DOI: 10.1002/cssc.201100588

## Catalytic Conversion of Inulin and Fructose into 5-Hydroxymethylfurfural by Lignosulfonic Acid in Ionic Liquids

Haibo Xie,<sup>\*[a, b]</sup> Zongbao K. Zhao,<sup>[a, b]</sup> and Qian Wang<sup>[a]</sup>

In this work, we found that lignosulfonic acid (LS), which is a waste byproduct from the paper industry, in ionic liquids (ILs) can catalyze the dehydration of fructose and inulin into 5hydroxymethylfurfural (HMF) efficiently, which is a promising potential substitute for petroleum-based building blocks. The effects of reaction time, temperature, catalyst loading, and reusability of the catalytic system were studied. It was found that a 94.3 % yield of HMF could be achieved in only 10 min at

Introduction

The development of the sustainable chemical industry requires the use of sustainable chemical feedstocks, green solvents, green catalysts, and sustainable energy sources for the production of valuable products through chemical reactions; these are key points of the recognized 12 principles of green chemistry.<sup>[1]</sup>With increasing concerns about global warming and energy security due to the overdependence on nonrenewable fossil resources, biomass, which is the largest renewable carbon source on the planet, has been regarded as an important alternative source for the production of fuels, chemicals, and materials.<sup>[2]</sup> Taking lessons from chemical production from fossil resources, currently, greenness is considered as one of the important aspects of new strategies for biomass conversion. For example, 5-hydroxymethylfurfural (HMF) has been recognized as a versatile and key precursor for the production of fine chemicals, polymeric materials, and biofuels.<sup>[3]</sup> In recent years, the preparation of HMF through the dehydration of biomass-based sugars has received much attention, especially in ionic liquids (ILs), due to the good solubility of carbohydrates in ILs.<sup>[3]</sup> Since Zhao et al.<sup>[4]</sup> reported that chromium(II) chloride could catalyze the dehydration of glucose into HMF in 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) with a good yield, much effort has been devoted to developing more efficient and environmentally friendly processes for the conversion of cellulose and glucose into HMF.<sup>[5]</sup> Compared to glucose and other carbohydrates, the production of HMF from fructose has high efficiency and selectivity. Fructose can be obtained by industrial isomerization of glucose or hydrolysis of inulin, which exists in many plants, such as in the roots of chicory.<sup>[6]</sup> Therefore, research into the production of HMF from fructose has been studied extensively for a long time. Many catalysts, such as acidic resin,<sup>[7]</sup> Lewis acids,<sup>[8]</sup> mineral acids,<sup>[9]</sup> organic carboxylic acids,<sup>[5a]</sup> and acidic ILs,<sup>[10]</sup> have been applied to this conversion successfully. Regardless of these developments, it remains 100 °C under mild conditions. The reusability study of the LS–IL catalytic system after removal of HMF by ethyl acetate extraction demonstrated that the catalytic activity decreased from 77.4 to 62.9% after five cycles and the catalytic activity could be recovered after simply removing the accumulated humins by filtration after adding ethanol to the LS–ILs. The integrated utilization of a biorenewable feedstock, catalyst, and ILs is an example of an ideal green chemical process.

a challenge to obtain HMF from carbohydrates in terms of efficiency and greenness. With the aim of developing a green pathway to use biomass in our lab, we are devoted to using green solvents and developing new green catalysts for this purpose.<sup>[11]</sup>

Lignosulfonic acid (LS) is also called sulfonated lignin, which is a highly cross-linked polyphe-

nolic polymer containing sulfonic acid groups. It is an abundant renewable resource and a waste byproduct from the paper industry (Figure 1).<sup>[12]</sup> The development of high-value applications of LS or lignin is one of the most important directions of modern biorefinery.<sup>[13]</sup> Recent research demonstrated that they can be used as proton-transfer materials for fuel cells<sup>[14]</sup> or electrochemistry materials due to their sulfonic acid func-



**Figure 1.** Representative structure of LS.

tionality.<sup>[15]</sup> However, as an acidic renewable polymer, the application of LS as an acidic catalyst is seldom reported.

Herein, we report a novel application of LS as an acidic catalyst for the dehydration of fructose and inulin into HMF in 1butyl-3-methylimidazolium chloride ([Bmim]Cl) (Scheme 1). The combination of using biorenewable resources as feedstocks

 [a] Prof. H. Xie, Prof. Z. K. Zhao, Q. Wang Dalian Institute of Chemical Physics CAS, 457 Zhongshan Road Dalian (P.R. China) Fax: (+ 86) 411-84379211
 E-mail: hbxie@dicp.ac.cn

[b] Prof. H. Xie, Prof. Z. K. Zhao Dalian National Laboratory for Clean Energy Dalian 116023 (P.R. China)



Scheme 1. Conversion of fructose and inulin into HMF catalyzed by LS in ILs.

and catalysts, using green solvents, and the production of valuable chemicals presents an ideal green chemical process.

### **Results and Discussion**

Lignin is an amorphous, polyphenolic polymer arising from the polymerization of phenylpropanoid monomers, including coniferyl, sinapyl, and p-coumaryl alcohol. It was found that ILs of the [Bmim]<sup>+</sup> cation with a range of anions, such as [MeSO<sub>4</sub>]<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and PF<sub>6</sub><sup>-</sup>, had good solubility to kraft pulp lignin. The solubility was up to  $312 \text{ gL}^{-1}$  at  $50 \,^{\circ}\text{C}$  in [Bmim][MeSO<sub>4</sub>], whereas the solubility decreased to 13.9 g L<sup>-1</sup> in [Bmim]Cl even at 75 °C.<sup>[16]</sup> Lignosulfonic acid is sulfonated lignin; in this study, it was found that it was easy to prepare a 2.5 wt% solution of LS in [Bmim]Cl at 100 °C in 5 min and a brown-red homogeneous solution was obtained. However, an increase in LS concentration from 2.5 to 4.0 wt% required more time. Elemental analysis of the LS showed that there was one sulfonic acid group in every two C9 lignin representative units; therefore, the LS can be regarded as an acidic polyphenolic polymer with a degree of substitution of 0.5. The full solubilization of LS in [Bmim]Cl results in an acidic solution, which is anticipated to be potential reaction media for acid-catalyzed conversions. The dehydration of carbohydrate to produce valuable chemicals, such as HMF, is a typical acid-catalyzed process,<sup>[3]</sup> furthermore, the catalytic conversion of carbohydrate is attracting extensive attention because of the good solubility of carbohydrates in ILs and the unique properties of ILs for catalysis.<sup>[17]</sup> The first thought that comes to mind is whether LS is an effective catalyst for the dehydration of carbohydrates. As shown in Figure 2, an HMF yield of 88.5% was achieved in only 5 min when 10 wt% of fructose was added into the 2.5 wt% LS-[Bmim]Cl solution at 100 °C. Prolonging the reaction time to 10 min resulted in an increase in HMF yield of 93.4%. However, further prolongation of the reaction time led to decreased yields; this was likely to result from degradation and polymerization of HMF,<sup>[18]</sup> as evidenced by the formation of visually observed black humins. The yields were sustained at around 85% after 15 min.

It was found that the application of [Bmim]Cl as a solvent was significant and promoted the dehydration of fructose into HMF. Other conventional solvents, such as DMA, DMSO, and NMP, were also relatively good because the dehydration reaction was slower (Figure 2). HMF yields of 50.9, 30.9, and 16.6% are achieved in 10 min under identical conditions in DMSO, NMP, and DMA, respectively. A maximum HMF yield of 79.6% was obtained in DMSO after 40 min. Clearly, NMP and DMA

are less effective in this study with HMF yields of 52.7 and 39.6%, respectively, after 60 min. As shown in Figure 3, ion chromatography analysis demonstrated that the conversion of fructose and selectivity to HMF were 98.3 and 95.0%, respectively, after 10 min at 100 °C in ILs, and the dehydration of fructose into HMF was almost quantitative. As the yields decreased



**Figure 2.** The effect of solvents on the catalytic conversion of fructose into HMF by LS. Experimental conditions: solvent (2.0 g), fructose (0.2 g), LS (0.05 g), 100 °C. DMA = dimethylacetamide, DMSO = dimethylsulfoxide, and NMP = *N*-methyl-2-pyrrolidone.



Figure 3. HMF yields, selectivity, and conversion of fructose catalyzed by LS in ILs. Experimental conditions: [Bmim]Cl (2.0 g), fructose (0.2 g), LS (0.05 g),  $100^{\circ}$ C.



Figure 4. Conversion of fructose, selectivity, and yields of HMF in different solvents. Experimental conditions: solvent (2.0 g), fructose (0.2 g), LS (0.05 g), 100 °C, 40 min.

after 10 min, the selectivity also decreased to 85.9% after 40 min.

The conversion of fructose in DMSO, NMP, and DMA was consistent with the trends in HMF yields in these solvents and a series of comparative results are shown in Figure 4. It was found that although the reaction rate was slower in DMSO than that in [Bmim]Cl, a satisfactory conversion of 97.4% and a moderate selectivity of 81.7% were achieved in 40 min, which led to a yield of 79.6%. Although the conversion of fructose was up to 91% in NMP, an HMF yield of only 52.4% was obtained due to a low selectivity of 57.6%. In DMA under identical conditions, only 72.4% conversion and 48.3% selectivity were obtained; these values were consisted with the low HMF yield of 35.0%. The results demonstrate that [Bmim]Cl and DMSO can suppress the formation of humins during the dehydration of fructose into HMF catalyzed by LS; furthermore, ILs can facilitate the dehydration process, which presents a faster dehydration reaction than that in traditional organic solvents and is consistent with previous publications.<sup>[19]</sup>

With the aim of optimizing the catalytic system, the effect of catalyst loading was studied (Figure 5). An HMF yield of only



**Figure 5.** The effect of catalyst loading on the dehydration of fructose into HMF in ILs. Experimental conditions: [Bmim]Cl (2.0 g), fructose (0.2 g), LS (0.05 g), 100  $^{\circ}$ C, 10 min.

75.2%, a selectivity of 77.0%, and a conversion of 97.7% were obtained when 10 mg of LS (0.5 wt% LS–IL solution) was used for 10 min. It seems that 20–50 mg of LS (1.0–2.4 wt% LS–IL solution) is a favorable catalyst loading for satisfactory fructose conversion, HMF yield, and selectivity, for example, a yield of 90.3%, fructose conversion of 98.7%, and a selectivity of 91.5% was obtained for the dehydration in 1.0 wt% LS–IL solu-

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tion. Further increasing the catalyst loading to 80 mg resulted in a decrease in HMF yield to 86.7%; this demonstrated that the higher catalyst concentration could facilitate both the dehydration of fructose and the degradation of HMF. Although the conversion of fructose increased to 98.8%, the selectivity decreased to 87.8%.

The effect of temperature was also studied (Figure 6). Lower reaction rates were observed when the reaction was performed at  $80^{\circ}$ C, for example, an HMF yield of only 53.7% was



Figure 6. The effect of reaction temperature on the yield of HMF from fructose catalyzed by LS. Experimental conditions: [Bmim]Cl (2.0 g), fructose (0.2 g), LS (0.05 g),  $100 \degree$ C, 10 min.

obtained in 10 min; however, HMF yields were 93.4 and 88.0% in 10 min at 100 and 120 °C, respectively. High temperature not only facilitated the dehydration of fructose to HMF, but also facilitated the formation of humins, as proved by the lower yields obtained when the reaction was performed at 120 °C. Although a low reaction rate was observed at 80 °C, the yield reached 89.7% after 40 min, which was higher than those at 100 and 120 °C after 40 min. This further demonstrates the effect of reaction temperature on the formation of humins.

The tolerance for the concentration of feedstock is an important aspect to evaluate a catalytic conversion process from an economical point of view. The effect of fructose concentration was also investigated, and the results are shown in Figure 7. It was found that the HMF yield decreased with increasing fructose concentration. For example, the yields were 92.7, 88.0, 84.1, and 73% in 10 min, respectively, when 5, 10, 25, and 50 wt%, respectively, of fructose were used. After 40 min, the remaining fructose was analyzed by ion chromatography, and the results showed that over 98% of fructose was consumed;



**Figure 7.** The effect of fructose concentration on the dehydration of fructose into HMF in ILs catalyzed by LS. Experimental conditions: [Bmim]Cl (2.0 g), LS (0.05 q), 120  $^{\circ}$ C.

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however, the corresponding HMF yields were 91.7, 85.9, 80.2, and 74.0%. High concentrations of HMF in ILs can promote the degradation and/or polymerization of HMF; this is supported by the increasing amount of humins (0.007, 0.019, and 0.046 g) precipitated by the addition of water (20 mL) to the reaction mixture.

Inulin is an indigestible oligosaccharide consisting of fructose and is available in large quantities. The hydrolysis of inulin can produce fructose that can be further converted into HMF. Both processes can be catalyzed by acids; therefore, the integration of the hydrolysis of inulin and the dehydration of fructose in one pot is logically possible and avoids the production of fructose and the corresponding operation costs. Therefore, the one-pot conversion of inulin into HMF has been investigated widely.<sup>[5a]</sup> In this study, we found that inulin had a good solubility in [Bmim]Cl at 100 or 120 °C, and a 10 wt% viscous solution of inulin in ILs can be easily prepared in 5 min. Figure 8 demonstrates the relationship between HMF yields and reac-



Figure 8. Catalytic conversion of inulin into HMF by LS in ILs. Experimental conditions: [Bmim]Cl (2.0 g), inulin (0.2 g), water (40  $\mu$ L), LS (0.05 g), 120 °C, 10 min.

tion times under identical conditions for the integrated catalytic conversion of inulin in a 2.5 wt% IL solution. It was found that consecutive hydrolysis was very fast, with a maximum yield of 47.0% achieved in only 5 min, and the yield could be sustained at this level, even with prolonging the reaction time to 90 min. It is worthy mentioning that, as the hydrolysis of inulin needs the participation of water, the comparative results in Figure 8 demonstrate that the addition of H<sub>2</sub>O (40  $\mu$ L) does not affect the reaction, with comparative yields obtained. It is believed that the dehydration of one molecule of fructose produces three molecules of H<sub>2</sub>O, which is sufficient for the previous hydrolysis of inulin into fructose; therefore, external water is not necessary.

The recycling of the LS–IL system was investigated after extracting HMF with ethyl acetate ( $3 \times 10$  mL) and adding fresh fructose to the mixture. The HMF yields for each reaction run in ILs and the amount of HMF extracted by ethyl acetate are shown in Figures 9 and 10, respectively. The results in Figure 9 show that, after reusing the LS–IL catalytic system four times, the HMF yield decreases from 77.4 to 62.9%, which demonstrates that the humins formed and accumulated during the reaction affect the catalytic activity of LS in ILs. Hu et al. reported that the accumulated residues can be precipitated from the IL phase by adding ethanol because ILs are soluble, whereas



Figure 9. Reusability of the catalytic system after HMF separation by ethyl acetate extraction. Experimental conditions: [Bmim]Cl (2.0 g), LS (0.05 g), fructose (0.5 g), 120 °C, 10 min.

the humin formed is insoluble in ethanol.<sup>[20]</sup> Therefore, ethanol (10 mL) was added into the LS–IL system after five cycles. The precipitated humins were filtered and the catalytic system was submitted to the next reaction after removal of ethanol and a 76.7% yield of HMF was obtained (Figure 9, run 5), which demonstrated that the LS–IL system could be reused after simply removing the accumulated humins after five cycles.

Although many publications demonstrated that the separation of HMF from ILs could be fulfilled by extraction with ethyl acetate and THF, more details of the real extraction process are limited.<sup>[5a]</sup> Our results presented in Figure 10 show that the extraction efficiency of ethyl acetate depends on the concentration of HMF in the IL. It was found that for the first run, there



Figure 10. The amount of HMF separated by extraction with ethyl acetate (3  $\times$  10 mL). Experimental conditions: [Bmim]Cl (2.0 g), LS (0.05 g), fructose (0.5 g), 120 °C, 10 min.

was 0.27 g HMF after the reaction, but only 0.08 g HMF could be extracted with ethyl acetate ( $3 \times 10$  mL). After removing the remaining ethyl acetate in the IL in vacuo, fresh fructose was added into the LS–IL solution, and the mixture was treated under identical conditions. With the accumulation of HMF in the IL, the extraction efficiency increases. The amounts of HMF extracted with ethyl acetate for runs 1–4 were 0.18, 0.25, 0.30, and 0.28 g, respectively.

## Conclusions

The dissolution of LS in ILs is efficient for the acid-catalyzed dehydration of fructose into HMF and even inulin into HMF in a one-pot reaction. The yield of HMF from fructose was up to 93.4% in only 10 min under mild conditions. The reusability study of the LS-IL catalytic system after removing HMF with ethyl acetate extraction demonstrated that the catalytic activity decreased from 77.4 to 62.9% after five cycles, and the catalytic activity can be recovered after simply removing the accumulated humins by filtration after adding ethanol to the LS–ILs. The combination of using renewable feedstocks, renewable organic catalysts, green solvents, and the production of valuable platform chemicals in this study presents an ideal chemical conversion process following the principles of green chemistry. We believe that this highly efficient and green route for the production of valuable chemicals from biomass has great potential for applications.

## **Experimental Section**

#### Materials

The ionic liquid (IL) 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) was supplied by Lanzhou Greenchem ILS, LIPC, CAS (Lanzhou, China). Drying was performed under vacuum at 80 °C for 10 h to remove absorbed water in the IL. Fructose was purchased from Sanland-Chem International (Xiamen, China). Inulin was purchased from Acrose. Acetonitrile (HPLC grade) was purchased from Merck (Darmstadt, Germany). All other chemicals were supplied by local suppliers and used without further purification. The sodium salt of LS was purchased from Sigma Aldrich. The acidic cation exchange resin (001  $\times$ 7) was purchased from the Chemical Plant of Nankai University (Tianjin, China).

#### Preparation of lignosulfonic acid

The acidic resin was activated in a saturated aqueous solution of NaCl for 1 day, followed by treatment with a 2.5 wt% aqueous solution of NaOH for 80 min, then it was washed with distilled water until the pH became 7, and finally it was treated with a 5 wt% aqueous solution of HCl for 12 h. Then the resin was transferred to a column and washed with deionized water until the eluent had a pH value of 7. The sodium salt of lignosulfonic acid (LS, 10.0 g) was dissolved in water (200 mL), and the solution was allowed to flow through the acidic resin column at a speed of 60 drops per minute. The acidic eluent was collected and yellow LS (7.8 g) was obtained after freeze-drying the solution. Yield: 78.3%; elemental analysis of  $[C_{18}H_{22.4}O_{11}SN_{0.14}]_n$ : found: C 47.77, H 4.94, O 39.14, S 7.69, N 0.46.

#### 5-Hydroxymethylfurfural production

In a typical run, LS (50 mg) was added to [Bmim]Cl (2.0 g) to produce a homogenous LS–IL solution in 5 min. Fructose (0.2 g) was added to the mixture, which was heated at a specified temperature for the desired time under atmospheric pressure with a magnetic stirrer. Samples were withdrawn, diluted with water, centrifuged at 10000 rpm for 5 min, and analyzed by means of HPLC.

#### Determination of 5-Hydroxymethylfurfural

HPLC analysis of 5-Hydroxymethylfurfural (HMF) was performed on a Dionex system (Dionex, CA, USA) equipped with Dionex P680 four-unit pump and UVD 170U detector. The samples were separated by using a reversed-phase C<sub>18</sub> column (200×4.6 mm) at  $\lambda$ = 280 nm. The column temperature was maintained at 30 °C. The optimized mobile phase consisted of acetonitrile and a 0.1 wt% aqueous solution of acetic acid with a volume ratio of 15:85. The flow rate was set at  $1.0 \text{ mLmin}^{-1}$ .

#### **Determination of fructose**

The ion chromatography system was from Dionex. The hardware consisted of an ICS-2500 system equipped with a GP50 gradient pump, an ED50A integrated amperometry detector, a CarbonPac PA10 guard column (4 mm×50 mm), a high capacity CarbonPac PA20 analytical column (3 mm×150 mm), and a 25 mL sample loop. Samples were eluted with 30 mm NaOH at a rate of 0.5 mLmin<sup>-1</sup>.

**Keywords:** biomass · green chemistry · ionic liquids · 5hydroxymethylfurfural · lignosulfonic acid

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Received: September 22, 2011

Revised: December 1, 2011

Published online on April 19, 2012