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Short communication

An effective pathway for converting carbohydrates to biofuel 5-ethoxymethylfurfural *via* 5-hydroxymethylfurfural with deep eutectic solvents (DESs)

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ABSTRACT

In this study, we put forward an effective two-step method of producing biofuel 5-ethoxymethylfurfural (5-EMF) from carbohydrates with DES mixture. With the catalysis of Amberlyst-15, 77.3% and 65.2% yield of 5-EMF were obtained respectively from the fructose and inulin in mild conditions. In addition, $CrCl_3$ modified Amberlyst-15 showed excellent catalytic performance in the aldoses dehydration, 46.7% and 50.2% of 5-EMF yield could be obtained from glucose and sucrose in the two-step reactions. Moreover, all catalysts used in this study could be effectively reused for several times.

1. Introduction

With the growth of environmental problems and the excessive consumption of fossil fuels, people are facing with ecological and environmental challenges. Those issues promote renewable and sustainable energy alternatives, which is imperative for the following energy transition and revolution decades(Ragauskas et al., 2006). Carbohydrates were considered as the most abundant renewable and cheapest resource in nature, which were considered as an important feed stock producing fossil chemical alternatives and platform compounds, such as 5-hydroxymethylfurfural (HMF), γ-valerolactone, levulinic acid, and 2,5-Dimethylfuran, *etc* (Huber et al., 2006; Román-Leshkov et al., 2006).

As a widely studied molecule, 5-HMF was always reported as an important bio-based platform compound. 5-HMF can be prepared from carbohydrates including monosaccharides, disaccharides and polysaccharides in different reaction systems(Eminov et al., 2014; Tucker et al., 2013; Zhao et al., 2007). Moreover, 5-HMF is a multifunctional molecule, which can be converted to varies of value-added chemicals (Girisuta et al., 2006; Hu et al., 2013). However, it is facing the problem of hydrolysis and polymerization in the preparation, as well as the difficulty in separation and storage(Galkin et al., 2016). In order to solve these issues, direct conversion of biomass to stable biofuels *via* 5-HMF was considered as a feasible way. In the current bio-refinery routes, 2, 5-dimethylfuran (DMF) and 5-(ethoxymethyl) furfural (5-EMF) are studied as potential biofuel alternative compounds(Kim et al., 2010; Kong et al., 2014). Compared with the complex hydrogenation-production process of the DMF, 5-EMF has distinct advantages in the preparation(Liu et al., 2014; Liu and Zhang, 2013). Generally, 5-EMF could be prepared from 5-HMF with much mild conditions and low-cost pathways, the etherification of 5-HMF with ethanol was considered as a principal approach for the production of 5-EMF. Some researchers showed that carbohydrate substances could be effectively converted to 5-EMF in different reaction systems, such as ethanol-biphasic system, single ethanol system and ionic liquids (ILs) (Imteyaz Alam et al., 2012; Li et al., 2016; Wang et al., 2013a,b). Several catalysts showed effective catalytic activities in the 5-EMF synthesis processes. Li et al. reported that 67% yield of 5-EMF could be obtained from fructose while 46% yield from glucose with catalysis of solid-acid(Li et al., 2016). Liu et al. indicated that the heteropoly acids showed significant perphormance in the 5-EMF preparation, and a yield of 90.3% could be obtained from fructose with the catalyst of $[MIMBS]_3PW_{12}O_{40}$ in ethanol(Bing et al., 2012). Guo et al. reported 83% yield of 5-EMF was obtained from fructose with ionic liquid as co-solvent and catalyst(Guo et al., 2017). Other catalysts such as Lewis acid and carbon-based catalysts also showed effective catalytic activities in the 5-EMF preparation(Liu et al., 2013; Wang et al., 2013a). For other substrate, 5-EMF could be easily prepared from 5-(chloromethyl) furfural (5-CMF) with nucleophilic substitution(Mascal and Nikitin, 2008).

Deep Eutectic Solvent (DES) is known as liquid mixture formed by

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solid hydrogen-bond donor (HBD) and hydrogen-bond acceptor (HBA), it has attracted much attention owing to its superior physical and chemical properties(de Morais et al., 2015; Zhang et al., 2012). Many previous reports confirmed that DESs share most of advantages of traditional ILs, but overcome many of their drawbacks, because the DES systems were usually formed by renewable, low toxicity/nontoxic compounds and cheap ingredients(Tang et al., 2017). Moreover, compared with conventional reaction systems (such as aqueous and organic solvent), the DES have superior biodegradability and biocompatibility. Recently, DESs have been adopted in many cases for the bio-refinery such as the conversion of carbohydrates(Abbott et al., 2004; Zuo et al., 2016). 5-HMF with desirable yields could be obtained in DES mixture when fructose was used as substrate(Ilgen et al., 2009; Zuo et al., 2017). Attracted by these studies, we attempt to develop a new means of 5-EMF synthesis from carbohydrates, of which the 5-HMF formation and 5-EMF production were integrated.

2. Materials and methods

2.1. Experiment materials

5-HMF (99%), and 5-EMF (97%) were supplied by Sigma-Aldrich China Co. Ltd. (Shanghai, China). EL (Ethyl levulinate) (98%) was supplied by TCI Co. Ltd. (Shanghai, China). Amberlyst-15, Amberlyst-732, Phosphotungstic acid ($H_3PW_{12}O_{40}$), Choline Chloride (ChCl), fructose, glucose and other carbohydrates were purchased from Aladdin Chemical Technology Co. Ltd. (Shanghai, China). Amberlyst-77 was purchased from Alfa Aesar Co. Ltd. The other chemicals of analytical grade were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used without further purification.

2.2. Preparation of Amberlyst-15-$CrCl_3$ cataslyst

The preparation of Amberlyst-15-$CrCl_3$ was carried out in a 150 ml glass flask with a water condenser pipe. Firstly, 5 g Amberlyst-15 resin was added into a certain amount of saturated ethanol solution of $CrCl_3$ and then the vessel hated at 78 °C for 6 h in oil bath. After the reaction finished and the vessel cooled down to the room temperature, the resin catalyst was separated from the ethanol solvent and washed by deionized water and acetone for three times, until there was no Cl^- detected from the washing solution. Lastly, the $CrCl_3$ coated Amberlyst-15 was dried in vacuum oven for 48 h at 110 °C, and then it could be used in the carbohydrate dehydrate experiments.

2.3. Step-1, dehydration of carbohydrates to 5-HMF in DES system

Under optimized conditions, the process for the synthesis of fructose-based sugars into 5-HMF was implemented in a glass flask (100 ml) with a condenser pipe in oil bath, the typical process for the synthesis of fructose is shown as follow, 0.9 g fructose and 0.18 g Amberlyst-15 (catalyst mass loading 20 wt%) were added into 3.6 g ChCl, 30 ml MeCN was added in the reactor as in-situ extracting solvent. With a condenser pipe, the reactor was then placed in oil bath and elevated to a suitable temperature for a certain time with stirring, after the reaction, the extraction of 5-HMF was carried out by repeated extraction with MeCN (60 °C), then separated the extracting solvent after the reactor cooled down to room temperature and an MeCN solvent of 5-HMF was obtained, which could be directly used in the next reaction step. The 5-HMF yield was analyzed with GC–MS.

The process for the synthesis of glucose-based sugars into 5-HMF was implemented in a stainless steel reaction still (100 ml, Parr, Germany), with 0.36 g Amberlyst-15-$CrCl_3$ catalyst, the reaction process was same with the fructose-based sugars synthesis processes.

2.4. Step-2, the etherification process from 5-HMF to 5-EMF

In a typical etherification step, after the separation of DES reaction system and extraction solvent, 20 ml of ethanol and 0.18 g of Amberlyst-15 were added into the obtained 5-HMF solvent and then started the etherification step directly. This reaction was also carried out in glass flask (100 ml) with a condenser pipe in oil bath, with a certain time reaction in a certain temperature, the yield of products in reaction solvent were analyzed by GC–MS after the reaction finished and cold down to room temperature.

During the above experiments, all the 5-HMF raw material was prepared from the DES reaction step, and these obtained 5-HMF solvent was directly etherified in ethanol without any other management. In this work, each experiment was tested at least for three times, and the experiment results were all mean values.

2.5. Products analysis

Considering that ChCl can damage the HPLC instrument, the quantification of 5-HMF yield was carried out by a Thermo-Fisher Trace 1300 & ISQ LT GC–MS instrument equipped with a TR- 5MS column (15.0 m × 250 μm × 0.25 μm). The following program was applied: 323 K (1 min) − 8 K/min − 423 K (1 min). He was used as carrier gas with a split ratio of 1:50 and a flow rate of 1.2 ml min^{-1}. The mass spectra were obtained by electron impact ionization (EI), with a 25 μA emission current and electron energy of 70 eV. The 5-HMF yield was calculated as following:

$$5-\text{HMF Yield}\ (\%)=\left(\frac{n_{5-\text{HMF}}}{n_{initial\ fructose}}\right)\times 100\%$$

$$5-\text{EMF Yield}\ (\%)=\left(\frac{n_{5-\text{EMF}}}{n_{initial\ fructose}}\right)\times 100\%$$

$$\text{EL Yield}\ (\%)=\left(\frac{n_{\text{EL}}}{n_{initial\ fructose}}\right)\times 100\%$$

It is necessary to point out that, without the standard substance of 2-(Diethoxymethyl)-5-(ethoxymethyl) furan (DEF, a main by-product of the 5-HMF etherification process), the yield of DEF was quantified by the comparison method of the peak area in gas chromatograph analysis, which was because the chemical characters of 5-EMF and DEF were very similar, therefore, this method might be a feasible way to determine the DEF yield in this reaction.

3. Results and discussion

Firstly, one-pot conversion of fructose to 5-EMF was attempted in a DES-based biphasic system. Different kinds of catalysts including Brönsted acids, Lewis acids, heteropoly acids and solid acids were applied in the reaction. In the experiment porcess, fructose was firstly formed a DES mixture with choline chloride (ChCl), and then organic extracting agent and catalyst were added into the DES mixture to start the dehydration. After the 5-HMF synthesis finished in 4 h reaction, additional ethanol was directly added in the reaction flask to carry out the etherification reaction. However, only a 5-EMF yield of 36.3% was obtained with 8.6% 5-HMF and 4.8% EL. This result was similar with some previous reports(Li et al., 2014), we speculated that an independent separation step of 5-HMF solution before the etherification process was necessary to reduce the by-ractions. Thus, the 5-EMF preparation process from fructose was designed with a two-step reaction.

We explored the reaction conditions of 5-HMF synthesis process. As the results illustrated in Fig. 1, extremely low Brönsted acid presented effective catalysis in the fructose dehydration, 90.3% mole yield of 5-HMF was obtained with 1.2 mol% HCl as catalyst. Amberlyst cation exchange resins showed desirable dehydration effects on fructose, with