Conversion of Sawdust into 5-Hydroxymethylfurfura by Using 1,3-Dimethyl-2-Imidazolidinone as the Solvent

Li, Ya-feng*+; Yuan, Yong-peng; Wang, Kai-Kai; Jia, Jun; Qin, Xiao-Lin; Xu, Yue

School of Chemical Engineering, Changchun University of Technology, Changchun 130012, P.R. CHINA

ABSTRACT: *The conversion of the cellulose into 5-HMF would experience three steps, cellulose to glycose, glycose to fructose and fructose to 5-HMF. Chloride ion can break down the hydrogen bond in cellucose, chromium can catalyze the isomerization of glycose to fructose, and the high temperature is helpful to cyclohydration of fructose to 5-HMF. In this paper, the sawdust has been directly degraded into 5-HMF in 1,3-dimethyl-2-imidazolidinone (DMI) solvent containing alkali halides or ionic liquid with chromium(III) as the catalyst. The factors including the reaction temperature, reaction time, amount of catalyst and liquid-solid ratio, are investigated. The results indicate that the additive —— alkali halides plays an important role in the degradation of sawdust, for example that NaCl and KCl give rise to 28% (140°C) and 25.5% (120°C) of the final yield calculated on m(5-HMF)/m(sawdust), respectively.*

KEY WORDS: *5-HMF, Sawdust, DMI, Alkali halide, Chromium catalyst.*

INTRODUCTION

In past decades, more efforts have made to transfer renewable biomass into chemicals because the diminishing fossil resources could not meet with the growing needs of humanity [1]. The renewable biomass is comprised of cellulose, hemi-cellulose and lignin, in which the main components are the pentose and hexose. A promising approach to utilizing the renewable biomass is to degrade plant cellulose into the saccharide which is further fabricated into all kinds of chemicals. As a cyclodehydrated product of hexoses, 5-HMF (5-hydroxymethylfurfural) [2] has been considered to be an important and renewable platform chemical in the bio-based renaissance, of which the derivatives including 2,5-furfuryldiamine, 5-hydroxymethyl furfurylidenester and 2,5-furfuryldiisocyanate are particularly suitable starting materials for the preparation of polymeric materials such as polyesters, polyamides and polyurethane[3-6].

With respect to the degradation of plant cellulose, several factors should be considered, including the solvents, catalysts, additives and reaction conditions. ILs can not only dissolve the plant cellulose and saccharide but also degrade the glucose and fructose into 5-HMF [2, 7-10]. However, ILs remain expensive and entail difficulties in terms of separation of products and possible byproducts. The water is an ecological and technological solvent but 5-HMF readily reacts in water to form levulinic acid and formic acid [8, 11-15]. DMSO [10,16,17] and DEF are effective organic solvents, but they easily decompose

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* *To whom correspondence should be addressed.*

\+ *E-mail: fly012345@sohu.com*

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at high temperature. Thus, it is required to search for a solvent that can dissolve organic and inorganic compounds and be stable at high temperature. 1,3-Dimethyl-2-imidazolidinone (DMI) as a high boiling point solvent (226°C) can conform to these requirements. The chloride ions play important role in converting biomass into saccharide because the chloride ions can form the hydrogen bonds with the hydroxyl groups of cellulose and further disrupt the extensive network of intra- and inter-chain hydrogen bonds [18]. The chromium catalyst can readily lead to the isomerization of glucose to fructose, followed by cyclodehydration to 5-HMF [7]. In our work, we have utilized the sawdust as raw material to prepare the 5-HMF in DMI containing alkali halides with chromium(III) as catalysts.

EXPERIMENTAL SECTION

Materials

The sawdust, used as raw materials was dried to constant weight in the oven for the experiments. 1,3-dimethyl-2-imidazolidinone (DMI, 98%) was purchased from Aladdin (Shanghai). 5-HMF was from Alfa Aesar (Shanghai). $Cr(NO_3)_3{\cdot}9H_2O$ from Aladdin (Shanghai) was used as catalyst. LiCl, NaCl, KCl and the ionic liquid synthesized according to literature [19] was used as additives.

Experimental procedure

Typically, 0.1g sawdust, 0.1g catalyst and 0.2g additive were added into 3g DMI. Then, the mixture was transferred into the 20mL autoclave and heated in a temperature-controlled oil bath with magnetic stirring at 140°C for 2h. Once the reaction was completed, the autoclave was cooled quickly with water.

The product was diluted with deionized water, and then centrifuged to get rid of insoluble sediment. U-3900UV-Vis spectrophotometer (2J2-0014) was used to analyze the liquid phase. The maximum absorption wavelength of 5-HMF was at 284 nm [10]. Since the degradation of the sawdust was very complicated, the yield of 5-HMF was calculated as below.

$$Y(\%)=m(5\text{-HMF})/m(\text{sawdust})\times 100\% \qquad (1)$$

The standard curve of 5-HMF

The different concentrations of 5-HMF, involving in 0 mg/mL, 0.008mg/mL, 0.016 mg/mL and 0.032 mg/mL, 0.064 mg/mL were used to obtain the curve of the concentration of 5-HMF vs. absorbance at 284nm by U-3900UV-Vis spectrophotometer. The linear relationship was described as follows:

$$Y=104.24x+0.0754 \qquad R^2=0.996 \qquad (2)$$

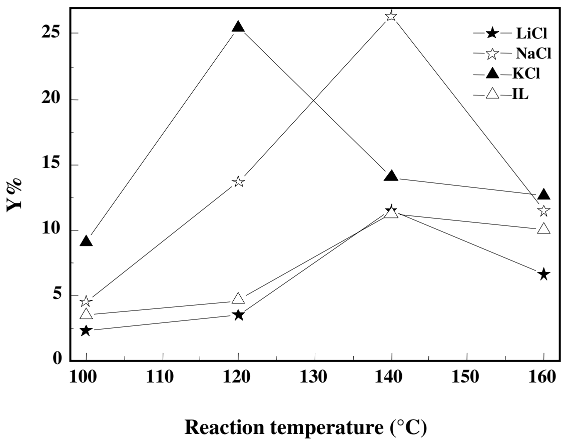

Fig.1 The effects of temperature on 5-HMF yield in DMI with $Cr(NO_3)_3{\cdot}9H_2O$ in the autoclave heated in a temperature-controlled oil bath with magnetic stirring: (★) 0.1g sawdust, 0.1g catalyst, 3g DMI, 0.2g LiCl for 2h; (☆) 0.1g sawdust, 0.1g catalyst, 3g DMI, 0.2g NaCl for 2h; (▲) 0.1g sawdust, 0.1g catalyst, 3g DMI, 0.2g KCl for 2h; (△) 0.1g sawdust, 0.1g catalyst, 3g DMI, 0.2g IL for 2h.

RESULTS AND DISCUSSION

Effect of temperature

The effect of the temperature is similar for 4 additives (Fig. 1). All four additives could prompt the cyclodehydration of sawdust and experience the same procedure. The cyclohydration is accelerated at the beginning step and gradually prohibited with temperature increasing. Two additives (NaCl and KCl) can prompt cyclodehydration more than the other two additives (LiCl and IL). The yield of 5-HMF for four additives increases fast at the beginning step and then decreases with the increase of temperature. In the case of NaCl, LiCl and IL, the maximum yields of 26.4%, 11.46% and 11.2% appear at 140°C, however in case of KCl the maximum yield of 25.5% appears at 120°C.

Effect of reaction time

High yield of 5-HMF can be obtained by optimizing reaction time (Fig. 2). As for different additives, the yield

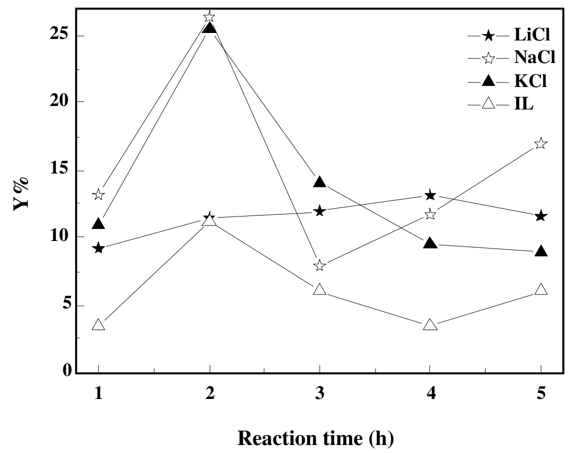

Fig.2: The effect of reaction time on 5-HMF yield in DMI with $Cr(NO_3)_3·9H_2O$ in the autoclave heated in a temperature-controlled oil bath with magnetic stirring: (★) 0.1g sawdust, 0.1g catalyst, 3g DMI, 0.2g LiCl at 140°C; (☆) 0.1g sawdust, 0.1g catalyst, 3g DMI, 0.2g NaCl and 140°C; (▲) 0.1g sawdust, 0.1g catalyst, 3g DMI, 0.2g KCl at 120°C; (△) 0.1g sawdust, 0.1g catalyst, 3g DMI, 0.2g IL at 140°C.

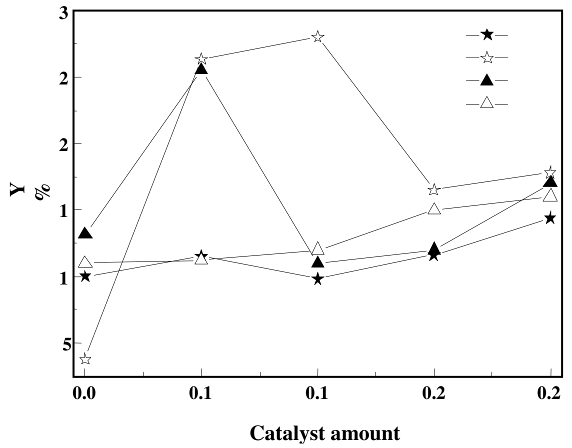

Fig. 3: Effect of catalyst amount on 5-HMF yield in DMI with $Cr(NO_3)_3·9H_2O$ in the autoclave heated in a temperature-controlled oil bath with magnetic stirring:(★)sawdust 0.1g, DMI 3g, LiCl 0.2g temperature 140°C for 4h;(☆) sawdust 0.1g, DMI 3g, NaCl 0.2g, temperature 140°C for 2h; (▲) sawdust 0.1g, DMI 3g, KCl 0.2g, temperature 120°C for 2h; (△) sawdust 0.1g, DMI 3g, IL 0.2g temperature 140°C for 2h.

varies similarly with time prolonging. In the beginning, the yield increases and then starts to decline with time prolonging due to the byproducts. The NaCl and KCl are superior to the LiCl and IL. When the additives are NaCl, KCl, IL, the maximum yields are achieved in 2h.They are respectively 26.4%, 25.5% and 11.2%. However, in case of LiCl, the maximum yield is obtained in 4h.

Effect of catalyst amount

The influence of the catalyst amount on the 5-HMF yield with different additives is shown in Fig.3. All four additives could be conducive to the cyclodehydration of sawdust and improve the yield of 5-HMF. At first, the yield increases remarkably with NaCl and KCl as additives, and then decreases with addition of catalyst. However, as for LiCl and IL, the yield increases slowly and continues to increase when the catalyst increased. In case of NaCl, KCl, the optimal catalyst amount is 0.15g and 0.1g, and the maximum yields are 28% and 25.5%. As for LiCl and IL, the catalyst amount is 0.25g, and the corresponding yields are 14.3% and 16%.

Effect of mass ratio of DMI to Sawdust

The effect of mass ratio of DMI to sawdust on 5-HMF yield is basically similar (Fig. 4). With increase of mass ratio of DMI to sawdust, the solubility increases and at the same time Cl^- concentration decreases. One additive (LiCl) is different from the other additives (NaCl, KCl, IL). As for LiCl, 5-HMF yield decreases gradually in the beginning and then increases with increasing mass ratio, and the maximum yield is 22% with 50:1 of mass ratio. In the case of NaCl, KCl, IL, the yield increases at first and then declines, and the maximum yield is obtained at 30:1 of the weight ratio. The maximum yields are 28%, 25.5% and 16%, respectively.

CONCLUSIONS

The catalytic cyclodehydration of sawdust to 5-HMF using $Cr(NO_3)_3·9H_2O$ as catalyst in DMI heated in a temperature-controlled oil bath with magnetic stirring is investigated. The experimental results show that 5-HMF yield was different with different additives. NaCl and KCl are the better additives. As for NaCl, a maximum yield of 28% could be achieved at 140°C for 2h. In case of KCl, the maximum yield of 25.5% could be obtained at 120°C for 2h. DMI is showed to be effective for dissolving and cyclodehydrating sawdust to 5-HMF.

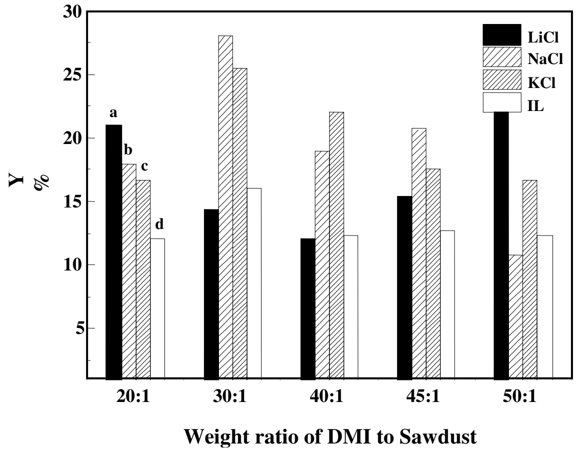

Fig. 4: Effect of mass ratio of DMI to sawdust on 5-HMF yield in DMI with $Cr(NO_3)_3{\cdot}9H_2O$ in the autoclave heated in a temperature-controlled oil bath with magnetic stirring: (a) 0.1g sawdust, 0.25g catalyst, 0.2g LiCl at 140°C for 4h; (b) 0.1g sawdust, 0.15g catalyst , 0.2g NaCl at 140°C for 2h; (c) 0.1g sawdust, 0.1g catalyst, 0.1g KCl at 120°C for 2h; (d) 0.1g sawdust, 0.2g catalyst, 0.2g IL at 140°C for 2h.

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