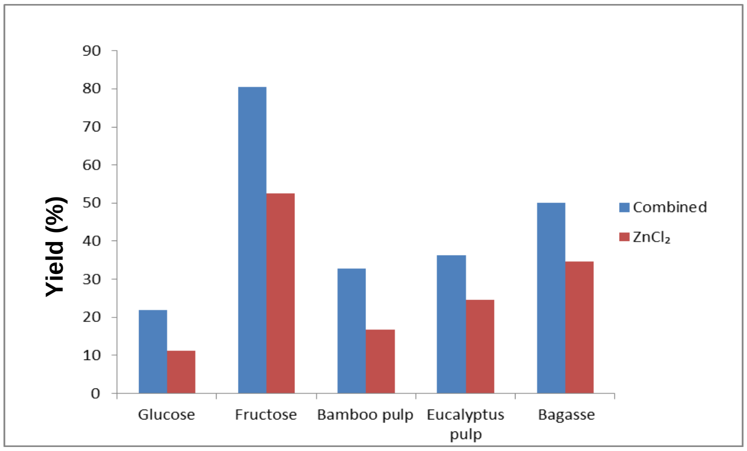

Fig. 3. Comparison between different catalyzed transformations. Ratio, 1:3; organic solvent, chloroform; temperature, 45 °C; time, 10 h

It can be seen clearly from Fig. 3 that each group of yield was improved greatly, no matter what the substrate was. The 5-CMF can be directly obtained at nearly 80% yield from the fructose under the mixed catalysts system. Bamboo pulp, eucalyptus pulp, and bagasse were also directly converted into 5-CMF under this system at the yield of 32.7%, 36.2%, and 50.1%, respectively. It might be indicated that, when a combination of metal chlorides was used, the transformations of glucose into fructose and fructose into 5-CMF were enhanced, since when the combined metal chlorides were used, the yield of 5-CMF from glucose and fructose both increased. In addition, the chance of producing humic material was reduced, as all are conducive to a higher yield of 5-CMF. However, the depolymerization process of celluloses into glucose still could not be assured, for all the transformations of 5-CMF from biomass involved the above mentioned processes. This needs to be further confirmed.

Product Identification

Sample product analyses were performed by means of gas chromatography/mass spectrometry (GC-MS) to insure the targeted product was obtained. The result is shown in Fig. 4.

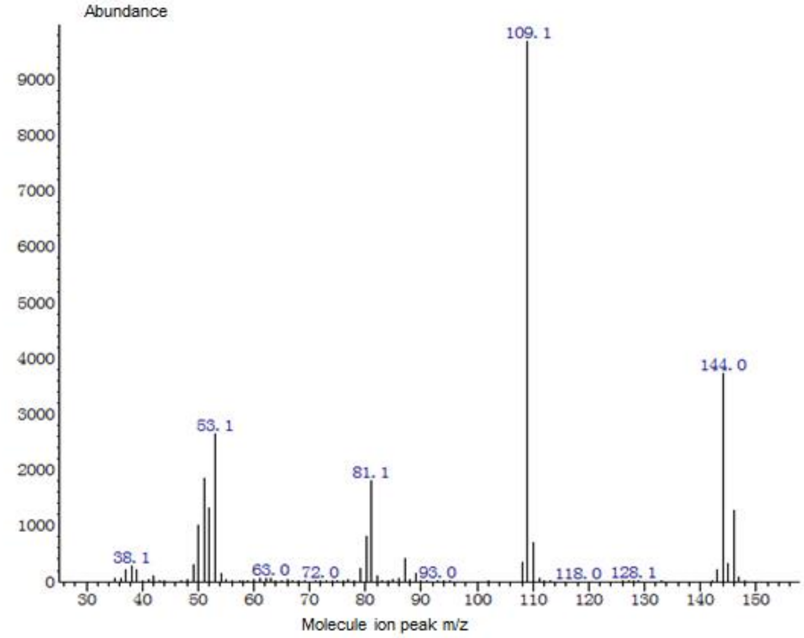

Fig. 4. GC-MS detection results

As shown in Fig. 4, the 5-CMF exhibited the expected distinct molecular ion peaks. The molecular ion peak m/z value of 5-CMF is 144, and the other major fragment ion peaks are also observed, including the m/z values at 109, 81, and 53, corresponding to the characteristic fragment ions of $[C_6H_5O_2]^+$, $[C_5H_5O]^+$, and $[C_4H_5]^+$, respectively. Therefore, it was firmly demonstrated that the synthesis product contained a chlorine atom, an aromatic aldehyde structure, and a furan ring; thus, the synthesis substance was exactly the targeted 5-CMF, and the molecular formula is $C_6H_5O_2Cl$.

The structure of 5-chloromethylfurfural was further confirmed by using ^{1}H-NMR, ^{1}H-NMR result is as follows: ^{1}H-NMR ($CDCl_3$): $\delta = 4.60$ (s, 2H), 6.58 (d, J = 3.6 Hz, 1H), 7.20 (d, J = 3.6 Hz, 1H), 9.64 (s, 1H) ppm.

CONCLUSIONS

1. 5-chloromethylfurfural (5-CMF) was directly synthesized using several different lignocellulosic raw materials. Over the process of optimization with monosaccharide, best performances were achieved at the conditions of a ratio of 1:3, temperature at 45 °C, and time of 10 h. Compared with $ZnCl_2$ catalytic efficiency (52.52%, fructose), $CrCl_3$ was higher (61.59%, fructose) in concentrated hydrochloric acid.
2. The transformation of raw materials into 5-CMF with single metal chloride was applied. It can be seen that the direct transformation of raw materials into 5-CMF in the presence of single metal chloride was unable to afford a very good yield.
3. When a combination of metal chlorides was used, the transformation of glucose into fructose and fructose into 5-CMF was enhanced; meanwhile, the generation of humic material was reduced. Therefore, the direct transformation of raw materials into 5-CMF with a combined catalyst was able to afford better yields.

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