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Rapid conversion of cellulose to 5-hydroxymethylfurfural using single and combined metal chloride catalysts in ionic liquid

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Abstract: Direct conversion of cellulose into 5-hydroxymethylfurfural (HMF) was performed by using single or combined metal chloride catalysts in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) ionic liquid. Our study demonstrated formation of 2-furyl hydroxymethyl ketone (FHMK), and furfural (FF) simultaneously with the formation of HMF. Various reaction parameters were addressed to optimize yields of furan derivatives produced from cellulose by varying reaction temperature, time, and the type of metal chloride catalyst. Catalytic reaction by using FeCl₃ resulted in 59.9% total yield of furan derivatives (HMF, FHMK, and FF) from cellulose. CrCl₃ was the most effective catalyst for selective conversion of cellulose into HMF (35.6%) with less concentrations of FHMK, and FF. Improving the yields of furans produced from cellulose could be achieved via reactions catalyzed by different combinations of two metal chlorides. Further optimization was carried out to produce total furans yield 75.9% by using FeCl₃/CuCl₂ combination. CrCl₃/CuCl₂ was the most selective combination to convert cellulose into HMF (39.9%) with total yield (63.8%) of furans produced from the reaction. The temperature and time of the catalytic reaction played an important role in cellulose conversion, and the yields of products. Increasing the reaction temperature could enhance the cellulose conversion and HMF yield for short reaction time intervals (5 ~ 20 min).

Key words: Microcrystalline cellulose; ionic liquids; 5-hydroxyfurfural; metal chlorides

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In recent years, world concerns have been emerged due to increasing of the current consumption and the demand of the limited natural resources such as petroleum and coal, etc. By 2030, it is predicted an increasing of the fuel consumption in USA by 25%, while fuel consumption is projected to 120% for rapidly growth developed countries such as China and India^[1]. The use of fossil fuel results in an increase of CO₂ to the atmosphere which is the major factor for the global climate change (CO₂ induced global warming). Biomass, as renewable source, is a part of natural carbon cycle and as result that, biomass will not contribute to increase the net CO₂ emissions to the atmosphere. Sustainable resources for energy and for the chemical industry require feedstock based on renewable source rather than the high rate depleting source. Cellulosic sources are one of the most important biomass resources due to their abundance in the nature and they are not included in the human food chain^[2,3]. Six and five-carbon carbohydrate derived from biomass cannot be used directly as building blocks in chemical industries or as a base of production of biofuel. The challenge is to transform six-carbon and five-carbon sugars into intermediates between biomass-based carbohydrate and petroleum-based organic substances. Efforts have focused for conversion of carbohydrate-derived from

biomass into furan derivatives such as 5-hydroxymethylfurfural (HMF) and furfural (FF)^[4-6]. Furan derivatives can replace the currently used petroleum-based building blocks for manufacture of plastics and fine chemicals^[7]. HMF is a promising intermediate to prepare liquid alkane from renewable resources^[8]. Current processes for preparation of HMF are mainly dependent on acid catalyzed dehydration reaction. Fructose is the most favored feed in case of acid catalysis processes. HMF yield is reduced when glucose is used instead of fructose^[9]. Using of acid catalysts in aqueous medium is not highly selective method for HMF preparation. Acid catalysts cause various side reactions, which result in decomposition of HMF into levulinic acid and formic acid^[10]. HMF yield has been improved by using of polar solvent such as DMSO in aqueous-organic reaction systems at high temperature^[11].

The crystallinity and complexity of cellulose super-molecular structure cause complete insolubility in aqueous and most of common organic solvents. The capability of ionic liquids to dissolve cellulose is a key of a promising selective method to produce HMF. Ionic liquids have some specific properties, such as very low vapor pressure, no flammability, high thermal and chemical stability, and efficient solvent power for organic and inorganic

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substances^[12]. Ionic liquids based on imidazolium salts were recently used to convert cellulose into HMF^[13]. It was reported that ionic liquids containing chloride ions have more dissolving power for cellulose, e. g. 1-butyl-3-methylimidazolium chloride [BMIM]Cl and 1-alkyl-3-methylimidazolium chloride [AMIM]Cl^[14]. The solubility of cellulose in ionic liquids is referred to its anion, which can disrupt the hydrogen bonds between the chains of cellulose, and then dissolving is taking place. Ionic liquids enabled us to carry out the dehydration reaction of cellulose at low temperature (80 ~ 120 °C) and ambient atmosphere and long reaction time^[15]. The conversion reaction of cellulose to produce HMF passes through three consecutive steps: hydrolysis, isomerization and dehydration. These consecutive steps can be performed in one-pot synthesis by using ionic liquids solvent. Using acidic ionic liquid, cellulose is hydrolyzed to oligosaccharides and then to glucose in short time, where ionic liquid solvent acts as hydrolyzing catalyst. Glucose should be isomerized into fructose followed by dehydration of fructose molecule by removing three water molecules^[16]. Ionic liquid can act as dehydrating agent, and then it can improve the selectivity towards HMF through suppression the rehydration reaction of HMF^[17]. It was reported that the dehydration reaction of cellulose in ionic liquids produced both HMF and FF. The yields of HMF and FF could be up to 40% and 23% respectively^[18].

Transition metal chlorides have been used as catalysts in ionic liquids solvents at temperatures of 80 ~ 120 °C for long time (up to 3 h) to produce HMF with high selectivity. Efficient isomerization catalysts e. g. CrCl₂ and CrCl₃ have been used in case of glucose conversion into HMF. Glucose isomerization to fructose has been proposed to proceed via enediolate intermediate with CrCl₂, where the glucose ring is opened and two oxygen species are coordinated with the hexa-coordination chromium (II) to form an intermediate complex^[6]. Several metal chlorides were used to catalyze the dehydration reaction in ionic liquids for fructose and glucose e. g. FeCl₂, FeCl₃, CuCl₂, VCl₃, MoCl₃, PdCl₂, PtCl₄, RuCl₃ or RbCl₃. HMF yields ranging from 60% to 83% were achieved in 3 h at temperatures 80 ~ 120 °C, the product yields were approximately free from levulinic acid (less than 0.08%), and so the purification and extraction of HMF would be facilitated^[19].

Most of the published work focused on using of ionic liquids for conversion of monosugars such fructose or glucose. Herein, the study is interesting in the direct conversion of cellulose into furan

derivatives such as HMF and FF by using 1-ethyl-3-methylimidazolium chloride [EMIM]Cl as solvent catalyzed by single or combined metal chlorides. The study aims to determine the optimum reaction conditions of time, temperatures, type of metal chloride catalyst, and the combination of two catalysts in order to maximize the yields of furan derivatives especially HMF.

1 Materials and Methods

1.1 Chemicals

All chemicals used in this study were purchased from commercial resources and used without further purification. Microcrystalline cellulose powder was purchased from Sigma, 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl, 98%), Furfural, HMF, CuCl₂, CrCl₃ were purchased from Sigma-Aldrich. FeCl₃, acetic acid, HPLC water, methylene chloride, methanol and glucose were purchased from Fisher scientific. CrCl₂ was purchased from Acros.

1.2 Cellulose conversion

Experiments were carried out in 50 mL graduated Pyrex glass tube immersed in an oil bath preheated at the required temperature using a hot plat with a digital magnetic stirrer (Fisher Scientific). In a typical experiment, 1 000 mg of [EMIM]Cl and the pre calculated amount of the single or combined catalysts were loaded in the glass tube and heated at 120 °C and 700 rpm for 30 min, then the contents were left over for cooling at room temperature. The amounts of added catalysts were 6% or 3%, based on the weight of cellulose, in case of using single or combined catalyst, respectively. After cooling, 100 mg of microcrystalline cellulose was added to the glass tube and the contents were heated again at the required temperatures (100, 120 or 140 °C) for a definite reaction time. At the end of the reaction, the contents of the glass tube were diluted to 15 mL using distilled water, stirred for 2 min, filtered with 0.2 μm syringe nylon membrane (Millex-GN) and used for determination of conversion products yields using HPLC.

1.3 Analytical methods

The filtered aqueous solution was analyzed by 1100 Agilent High Performance Liquid Chromatography (HPLC) equipped with ZORBAX eclipse C₁₈ Column and UV detector. During this process, The column temperature remain constant at 30 °C, and the mobile phase was methanol water (1:5, v/v acidified by 5% acetic acid) at flow rate of 1 mL/min with UV detection at 282 nm, and 10 μL of each sample was injected manually. The concentrations of HMF and FF were calculated based

on standard calibration curve obtained with standard prepared solutions contained HMF and FF. The third observed peak related to Furylhydroxymethyl ketone (FHMK), as identified by GC/MS chromatogram, was quantified using HMF calibration data since FHMK has similar HMF structure and could not be obtained commercially.

For the identification of third observed HPLC peak, the diluted cellulose conversion solution was extracted with methylene chloride (1:1 v/v) to separate organic and aqueous layers using a separating funnel. The organic layer was filtered and analyzed by a Hewlett-Packard 5972A quadruple mass spectrometer integrated with a HP5890 gas chromatograph equipped with a J&W Scientific Durabond HP-5MS, 30 m fused silica capillary column, 0.25 mm i. d. and 0.25 μ m film thickness, using helium as the carrier gas on a constant flow rate mode at 1 mL/min. The injection port was maintained at 250 $^{\circ}$ C, and the sample was injected with splitless mode followed by purge 1 min after the injection. Column temperature was held at 40 $^{\circ}$ C for 4 min, then programmed at 4 $^{\circ}$ C/min to 280 $^{\circ}$ C, and held for 10 min. A selected ion monitoring method was employed after a delay of 4 min and sharp peak related to FHMK was identified after 14.85 min retention time.

For the determination of unreacted cellulose, each sample was subjected to hydrolysis process by 72% H_2SO_4 with definite volume added according to pH of the sample^[20]. The concentration of glucose resulted from the hydrolysis process which indicate the amount of unreacted cellulose was analyzed by high performance liquid chromatography (HPLC) using Agilent 1200 instrument equipped with a refractive index detector and Biorad column HPX 87H (7.8 mm \times 300 mm) at 60 $^{\circ}$ C. The sample was analyzed with 0.001 mol/L sulfuric acid as eluent at flow rate of 0.6 mL/min for 20 min.

1.4 Calculations

The product yields, conversion and selectivity of the process were calculated as follows:

$$\text{Product Yield, \%} = \frac{\text{moles of product obtained}}{\text{moles of initial cellulose}} \times 100$$

$$\text{Cellulose conversion, \%} = \frac{\text{moles of reacted cellulose}}{\text{moles of initial cellulose}} \times 100$$

$$= \frac{\text{moles of initial cellulose} - \text{moles of initial cellulose} \times \left[\frac{\text{moles of final glucose} \times (162/180)}{\text{moles of initial cellulose}} \right]}{\text{moles of initial cellulose}} \times 100$$

$$\text{Product selectivity, \%} =$$

$$\frac{\text{moles of product obtained}}{\text{moles of reacted cellulose}} \times 100$$

2 Results and Discussion

2.1 Identification of conversion products

HPLC chromatogram for the most cellulose conversion experiments catalyzed by metal chlorides exhibit production of major three furan derivatives HMF, FF and FHMK. Figure 1 represents an example for these chromatograms. Two of the three obtained products (HMF and FF) were identified by coincidence their retention time with the retention time of HMF and FF in the calibration standard solution at 2.37 and 3.39 min, respectively. For the identification of the unknown compound exhibited absorbance at 1.68 min, the organic compounds were extracted from the ionic liquid conversion solution by using dichloromethane and injected in the GC/MS column as explained in the experimental part. The obtained GC/MS chromatogram (Figure 2) shows clear distinct peaks for FHMK and 2-furanmethanol at 14.85 and 15.8 min, respectively.

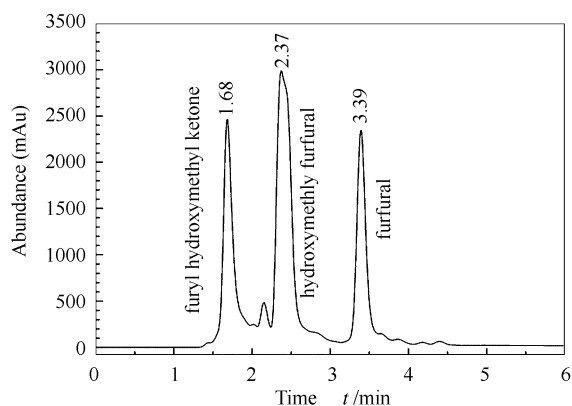


Figure 1 HPLC chromatogram for the products mixture produced from a catalytic run of cellulose conversion

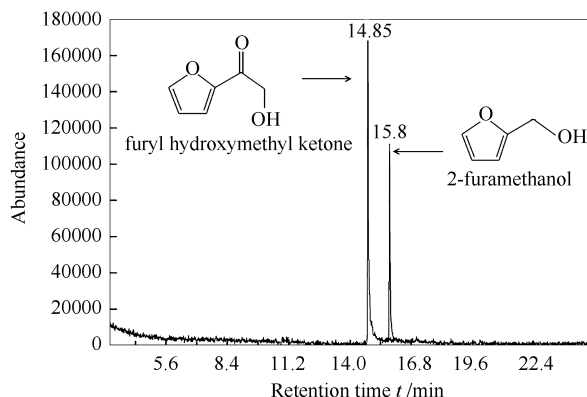


Figure 2 GC-Mass chromatogram for the dichloromethane extracted organic compounds showing 2-furylhydroxymethyl ketone as a major compound

Injecting 2-furanmethanol in the HPLC give pronounced peak at different retention time than the unknown product. This experiment proof that the unknown peak is most probably are related to the formation of FHMK in the conversion product. This result consistent with the same result obtained by Chidambaram et al^[21], indicating the formation of FHMK during the conversion of glucose. The absence of HMF and FF peaks from GC/MS chromatogram may be related to the higher affinity of FF and HMF to dissolve in the ionic liquid than the organic solvent.

2.2 Single metal chloride for catalytic cellulose conversion

The Complexity of direct conversion of cellulose into 5-hydroxymethylfurfural requires using a reaction system can enhance the three simultaneous steps

hydrolysis, isomerization, and dehydration performed on cellulose. In our work, we evaluated cellulose conversion by using of high efficient solvent, 1-ethyl-3-methylimidazolium chloride [EMIM]Cl with single metal chloride catalysts including FeCl₃, CrCl₂, CrCl₃, CuCl₂, and combination of two metal chlorides catalysts involving FeCl₃/CuCl₂, FeCl₃/CrCl₂, FeCl₃/CrCl₃, CrCl₂/CrCl₃, CrCl₃/CuCl₂, CrCl₂/CuCl₂. The design of this reaction system was based on high capability ionic liquid solvent for dissolving cellulose and then to promote the hydrolysis step resulting in glucose units. Also, the multifunctional metal chlorides catalysts were selected according to their principle role in isomerization and dehydration of glucose. Table 1 summarizes the results of single metal chloride catalyzed conversions of cellulose to HMF.

Table 1 Effect of catalyst type on the yield, conversion and selectivity of cellulose

Catalyst	Temp. <i>t</i> /°C	Time <i>t</i> /min	HMF yield <i>w</i> /%	FHMK yield <i>w</i> /%	F yield <i>w</i> /%	Total yield <i>w</i> /%	Cellulose conversion <i>x</i> /%	HMF selectivity <i>s</i> /%
FeCl ₃	100	60	16.0	–	–	16.0	35.0	45.8
	100	120	18.7	10.5	1.7	31.0	51.5	36.3
	120	20	20.1	12.7	15.9	48.7	65.7	30.6
	120	30	21.2	9.9	14.4	45.5	74.3	28.5
	120	60	13.2	6.7	12.5	32.5	82.8	16.0
	120	120	6.8	–	7.1	14.0	88.7	7.7
	140	10	23.6	21.9	14.3	59.9	72.4	32.4
	140	20	18.4	8.7	12.5	39.6	84.9	21.6
CrCl ₂	100	60	15.6	5.3	–	20.9	31.0	50.3
	100	120	24.4	–	–	24.4	41.6	58.6
	120	20	28.9	4.1	0.7	33.7	66.3	43.6
	120	30	28.9	3.7	–	32.7	75.3	38.4
	120	60	26.6	–	–	26.9	83.3	32.0
	120	120	22.5	–	–	22.5	88.8	25.4
	140	10	31.8	3.4	1.6	36.8	82.9	38.4
	140	20	28.1	3.0	–	31.2	89.1	31.6
CrCl ₃	100	60	16.0	0.9	–	16.9	28.5	56.2
	100	120	17.2	–	–	17.2	40.0	43.0
	120	20	33.9	4.9	1.4	40.2	69.0	49.4
	120	30	27.2	3.8	0.1	31.0	69.8	38.9
	120	60	26.8	–	–	26.8	75.3	35.5
	120	120	23.8	–	–	23.8	87.4	27.0
	140	10	35.6	6.5	0.7	42.9	84.9	42.0
	140	20	34.1	3.8	2.5	40.4	88.0	38.7
CuCl ₂	120	60	0.1	–	–	0.12	39.2	0.3
	120	120	3.9	–	–	3.95	48.7	8.1
	140	10	11.3	–	–	11.3	54.3	20.8
	140	20	10.7	–	–	10.7	59.8	17.8

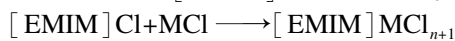
The catalytic runs were carried out at different temperatures 100, 120, 140 °C for different time intervals specified based on the temperature used. In addition to type of metal chloride catalyst, the reaction temperature and time are critical parameters that play an important role in cellulose conversion to HMF. Low yields of HMF are observed for runs performed at 100 °C for 60 min with low cellulose conversions. At 100 °C, the yields of HMF could be improved with increasing reaction time from 60 to 120 min for catalysts FeCl₃, CrCl₂ and CrCl₃. At 100 °C, the highest HMF yield (24.4%) with the highest selectivity (58.6%) could be produced by using CrCl₂ for 120 min, while the highest total yield (31.0%) could be obtained by using FeCl₃ due to producing of both FHMK and FF. It was obvious the reaction temperature 100 °C was not sufficient to produce HMF with good yield. Therefore, raising the reaction temperature to 120 °C was an attempt to improve both HMF yield and total yield of products obtained from the cellulose conversion reaction.

At reaction temperature 120 °C, cellulose conversion experiments were performed at different times ranging from 20 to 120 min. In case of CuCl₂ catalyst, cellulose conversion was performed only at 60 and 120 min. Very low HMF yield and selectivity were obtained at both reaction times. This result indicates that CuCl₂ has poor catalytic activity towards cellulose conversion to HMF. For other catalysts (FeCl₃, CrCl₂ and CrCl₃), high HMF yields was obtained at 20 and 30 min. The highest HMF yield (33.9%) and selectivity (49.4%) were obtained with CrCl₃ catalyst after 20 min. At longer reaction time (60 and 120 min) the yield of HMF was decreased. Increasing the reaction time from 20 to 120 min resulted in decrease in the selectivity of cellulose towards HMF production. In case of FeCl₃ catalyst, the yield of (FHMK and FF) and the total yield of furan derivatives were higher than those for CrCl₂ and CrCl₃ catalysts. The highest total yield (48.7%) was obtained with FeCl₃ catalyst after 20 min. Increasing the reaction temperature from 100 to 120 °C raised the yield of HMF from 24.4% after 120 min to 33.9% after 20 min. Also, after 20 min reaction time, the total yield was increased from 31% at 100 °C to 48.7% at 120 °C. This result indicates that raising the temperature with 20 °C was very effective for increasing the yield of HMF with significant decrease in the reaction time.

The catalytic runs performed at 120 min revealed the negative effect of increasing time and the positive effect of increasing temperature upon HMF yield and selectivity. Thus, in order to improve HMF yield

and/or total yield, the reaction was performed at higher temperature (140 °C) and shorter times (10 and 20 min). At 140 °C and 10 min, the highest HMF yield (35.6%) and selectivity (42.0%) were obtained with CrCl₃ catalyst while the highest total yield (59.9%) and selectivity (32.4%) were obtained with FeCl₃ catalyst. The higher total yield and low selectivity shown with FeCl₃ are actually related to the formation of FF and FHMK with high yields compared to those formed with CrCl₂ and CrCl₃ catalysts. This result indicates that CrCl₃ and CrCl₂ catalysts are more selective toward HMF production while FeCl₃ catalyst can produce more total furan derivatives with less selectivity toward HMF. Increasing the reaction time to 20 min at 140 °C resulted in decrease in both HMF yield and selectivity. CuCl₂ catalyst produced low HMF yield and low selectivity compared to other metal chloride catalysts.

In order to explain how the reaction of cellulose conversion can proceed, we built on the previous studies which support the reaction mechanism through our system. Supermolecular structure of cellulose was disassembled completely by solubilization in [EMIM]Cl, since the chloride anions were more involved in disruption of hydrogen bonds system than cations. Then, the reactivity of cellulose could be strongly improved^[22,23]. Splitting of cellulose chain into glucose units could be occurred by metal chloride (Lewis acid) binding with a glycosidic oxygen in a similar manner to protic acid and hence the glycosidic bonds became weak leading to conversion of polysaccharide to monosaccharide^[18]. According to NMR spectroscopy study^[6], It was found that the produced glucose units after hydrolysis in ([EMIM]Cl) were predominately in α anomer form. Conversion from α to β anomer (mutarotation) is necessary for completion the conversion reaction of glucose unit to HMF. It was proposed that an equilibrium was established between metal chloride and [EMIM]Cl as follows:



The catalytic role of metal chloride is essential to achieve mutarotation and isomerization has been shown in Figure 3.

The metal enolate is the key intermediate for formation of HMF via isomerization of glucose to fructose^[24]. The formation of metal enolate intermediate is followed rapidly with dehydration step to produce fructofuranose and accordingly HMF. Based on this mechanism, the weak catalytic action of CuCl₂ for HMF production may be referred to

presence of coordination between CuCl_2 and β -glucose anomer was different from that of the other metal chlorides used in our study. i. e. the interaction between CuCl_2 and sugar was unable to form fructofuranose ring. In order to clarify the pathway through which FHMK was formed, we emerged the results of two studies^[6,21]. The formation of the key intermediate, metal enolate, was undergone for successive dehydration steps leading to diketone compound, and consequently rings closing to form FHMK. In our study, we can suggest that the

probability could be increased for the enolate intermediate to be undergone in this pathway, Figure 4, in case of using FeCl_3 catalyst. Also, this pathway can support the formation of FF. We suggest that the formation of FF could be achieved via the diketone intermediate (formed from metal enolate). Diketone may be undergone for furan ring formation in addition to loss of formaldehyde molecule. This pathway for FF formation may be confirmed by the results of our work, since the formation of FF was related to formation of FHMK in comparable concentrations.

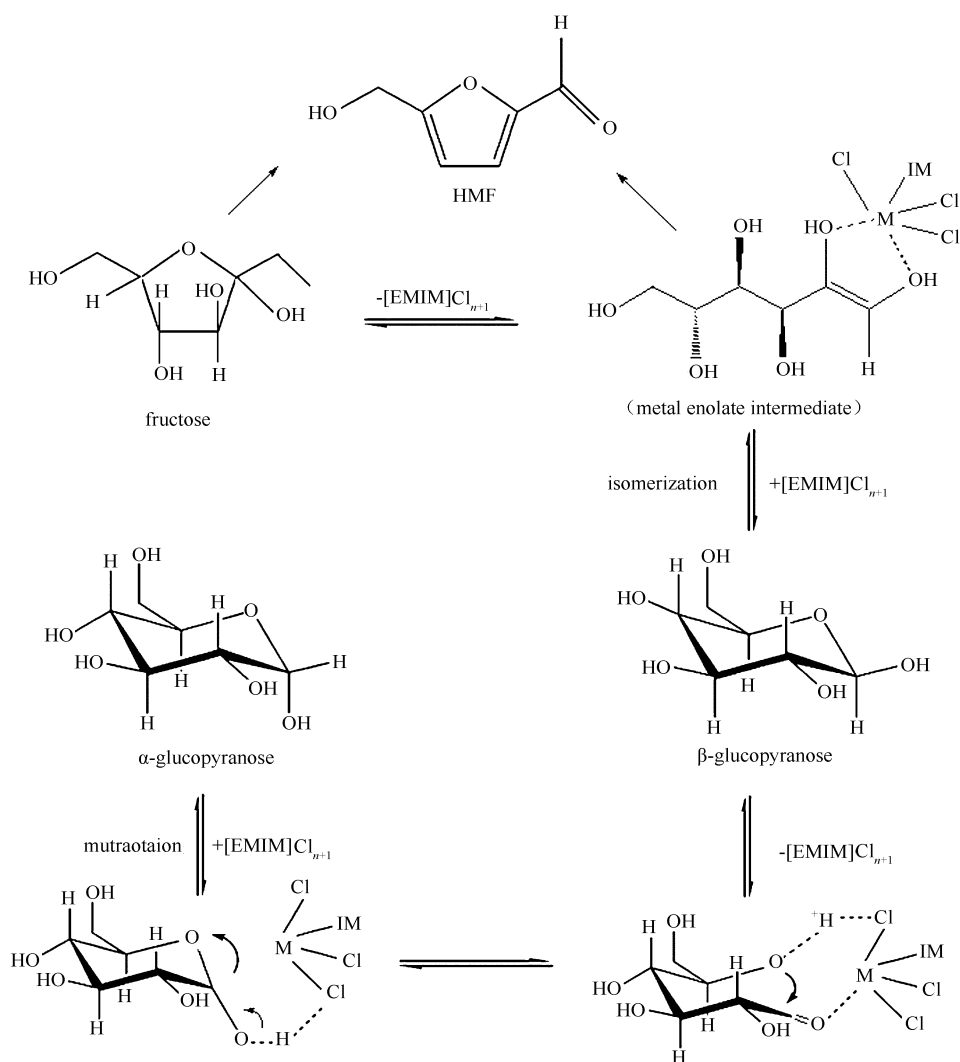


Figure 3 Role of metal chloride catalyst in mutarotation of glucopyranose, isomerization and dehydration to HMF^[6]

2.3 Combination of two metal chlorides for catalytic conversion of cellulose

In order to evaluate the effect of combination of two metal chlorides, catalytic runs were carried out by using of different pairs of metal chlorides with equal molar percentage at $140\text{ }^\circ\text{C}$ for different time intervals. Figure 5 shows the results of using six pairs

of metal chloride catalysts to convert cellulose into HMF, and furan derivatives FHMK, FF at $140\text{ }^\circ\text{C}$ for 5 min reaction time. From Figure 5, the catalyst combination $\text{CrCl}_3/\text{CuCl}_2$ resulted in the highest HMF yield (39.86%) with highest HMF selectivity (49.85%), while the highest total yield (79.93%) was obtained by using combination $\text{FeCl}_3/\text{CuCl}_2$. The

high concentrations of FHMK (25.25%) and FF (16.68%) were produced by using $\text{FeCl}_3/\text{CuCl}_2$ combination leading to highest total yield. The

total yield of combinations $\text{CrCl}_3/\text{CuCl}_2$ and $\text{CrCl}_3/\text{CrCl}_2$ (63.75% and 56.12% respectively) are comparable to that of $\text{FeCl}_3/\text{CuCl}_2$ combination.

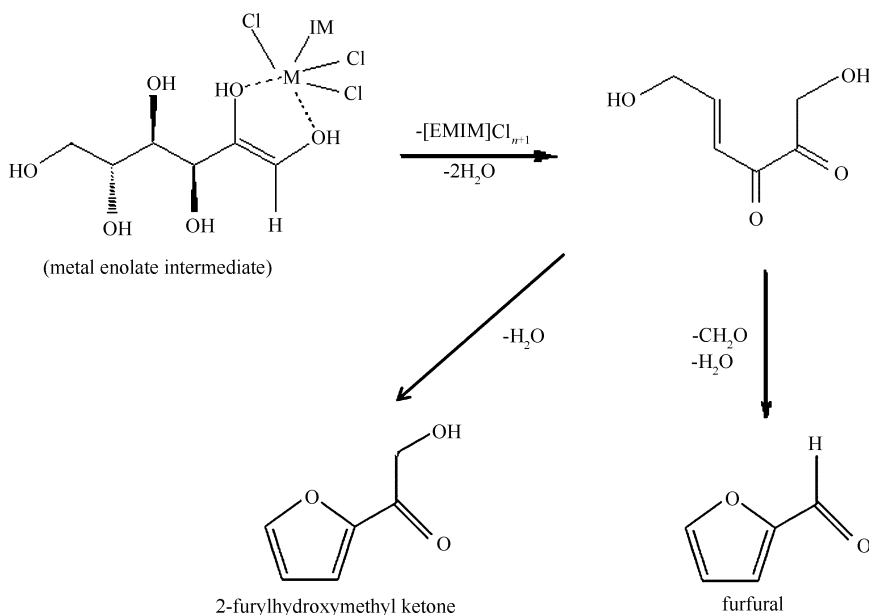


Figure 4 Proposed mechanism for the formation of FF and FHMK from the metal enolate intermediate

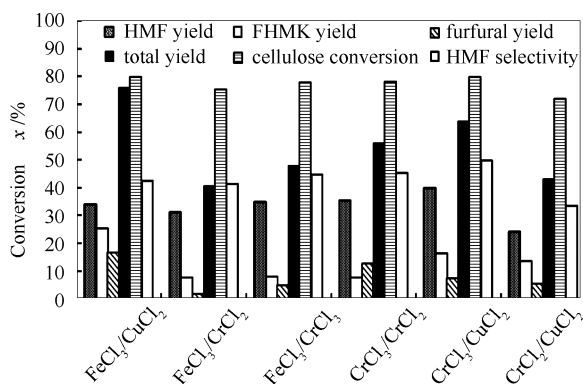


Figure 5 Conversion of cellulose by different combination of metal chloride catalysts at 140 °C, for 5 min

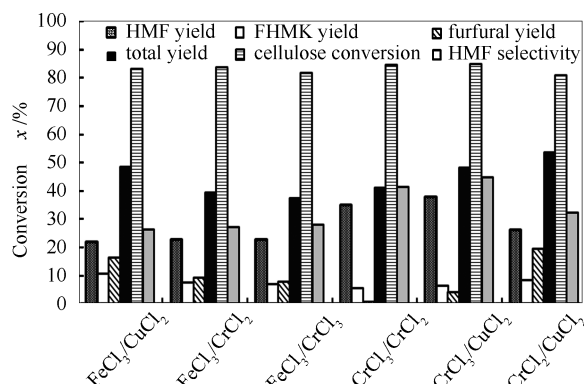


Figure 6 Conversion of cellulose by different combination of metal chloride catalysts at 140 °C for 10 min

As shown from Figure 6, the highest HMF yield (37.72%) with highest selectivity (44.50%), at 140 °C for 10 min, was obtained by using of $\text{CrCl}_3/\text{CuCl}_2$, while the highest total yield (53.58%) was resulted by using $\text{CrCl}_2/\text{CuCl}_2$ due to the high FF concentration (19.43%) produced. The total yields produced by combinations $\text{FeCl}_3/\text{CuCl}_2$ and $\text{CrCl}_3/\text{CuCl}_2$ (48.25 and 48.04% respectively) are comparable to that resulted by using $\text{CrCl}_2/\text{CuCl}_2$ combination at 140 for 10 min. The high concentrations of FHMK and FF produced at 140 °C for 10 min were obtained by using either $\text{FeCl}_3/\text{CuCl}_2$ or $\text{CrCl}_2/\text{CuCl}_2$.

Figure 7 shows that the highest HMF yield (26.52%) was obtained by using $\text{CrCl}_2/\text{CuCl}_2$ at 140 °C for 20 min. Also, the performance of the catalytic reaction at 20 min was associated with both low HMF selectivity, and low FHMK and FF concentration resulted from the reactions.

The results of catalytic runs performed at 140 °C for 5, 10 and 20 min revealed that the high yields of reaction products, and high HMF selectivity of products were achieved in short reaction time (5 min). The cellulose conversion increased with increasing the reaction time. There are promising three pairs of metal chlorides combinations to convert cellulose into HMF, FHMK and FF. One of them is

$\text{FeCl}_3/\text{CuCl}_2$, which is characterized by the capability for producing of FHMK and FF in comparable concentrations to HMF leading to high total yield of furan derivatives mixture. The other two pairs are $\text{CrCl}_3/\text{CuCl}_2$ and $\text{CrCl}_3/\text{CrCl}_2$. They are characterized by high selectivity to convert cellulose to HMF with minimizing the concentrations of the associated furan derivatives (FHMK and FF) produced from the catalytic reactions.

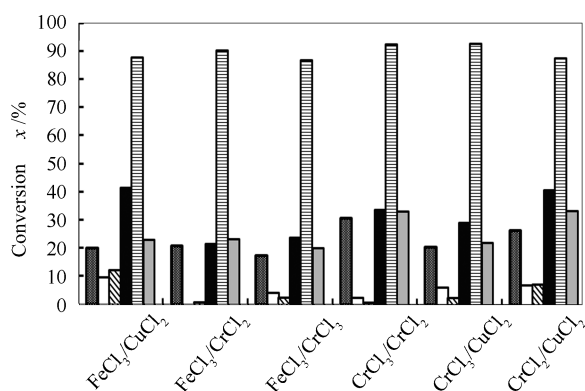


Figure 7 Conversion of cellulose by different combination of metal chloride catalysts at 140 °C, for 20 min

▨ : HMF yield; □ : FHMK yield; ▩ : furfural yield;
 ■ : total yield; ▨ : cellulose conversion; ▮ : HMF selectivity

3 Conclusions

The present study demonstrated efficient

conversion of cellulose to HMF, FHMK and FF in ionic solvent [EMIM]Cl through short time, where the reaction was catalyzed by different single and combined metal chlorides. FeCl_3 was found to be the most effective catalyst in production of FHMK and FF simultaneously with HMF. The highest total furan yield (59.9%) was achieved with FeCl_3 catalyst at 140 °C and 10 min. The selectivity of HMF production was enhanced with CrCl_3 or CrCl_2 catalysts due to less formation of FHMK and FF. Although the highest yield of HMF (35.6%) was resulted with CrCl_3 catalyst at 140 °C and 10 min, the highest HMF selectivity (58.6%) was achieved by CrCl_2 at 100 °C and 120 min. At the optimum reaction conditions (140 °C and 10 min), the selectivity of CrCl_3 was higher than that for CrCl_2 . Among the different metal chloride combinations, $\text{CrCl}_3/\text{CuCl}_2$, $\text{CrCl}_3/\text{CrCl}_2$ and $\text{FeCl}_3/\text{CuCl}_2$ were the most efficient combinations to improve the total yield and HMF yield at 140 °C and after 5 min. The total yield 75.9% was achieved with $\text{FeCl}_3/\text{CuCl}_2$ combination due to high concentrations of FHMK and FF associated with HMF production. The combination $\text{CrCl}_3/\text{CuCl}_2$ produced highest HMF yield (39.9%) with highest HMF selectivity (49.9%) and total yield (63.8%). The combination of two metal chloride catalysts was more effective for conversion of cellulose into HMF, FHMK and FF than single metal chloride catalysts.

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