



# Direct conversion of lignocellulose to levulinic acid catalyzed by ionic liquid

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## ABSTRACT

Acidic ionic liquid (IL) [C<sub>3</sub>SO<sub>3</sub>Hmim]HSO<sub>4</sub> was applied to catalyze lignocellulose conversion to levulinic acid (LA) in one pot with high selectivity under hydrothermal conditions. Through the optimization of reaction conditions, the highest yield of LA is 96.6 mol% (21.6 wt%) based on the amount of C<sub>6</sub>-sugars in the straw. The relationship between IL structure and LA yield was established, disclosing that acidity and hydrogen bonding ability of anions are crucial to the yield of LA. Moreover, the LA product can be readily separated through extraction by methyl isobutyl ketone (MIBK) and IL can be reused over 5 cycles without loss of activity. In addition, the chemical structures and morphologies of the solid residues were investigated by DTG, SEM and IR, demonstrating the gradual conversion process of cellulose and hemicellulose accompanied by the formation of humin byproducts, whereas the lignin fraction of the straw sustains the scaffold structure without modifications during the reaction.

## 1. Introduction

Lignocellulosic biomass is the most abundant natural feedstock and the only renewable resource of fixed carbon as well. Due to diminishing fossil resources and increasing concern about sustainable development, production of fuels and chemicals from lignocellulosic biomass has come to prominence (Ragauskas et al., 2006). As one of the twelve platform chemicals proposed by the US Department of Energy, levulinic acid (LA) is a versatile building block for the synthesis of various organic compounds that can be used as fuel additives, herbicides, pharmaceutical agents, flavor substances, or precursors in the polymer and resin industries (Rackemann & Doherty, 2011). Recent work further demonstrated that LA can supplement as initial feedstock for existing petrochemical processing operations, connecting biomass and petroleum processing together (Bozell, 2010). Therefore, production of LA from lignocellulose has become one of the key steps in biomass conversion.

Lignocellulose is comprised of three major constituents, including cellulose, hemicellulose and lignin. The recalcitrant structure of lignocellulose requires pretreatment in biochemical transformation to enhance the enzyme accessibility so as to catalyze the conversion more efficiently. Meanwhile, chemical transformation has attracted increasing attentions. Initially converting lignocellulose to LA (Morone, Apte, & Pandey, 2015; Rackemann & Doherty, 2011) has been achieved by using mineral acids, such as H<sub>2</sub>SO<sub>4</sub> (Chang, Cen, & Ma, 2007; Girisuta, Danon, Manurung, Janssen, & Heeres, 2008; Runge & Zhang, 2012) and HCl (Galletti, Antonetti, De Luise, Licursi, & Di Nasso, 2012;

Yan, Yang, Pang, & Liao, 2008), whereas the acids are difficult to recycle and additional steps of neutralization are necessary. To overcome the disadvantage, many other catalysts were developed to convert lignocellulose biomass to LA. A solid superacid, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/ZrO<sub>2</sub>-SiO<sub>2</sub>-Sm<sub>2</sub>O<sub>3</sub>, has been used to produce 70 mol% of LA from steam exploded rice straw (Chen, Yu, & Jin, 2011). Ya'aini, Amin, and Asmadi (2012) proposed a new hybrid catalyst comprising CrCl<sub>3</sub> and HY zeolite to convert empty fruit bunch and kenaf, leading to 53 mol% and 66 mol% of LA, respectively. Alonso, Gallo, Mellmer, Wettstein, and Dumesic (2013) applied Amberlyst 70 to convert corn stover into LA (54 mol%) using gamma-valerolactone (GVL)/water (90/10 wt%) as the solvent. However, it is still challenging to recycle the heterogeneous catalysts mainly due to the presence of unconverted lignin fraction and solid byproduct humins, which are inclined to mix with the solid catalysts and difficult to separate.

Ionic liquids (ILs) are distinctive of tunable solubility so as to recyclability, which have opened up vast possibilities in biomass research (Brandt, Grasvik, Hallett, & Welton, 2013; da Costa Lopes et al., 2013; Song, Fan, Ma, & Han, 2013; Verdia, Brandt, Hallett, Ray, & Welton, 2014; Zakrzewska, Bogel-Lukasik, & Bogel-Lukasik, 2011), ever since the pioneer report of dissolving cellulose in [C<sub>4</sub>mim]Cl by Swatloski, Spear, Holbrey, and Rogers (2002). So far, a great number of studies have been directed upon applying ionic liquids to convert lignocellulosic biomass into chemicals (Zhang, Song, & Han, 2017). For example, Li, Wang, and Zhao (2008) used [Bmim]Cl as solvent and HCl as catalyst to hydrolyze lignocellulosic biomass into total reducing sugars (TRS) of 81 wt%. Binder and Raines (2010) hydrolyzed corn stover

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leading to 66 mol% yield of glucose and 75 mol% of xylose, using HCl in [Emim]Cl. Watanabe (2010) reported that yields of TRS, glucose and ethanol are 25.6 wt%, 11.5 wt% and 7.7 wt%, respectively, by use of Dowex 50WX8 to depolymerize wood in [Bmim]Cl. Sievers et al. (2009) applied trifluoroacetic acid (TFA) in [Bmim]Cl to hydrolyze pine wood and obtained water-soluble products including monosaccharides, oligosaccharides, furfural, and 5-hydroxymethylfurfural (HMF). Vanoye, Fanselow, Holbrey, Atkins, and Seddon (2009) adopted methanesulfonic acid in [Emim]Cl for hydrolysis of Miscanthus grass yielding glucose, xylose, furfural and HMF. The selective production of HMF from corn stover in 48 mol% yield has been reported using  $\text{CrCl}_3/\text{HCl}/[\text{Emim}]\text{Cl}$  in DMA-LiCl (Binder & Raines, 2009). In the absence of Brønsted acid HCl, the catalytic system  $\text{CrCl}_3/[\text{Bmim}]\text{Cl}$  was reported leading to higher HMF yield of 52 mol% from pine wood under microwave irradiation for 3 min (Zhang & Zhao, 2010). A combination of  $\text{CrCl}_3/\text{LiCl}/[\text{Bmim}]\text{Cl}$  could raise the HMF yield to 61.4 mol% from wheat straw under microwave irradiation for 15 min (Wang, Yu, Zhan, & Wang, 2011).

Recently, we employed  $\text{SO}_3\text{H}$ -functionalized acidic ionic liquids in the direct conversion of cellulose to LA, leading to a high yield of 86 mol% (Ren, Zhou, & Liu, 2013). Our efforts highlighted the tributes of ionic liquids capable of combining the advantages of homogeneous and heterogeneous catalysts, facilitating the product separation and catalyst reuse (Amarasekara, 2016; da Costa Lopes & Bogel-Lukasik, 2015). Herein, we explored the direct conversion of lignocellulosic biomass to LA by catalysis of acidic ionic liquids. The selection of the biomass feedstock is of paramount importance from both techno- and socio-economical points of view. In this work, straw was chosen because it does not compete with food production. On the other hand, as agriculture wastes, millions of tons of straw produced are discarded or incinerated in the fields, which cause severe environmental pollution problems. If the straw could be directly used to produce chemicals, costs will decrease greatly, which is also significantly beneficial to the environmental protection.

## 2. Materials and methods

### 2.1. Materials and equipments

The rice straw was obtained from local farmland (Dalian, China), which was washed with water to remove dirt and dried at 80 °C for 24 h. The dried straw was then milled and sieved to 80-mesh (0.18 mm) before use. 1,3-Propane sultone and 1-methylimidazole were purchased from Energy Chemical Co., Ltd. (Shanghai, China) and freshly distilled before use. Six ionic liquids including 1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate ( $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$ ), 1-methyl-3-(3-sulfopropyl)imidazolium dihydrogen phosphate ( $[\text{C}_3\text{SO}_3\text{Hmim}]\text{H}_2\text{PO}_4$ ), 1-methyl-3-(3-sulfopropyl)imidazolium methanesulfonate ( $[\text{C}_3\text{SO}_3\text{Hmim}]\text{CH}_3\text{SO}_3$ ), 1-methyl-3-(3-sulfopropyl)imidazolium phenylsulfonate ( $[\text{C}_3\text{SO}_3\text{Hmim}]\text{PhSO}_3$ ), 1-methyl-3-(3-sulfopropyl)imidazolium 1-naphthalenesulfonate ( $[\text{C}_3\text{SO}_3\text{Hmim}]\text{1-NS}$ ) and 1-methyl-3-(3-sulfopropyl)imidazolium chloride ( $[\text{C}_3\text{SO}_3\text{Hmim}]\text{Cl}$ ) were prepared according to literature (Ren, Girisuta, Zhou, & Liu, 2015) and characterized by NMR prior to use (Supplementary data). Other chemicals were purchased from local suppliers and used without further purification. The NMR spectra were recorded on Bruker Avance II 400 MHz spectrometer. The scanning electron microscopy images were obtained on NOVA NanoSEM 450 field emission scanning electron microscopy, wherein samples were pre-coated with a thin Aurum film. The infrared spectra were recorded on Bruker Equinox 55 infrared spectrometer. UV–vis spectra were recorded on HP-8453 spectrophotometer. Dionex ICS-5000 ion chromatography was equipped with IPAD detector and CarboPac PA20 column (30 °C), whereas an aqueous solution of NaOH (2.0 mM) at a flow rate of 0.45 mL/min was used as mobile phase. Thermogravimetric analysis (TGA) was done using a Mettler Toledo model SDTA 815 under nitrogen flows from room temperature to 600 °C with a heating ramp of 10 °C  $\text{min}^{-1}$ .

### 2.2. Characterisation of the straw

Initially, the straw was extracted using ethanol in Soxhlet apparatus for 24 h, whereby the extractives were dried under vacuum at 80 °C for 8 h. Then two-stage acid-catalyzed hydrolysis (Sluiter et al., 2010) was used to quantify the amounts of C5- and C6-sugars. At the first stage, the straw was hydrolyzed in a concentrated solution of sulfuric acid (72 wt%) at 30 °C for 4 h. At the second stage, the reaction mixture was diluted to obtain an acid concentration of 4 wt%, and hydrolyzed at 130 °C for 4 h. The liquid phase was filtered, neutralized with  $\text{CaCO}_3$ , and then sent to ion chromatography for determining the carbohydrate contents.

### 2.3. General procedure for straw conversion

In a typical procedure, straw, ionic liquid and de-ionized water were mixed in an autoclave of stainless steel with Teflon lining and heated in an oil bath maintained at the desired temperature for a specified length of time with magnetic stirring. And then the reaction was quenched in an ice bath. After filtration of solid residues and removal of water by rotary evaporation at 50 °C for 5 min, the crude product was analyzed by  $^1\text{H}$  NMR using ionic liquid as internal standard, whereas  $\text{H}_2$  and  $\text{H}_{\text{c,d}}$  were used for integration of LA (Fig. A.1, Supplementary data) and IL, respectively (Fig. 1). The  $^1\text{H}$  NMR spectra were attained at  $296 \pm 0.5$  K, using 12  $\mu\text{s}$  pulse width and 1 s delay time. A total of 32 scans were collected. All spectra were referenced relative to residual HOD at 4.79 ppm. The yield of LA on a weight base was calculated from the equation:  $Y_{\text{LA}} (\text{wt}\%) = (\text{mass of LA})/(\text{total mass of the straw}) \times 100\%$ . The yield of LA on a molar base was calculated from the equation:  $Y_{\text{LA}} (\text{mol}\%) = (\text{mol of LA})/(\text{mol of C6-sugars in the straw}) \times 100\%$ . All the results were replicated at least three times. The analytical error was evaluated to be within 5% on the basis of standard samples of known concentrations. The solid residues were separated from the reaction mixture by filtration, oven-dried, and weighed.

### 2.4. Reuse of IL

For the first run, the reaction of straw (250 mg),  $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$  (1.000 g) and de-ionized water (2.000 g) were heated in a 10 mL autoclave at 180 °C for 1.5 h, whereby the crude product was analyzed by  $^1\text{H}$  NMR using ionic liquid as internal standard. After filtration of solid residue, the aqueous solution of IL was extracted by MIBK 60 mL  $\times$  3, and dried under high vacuum. Afterwards, the IL was added to 1.000 g by supplementing fresh IL of no more than 5% and reused in the next cycle as above.

## 3. Results and discussion

### 3.1. The effects of reaction conditions on LA yield

To gain insights into the effects of reaction temperature and time on lignocellulose conversion, a series of experiments were carried out in 10 mL autoclaves at temperatures ranging from 160 to 180 °C, during the reaction course of 0.5–2.5 h, with 1.000 g of  $[\text{C}_3\text{SO}_3\text{Hmim}]\text{HSO}_4$ , 2.000 g of  $\text{H}_2\text{O}$  and 250 mg of straw. As shown in Fig. 2, the yield of LA increased with the rise of reaction temperature from 160 to 180 °C within the first hour, indicating faster reaction at higher temperature. Then the yields of LA reached a maximum plateau of ca. 17 wt% after 1.0 h, 1.5 h and 2.0 h, for 180, 170 and 160 °C, respectively, suggesting it takes longer period of reaction time to achieve the maximum yield at lower temperature. When the reaction temperature ascended further to 190 °C, the maximum yield decreased slightly to 16.3 wt%. To assure the completeness of the reaction concurrently with shortening the reaction time, the optimum reaction temperature was determined to be 180 °C.

Water is vital to the hydrothermal conversion of lignocellulose to LA

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