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Original article

Conversion of xylose and xylan into furfural in biorenewable choline chloride–oxalic acid deep eutectic solvent with the addition of metal chloride

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ABSTRACT

An environmentally benign processing approach for furfural production from xylose and xylan under very mild conditions (353–373 K) was developed with the addition of metal chlorides in ChCl–oxalic acid (a deep eutectic solvent (DES)) synthesized from cheap and renewable starting materials). ChCl–oxalic acid acted as both a Brønsted acid catalyst and a reaction medium in this catalytic route. In addition, a biphasic system with methyl isobutyl ketone as an extracting reagent (DES/MIBK) to further increase furfural yield was also proposed. This processing approach for producing furfural eliminated the large energy consumption for high pressure saturated steam and the generation of acidic effluent, which was very difficult to handle. The whole catalytic system was more environmentally friendly compared with the commercial process for furfural production.

1. Introduction

As petrochemical resources deplete in an alarming rate, producing fuel and other high-value chemicals from renewable biomass has generated sustained interest worldwide. It is an important and challenging path for biomass utilization using selective catalytic routes to process the carbohydrate fractions of lignocellulose to produce valuable platform chemicals [1]. Furfural, derived from lignocellulosic biomass, is a very versatile and key bio-based platform chemical used for the production of important non-petroleum-derived chemicals and the development of new generation of bioplastics [2]. Besides, it is a biofuel precursor and also in high demand in industries including plastics, petroleum refining, agrochemical and pharmaceutical industries [3]. Industrial process for furfural production *via* mineral acid treatment of hemicellulose and high pressure saturated steam stripping of furfural suffered from disadvantages such as low efficiency, high energy consumption, equipment corrosion, severe yield loss due to side-reactions and the generation of acidic effluent, *etc*. Alternative approaches for furfural production investigated recently focused on the development of a variety of different catalysts [4,5] and reaction medium [6,7]. Besides, systems using simultaneous stripping (*e.g.*, N_2 stripping [8]) or extraction (*e.g.*, water/organic solvent biphasic systems [9–11]) for furfural have also been proposed. All the above-mentioned approaches have improved furfural yield and selectivity. However, the production of furfural with minimal carbon footprint route is still a challenging undertaking. Water is definitely a cheap and green solvent for furfural formation. However, the use of water as reaction medium suffers from disadvantages such as low furfural yields and the generation of a large amount of acidic effluent. Recently, due to the negligible vapour pressure, ionic liquids have been widely considered as "green" solvents instead of water or other organic solvents for many reactions including furfural production [7,12,13]. Besides, other unique properties of ionic liquid such as high thermal stability, non-flammability, and good solvent power also make ionic-liquid-phase reactions useful for producing biofuels and biochemicals. However, the inherent toxicity of commonly used ILs has not been investigated thoroughly. More importantly, the application of commonly used ionic liquids on industrial scale is limited, owing to their high costs. More recently, deep eutectic solvents (DES) have drawn increasing attention and are revealed to be a promising alternative to ILs as green media [14,15]. DESs are mixtures of two or three compounds that are capable of forming eutectic liquids, in which choline chloride

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(ChCl) is a commonly used component [16]. Deep eutectic solvents share many characteristics with ILs and have added advantages of low price, low toxicity, bio-degradability, environmental friendliness, ease to prepare on large scale and the elimination of the preliminary purification step. ChCl-based DESs could be obtained by mixing choline chloride with substances having hydrogen bond donors (urea, carboxylic acids, alcohols, *etc.*). In this manuscript, ChCl–oxalic acid, characterized by low toxicological risks, low pollution, reduced mobility, bulk renewable and acidic property, was selected as an alternative media for “greener” furfural production processes.

As for the catalysts employed in the production of furfural, both Brønsted acid and Lewis acid catalysts catalyze the reactions in furfural formation [17]. Recently, metal chloride as catalyst [12,18,19] or additive [20,21] for the conversion of lignocelluloses into furfural have been reported. Metal chloride clearly accelerated the reaction rate of the furfural formation from xylose and it was found that both metal cation and Cl^- ion are responsible for this reaction [20,22]. Additionally, although it had been established that metal chlorides had pronounced influence on xylose isomerization, the presence of Brønsted acid was recently found to facilitate both the dehydration reactions and the furfural selectivity [20]. Thus the combination of a metal chloride and an acid would probably achieve better furfural yields. The ChCl–oxalic acid mixture could play the role of both reaction medium and Brønsted acid catalyst, and it is also a Cl^- ion provider. In addition, industrial processes for furfural production are commonly carried out at temperatures >423 K. If the reactions could be conducted at lower temperatures, energy saving could be substantial. Based on all the reasons above, and with the aim to produce furfural in a milder and more environmentally friendly manner, metal chlorides enhanced production of furfural in ChCl–oxalic acid under mild conditions were investigated in this work. Moreover, one approach to inhibit the formation of humins and thus promote furfural yield and selectivity is to extract furfural simultaneously using an organic solvent as extractant (low boiling solvent is energetically more advantageous, such as MIBK). Therefore reactions in a DES/MIBK biphasic system was also studied in this work to selectively extract furfural from the DES phase to organic phase in order to further enhance the furfural yield.

2. Experimental

2.1. Materials

Xylan (from birch wood, ≥90%) was purchased from Sigma–Aldrich Ltd. D-Xylose (≥98%) and choline chloride (≥99%) were purchased from Acros. $CrCl_3{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$, $AlCl_3{\cdot}6H_2O$, $CeCl_3{\cdot}7H_2O$, $LaCl_3{\cdot}7H_2O$ and oxalic acid were purchased from Tianjin Jiangtian Chemical Co., Ltd. (Tianjin, China). All other chemicals were purchased from Sigma–Aldrich and used without further purification. ChCl–oxalic acid was synthesized according to procedures reported in the literature [23,24]. The molar ratio of choline chloride to oxalic acid was following the report by Hu *et al.* [24].

2.2. Procedure for the reaction in the monophase system

Substrate sample (0.25 mmol), ChCl–oxalic acid (6 mmol based on the acid) and a known amount of metal chloride were loaded into a sealed glass reactor (10 mL). The mixture was then heated in a preheated oil bath and stirred at different temperatures for the desired time. When using xylan as the starting material, 10 mg of H_2O was added into each reactor. After the desired residence time, the reaction was quenched by putting the reactor in cooling water immediately. Samples were then diluted, filtered and then analyzed using HPLC. Reactions heated by microwave irradiation were conducted according to the procedures reported in our previous work [12].

2.3. Procedure for the reaction in the DES/MIBK biphasic system

Experiments were carried out in 10 mL sealed thick-walled glass vessels in a preheated oil bath with magnetic stirring. In a typical experiment, the reactor was charged with required amounts of feedstock, metal chloride, ChCl–oxalic acid and MIBK, these materials were then mixed using a magnetic stirrer and heated to the desired temperature and time. After reaction, the reactor was cooled to room temperature by cooling water immediately. The DES phase and organic phase were separated and collected for analysis.

2.4. Quantification procedure for furfural and xylose

Furfural was determined using HPLC (Agilent 1200) with an Ultraviolet Detector and a XDB-C18 column at 280 nm. The column oven temperature was maintained at 303 K. The mobile phase was acetonitrile/water (15/85, v/v) at a flow rate of 1 mL/min. Quantitative analysis of xylose was performed using HPLC (Waters 1525) equipped with a refractive index detector (Waters 2412) and an aminex HPX-87H column. The column oven temperature was maintained at 338 K. H_2SO_4 (5 mmol/L) was used as the mobile phase at a flow rate of 0.6 mL/min. For HPLC analysis, the samples were filtered with a syringe filter (0.2 μm) prior to analysis.

Conversion of xylose and yields of products were defined as follows:

$$\text{xylose conversion} = \frac{\text{moles of xylose reacted}}{\text{mole of starting xylose}} \times 100\% \tag{1}$$

$$\text{furfural yield (from xylan)} = \frac{\text{moles of furfural produced}}{\text{moles of starting xylan}} \times 100\% \tag{2}$$

$$\text{furfural yield (from xylose)} = \frac{\text{moles of furfural produced}}{\text{moles of starting xylose}} \times 100\% \tag{3}$$

3. Results and discussion

We started our studies by investigating the effect of trivalent metal chlorides in ChCl–oxalic acid in converting xylose into furfural at 373 K. $CrCl_3{\cdot}6H_2O$, $FeCl_3{\cdot}6H_2O$, $AlCl_3{\cdot}6H_2O$, $CeCl_3{\cdot}7H_2O$ and $LaCl_3{\cdot}7H_2O$ were selected as a co-catalyst. As shown in Fig. 1, furfural was formed in ChCl–oxalic acid without an additional metal chloride affording a furfural yield of 14.6%, indicating that DES acted as both a Brønsted acid catalyst and a reaction media. The furfural yields could be improved by combining a metal chloride as the co-catalyst. Amongst all the trivalent metal chlorides tested, $AlCl_3{\cdot}6H_2O$ proved most efficient in producing furfural from xylose, with a 32.4% furfural yield achieved at 74.3% xylose conversion at 373 K in 30 min. For other trivalent metal chlorides, the furfural yields obtained under the typical reaction conditions followed the order of $FeCl_3{\cdot}6H_2O > CrCl_3{\cdot}6H_2O > CeCl_3{\cdot}6H_2O > LaCl_3{\cdot}7H_2O$, leading to furfural yields and xylose conversions in the range of 16%–23% and 61%–69%, respectively.

The mechanism of furfural formation from xylose is still debated and has not been unequivocally established. Specifically, furfural production mechanism may differ when the reaction was catalyzed by different catalysts under different reaction conditions. In this manuscript, a double catalytic effect was achieved by