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Liquefaction of sawdust in 1-octanol using acidic ionic liquids as catalyst

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HIGHLIGHTS

- A series of acidic ionic liquids (AILs) containing HSO_4^- were synthesized.
- The AILs was firstly applied to the liquefaction of sawdust in 1-octanol.
- The liquefaction of sawdust was improved with AILs acidity increasing.
- The acidic ionic liquid [BsMIM]HSO_4 exhibited excellent catalytic performance.

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ABSTRACT

Acidic ionic liquids (AILs) as a novel catalyst in biomass liquefaction can accord with the demand of green chemistry and enhance the development of biomass thermal chemical conversion. A series of AILs containing HSO_4^- were synthesized by the imidazolium cation functionalization and applied to the Chinese fir sawdust liquefaction in 1-octanol in this paper. The experimental results showed that the liquefaction rate was gradually improved with the AILs acidity increasing, and reached 71.5% when 1-(4-sulfobutyl)-3-methylmidazolium hydrosulfate was used as catalyst with the 6:1 mass ratio of 1-octanol to sawdust at 423 K after 60 min. Lignin, hemicellulose and cellulose were orderly desquamated, and then depolymerized and liquefied with the catalyst acidity increasing in the sawdust liquefaction process. The light oil was mainly composed of the octyl ether and the octyl ester compounds, suggesting that the solvent may play an important role in producing the high octane rating biofuel.

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1. Introduction

Sawdust of Chinese fir, an abundant residual forest biomass in Southern China, has not been utilized effectively and is often direct combustion, resulting in energy waste and environmental pollution. Therefore, it is significant to exploit the residual to acquire biofuel and valuable chemicals by the conversion techniques, including pyrolysis, gasification, liquefaction, fermentation. The liquefaction of biomass has attracted people's attention because of its relatively mild reaction conditions and high efficiency, particularly when sulfuric acid was used as catalyst in high-boiling point alcoholic solvents (Yip et al., 2009; Jin et al., 2011). It has been reported that 1-octanol as the liquefaction solvent could dramatically improve the octane rating of the liquefaction product (Zou et al., 2009, 2011). In these works, sulfuric acid was commonly used as catalyst and exhibited excellent catalytic performance. However, these conventional strong acid catalysts do not accord with the demand of the green chemistry due to their oxidation, corrosion and difficulty in recovery. Thus, much research work has been endeavored to explore the novel liquefaction catalyst such as ionic liquid (Zhang and Zhao, 2010; Nakamura et al., 2010) and solid acid (Fisk et al., 2009; Peng et al., 2009; Yang et al., 2011).

Recently, acidic ionic liquids (AILs) as green chemical solvents and catalysts have been applied to cellulose dissolution (Swatloski et al., 2002; Fukaya et al., 2008) and wood liquefaction (Xie and Shi, 2006; Guo et al., 2011; Wang et al., 2011; Long et al., 2011), owing to their excellent physicochemical properties, such as less corrosion, high acid density, uniform catalytic active center and so on. Xie (Xie and Shi, 2006) reported that wood could be completely liquefied in 3,3′-ethane-1,2-diylbis(1-methyl-1*H*-imidazol-3-ium) dichloroaluminate ionic liquid at 120 °C for 25 min, Whereas the terrible deliquescence of the ionic liquids with chloroaluminate anion always induces the acidity to vary. Recently, Wang (Wang et al., 2011) demonstrated the production of 5-hydroxymethylfurfural from cellulose catalyzed by solid acids and metal chlorides in the ionic liquid of 1-butyl-3-methylimidazolium chloride under microwave irradiation. Especially, Li group (Long et al., 2011) re-

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ported that SO_3H-, COOH-functionalized and HSO_4^- paired imidazolium ionic liquids are proved to be efficient catalysts for bagasse liquefaction in hot compressed water, that the liquefaction rate of bagasse is 96.1% and the selectivity of low-boiling biochemicals is 50.6% at 543 K in SO_3H-functionalized ionic liquid. These valuable results show that taking advantage of the functionalization technique, AILs can achieve the greater efficiency in the catalytic liquefaction process of biomass.

In order to explore an effective and green catalyst for biomass liquefaction in alcohol solvent, in this paper, a series of AILs containing HSO_4^- were synthesized by the imidazolium cation functionalization of and applied to the catalytic liquefaction of Chinese fir sawdust 1-octanol. In addition, the catalytic performance of the AILs and the liquefaction process of sawdust in 1-octanol were investigated by the analysis of the liquefaction product.

2. Methods

2.1. Materials

Prior to use, Fir sawdust, obtained from a wood processing factory in Fuzhou, China, was sieved to a particle size of 40–60 mesh, and then dried in an oven at 378 K until constant weight. According to Chinese GB/T 2677 standard, the composition of sawdust in terms of cellulose, hemicellulose, lignin and ash was performed for two samples, respectively. The final result obtained by averaging the experimental data showed that the dried sawdust composed of 41.01% cellulose, 27.09% hemicellulose, 30.24% acid-insoluble lignin and 1.66% ash. *N*-methylimidazole supplied by Alfa Aesar Co. Ltd., Beijing, China, was redistilled before used. Other chemicals were analytical reagent grade and used without any further purification.

2.2. Synthesization of acidic ionic liquids

Four kinds of the AILs (Fig. 1), 1-methylimidazolium hydrosulfate ([Mim]HSO_4), 1-butyl-3-methylimidazolium hydrosulfate ([Bmim]HSO_4), 1-(4-sulfopropyl)-3-methylimidazolium hydrosulfate ([Psmim]HSO_4) and 1-(4-sulfobutyl)-3-methylmidazolium hydrosulfate ([Bsmim]HSO_4) were synthesized according to the previous literatures (Naydenov and Bart, 2007; Tajik et al., 2009; Xie et al., 2008; Gui et al., 2004). Their molecular structures were confirmed by the data of ^{13}C NMR (126 MHz, MeOD) as follows: [Mim]HSO_4, δ (ppm) 137.29, 124.81, 121.25, 36.54; [Bmim]HSO_4, δ (ppm) 138.17, 125.26, 123.97, 50.90, 36.88, 33.40, 20.72, 14.03; [Psmim]HSO_4, δ (ppm) 138.53, 125.34, 123.95, 49.81, 36.83, 29.35, 27.31; [Bsmim]HSO_4, δ (ppm) 138.33, 125.29, 123.97, 51.80, 50.57, 36.79, 30.12, 22.94.

2.3. Liquefaction of fir sawdust

The liquefaction of sawdust was carried out in a 300 ml stainless-steel autoclave. In a typical run, 10 g of sawdust, 8.6 mmol catalyst (H_2SO_4 or AILs) and 60 g 1-octanol were loaded into reactor which was purged three times with N_2. The autoclave was heated to the desired temperature with 4 K/min first, and then cooled abruptly after maintained for 60 min. The procedure for the separation of liquefaction products is shown in Fig. 2. The products were rinsed from the autoclave with 30 mL acetone, and separated by a series of filtration and extraction into three fractions: solid residue (SR), biomass oil (BO) and water soluble products (WS). The AILs could be recycled partially after extracted from aqueous solution with CH_2Cl_2. The SR was dried in an oven at 378 K until constant weight. The liquefaction rate of sawdust (Y_L) was calculated according to Eq. (1), and the mass percentage of SR, BO and WS (Y_{SR}, Y_{BO} and Y_{WS}) in the liquefaction products were acquired from Eqs. (2)–(4), respectively.

$$Y_L = \left(1 - \frac{M_{SR}}{M_S}\right) \times 100\% \tag{1}$$

$$Y_{SR} = \frac{M_{SR}}{M_{LP}} \times 100\% \tag{2}$$

$$Y_{BO} = \frac{M_{BO}}{M_{LP}} \times 100\% \tag{3}$$

$$Y_{WS} = \frac{M_{WS}}{M_{LP}} \times 100\% \tag{4}$$

where, M_S is the mass of feed sawdust (10 g); M_{SR}, M_{BO} and M_{WS} are the mass of SR, BO and WS, respectively; M_{LP} equals the total mass of SR, BO and WS.

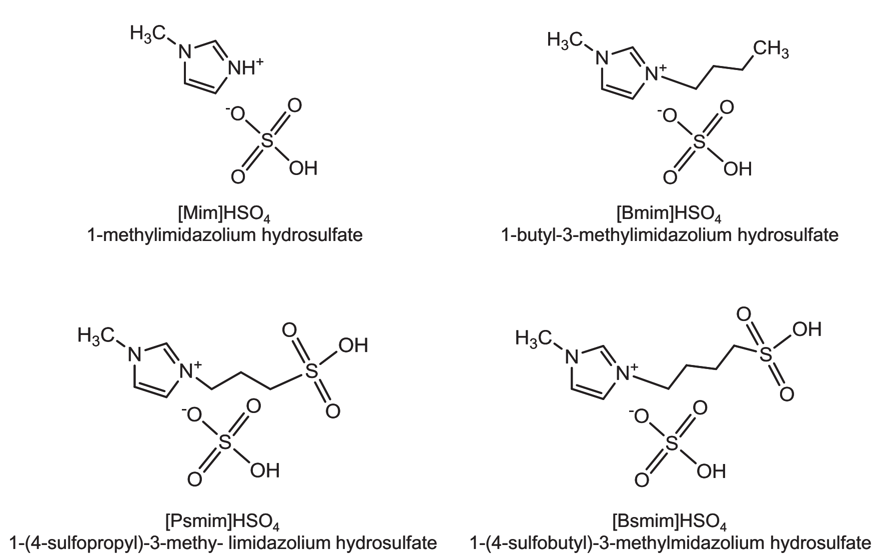

Fig. 1. The synthesized acidic ionic liquids ([Mim]HSO_4 and [Bmim]HSO_4 containing single acid site, [Psmim]HSO_4 and [Bsmim]HSO_4 containing double acid sites.)

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