



Preparation of ethyl levulinate from wheat straw catalysed by sulfonate ionic liquid

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ABSTRACT

Wheat straw, a typical lignocellulosic biomass, is difficult to be liquefied because of its complex structure, which limits its further conversion to valuable products. Ionic liquid can dissolve the cellulose, which can destroy the connection of biomass components. Ionic liquids, [BMIM][HSO₄], [BMIM][Cl], and [HSO₃-BMIM][HSO₄], were used in the liquefaction of wheat straw to produce ethyl levulinate (EL) in a one-pot reaction under mild conditions in ethanol, which served as both solvent and reactant. The highest conversion rate, 85.50%, was obtained following reaction at 200 °C for 60 min using the acidic ionic liquid 1-methyl-3-(4-sulfobutyl) imidazole bisulfate as the catalyst. Under optimal conditions, ethyl levulinate was obtained with a yield of 16.23% and its content in the liquid products was 28.11%. Without the acidic ionic liquid catalyst, the conversion rate of wheat straw and the yield of ethyl levulinate were only 22.33% and 6.23%, respectively. Of the catalysts evaluated, [HSO₃-BMIM][HSO₄] was the most effective, and its recovery rate was 64.71%. This study provides a theoretical basis for the development and utilisation of low-corrosion and environment-friendly catalysts for liquefaction processes for the preparation of high-grade chemicals.

1. Introduction

With the increasingly prominent energy crisis and environment problems, research into renewable and pollution-free resources is of great interest worldwide (Kang and Yu, 2015). One potential resource that fits these criteria is biomass, which can be converted into bio-based platform chemicals and fuels such as 5-hydroxymethylfurfural, levulinic acid (LA), lactic acid, and alkyl levulinate, e.g., methyl levulinate and ethyl levulinate (Saravanamurugan et al., 2011). LA is the main product of biomass hydrolysis and can be further converted into a series of valuable chemicals. Grilc and Likozar (2017), Grilc et al. (2016) reported the preparation of NiMo/Al₂O₃, Pd/Al₂O₃ catalysts, and investigated the hydrodeoxygenation of solvent-free levulinic acid and liquefaction of lignocellulosic biomass in hydrogen donor solvents by those catalyst, high yield of γ -valerolactone (GVL) was obtained. Ethyl levulinate (EL) is particularly versatile and can be used as an oxygenating fuel additive, raw material for γ -valerolactone (GVL) production, or a solvent for CO₂ absorption (Ahmad et al., 2016; Deng et al., 2015; Tan et al., 2017; Zhou et al., 2014). Producing ethyl levulinate typically requires an aqueous mineral acid catalyst, and the treatment of

carbohydrates with the mineral acid catalyst (H₂SO₄) can get a yield of 55% (Wu et al., 2012). Although such catalysts boast high EL yields at optimum conditions, they are nonrecyclable, corrosive, and difficult to separate from the products. Tiwari et al. (Tiwari et al., 2017) have successfully synthesized magnetically separable sulphated zirconia catalysts and compared their activity for the synthesis of ethyl levulinate from furfuryl alcohol (FAL), the results implied that it gives a 96% yield of EL with 100% conversion of FAL with a 1: 15 mol ratio in 2 h. Chang et al. (2015a) used zeolite USY as catalyst to convert glucose and furfural residues (content of cellulose is more than 85%), and got a 51.47% and 18.68% yield of EL respectively. Solid acid catalysts have shown good catalytic performance in the production of EL (Saravanamurugan and Riisager, 2012) but suffer from fast deactivation, difficult regeneration, and a complex reaction product distribution, which makes them unsuitable for large-scale applications. Ion-exchange resins have also been used to fabricate EL but are hindered by low thermal stability.

Ionic liquid, which may be used as both solvent and catalyst, has generated a great deal of interest because of their noncorrosive properties, high thermal stability, and low melting points (Yoo et al., 2017;

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Nomenclature

Notation

[BMIM][HSO ₄]	1-Butyl-3-methylimidazolium hydrogen sulfate
[BMIM][Cl]	1-Butyl-3-methylimidazolium chloride
[HSO ₃ -BMIM][HSO ₄]	1-Methyl-3-(4-sulfobutyl) imidazole bisulfate
MIM-BS	1-Methyl-3-(4-sulfobutyl) imidazole

¹³ C NMR	Carbon nuclear magnetic resonance
LA	Levulinic acid
EL	Ethyl levulinate
FTIR	Fourier transform infrared spectroscopy
GC-MS	Gas chromatography–mass spectrometer
TG-DTG	Differential thermal gravity
EG	Ethyl glycoside
EMF	5-Ethoxymethylfurfural

Zhang et al., 2015). Besides, ionic liquid is innocuous for the environment, and the addition of antisolvent give the benefit for an easy separation of ionic liquid (Andre M da Costa Lopes et al., 2013). Many of ionic liquids are currently being evaluated as substitutes for conventional catalysts and are used in biomass dissolution and in the formation of various chemicals, including EL and levulinic acid. In particular, sulfonic acid-functionalised ionic liquids have a higher acid site (Chang et al., 2017; Vancov et al., 2012) that breaks hydrogen bonds in the biomass feedstock and promotes the degradation of cellulose. Nakamura et al. (2010) reported that the polymer chain of cellulose becomes amorphous when mixed in an ionic liquid. Amarasekara and Wiredu (Amarasekara and Wiredu, 2014) obtained ethyl levulinate in a yield of 19% following a reaction at 170 °C for 12 h in a water/ethanol solvent containing a 1-(1-propylsulfonic)-3-methylimidazolium chloride catalyst. Long et al. (Long et al., 2015) liquified bagasse lignin catalysed by [C₄H₈SO₃Hmim][HSO₄] and obtained satisfactory conversion rates and phenol yields without coke formation. Grilc et al. (2015) liquified the wood and its main components in glycerol under the presence of heterogeneous imidazolium-based ionic liquid catalysts, and the conversion of beech wood reached to 91.5 wt% at 200 °C within 60 min. Thus, ionic liquid has a promising application in the degradation of biomass and formation of high value-added products.

Despite the various studies to date including the preparation of hydroxymethyl furfural and levulinic acid catalysed by ionic liquids, to the best of our knowledge, there have been very few detailed studies on the preparation of levulinates with this type of catalyst from agricultural residues, such as wheat straw. We report here the catalytic performance of [BMIM][HSO₄], [BMIM][Cl], and [HSO₃-BMIM][HSO₄] (chemical structures are seen in Fig. 1) in the liquefaction of biomass in ethanol, which served as both a reactant and solvent. Of the ionic liquids included in this study, [HSO₃-BMIM][HSO₄] exhibited the highest catalytic performance and was used to further evaluate the effects of ionic liquid concentration, reaction time, and temperature on the conversion rate of wheat straw and the EL yield. Liquefied products were analysed, and the separation of target product and recycle of ionic liquid were researched. Finally, reaction scheme of ethyl levulinate formation is discussed.

2. Methods and materials

2.1. Materials

All chemicals obtained from reagent companies were of analytical

grade and were used as received. 1-Methylimidazole was purchased from the Aladdin Reagent Company. 1,4-Butanesultone was supplied by the Adamas Reagent Company. Toluene was obtained from Shanghai Lingfeng Chemical Reagents, Ltd. Sulfuric acid and ethanol were purchased from Nanjing and Xilong Chemical Reagent Companies, respectively. Ethyl acetate was purchased from Chinasun Specialty Products Co., Ltd. Wheat straw was collected from a farm in Henan province, China; smashed with a grinder; and sieved through a 40–60 mesh. The wheat straw was further characterized, the results were as follows: cellulose, 38.39%; hemicellulose, 23.01%; lignin, 15.00%, ash, 8.59%; moisture, 13.04%.

[BMIM][HSO₄] and [BMIM][Cl] were purchased from the Lanzhou Institute of Chemical Physics. [HSO₃-BMIM][HSO₄] was synthesised in our laboratory according to a previously reported procedure (Li et al., 2009). The synthesised ionic liquid was verified and characterised by Fourier transform infrared (FTIR) and carbon nuclear magnetic resonance (¹³C NMR) spectroscopies.

2.2. Experimental procedure

2.2.1. Preparation of ionic liquid

Twenty grams of 1,4-butanediol and 100 mL toluene were added to a three-necked flask for dissolution. Twelve grams of 1-methylimidazole was added to the flask dropwise, with continued magnetic stirring in an ice bath. Then we slowly raised the reaction temperature to 80 °C with a speed of 3 °C min⁻¹. After 2 h, the reaction mixture was subjected to suction filtration, and the white solid was washed three times with ethyl acetate and dried for 5 h below 100 °C. The resulting white powder (28.85 g, yield of 90.16%) was 1-methyl-3-(4-sulfobutyl) imidazole (MIM-BS), an intermediate in the synthesis of many ionic liquids. Twenty grams of MIM-BS, prepared as above, was dissolved in 100 mL deionised water in another three-necked flask. Sulfuric acid, same amount of substance with MIM-BS, was added with constant magnetic stirring at room temperature. Then we slowly raised the reaction temperature to 90 °C with a speed of 3 °C min⁻¹ and kept it there for 2 h. After drying for 3 h in a vacuum oven, a pale yellow viscous liquid ([HSO₃-BMIM][HSO₄]) was obtained, and its characterization results were as following: IR (KBr disc, cm⁻¹): 3380, 3157, 3116, 2961, 1715, 1575, 1169, 1036, 889, 854, 576; ¹³C NMR (500 MHz, D₂O): δ20.55, 27.67, 35.35, 48.48, 49.74, 121.77, 123.29, 135.48. ¹H NMR (500 MHz, D₂O): δ1.36 (m, 2H), 1.67 (m, 2H), 2.57 (t, 2H), 3.53 (s, 3H), 3.86 (m, 2H), 7.08 (s, 1H), 7.13 (s, 1H), 8.34 (s, 1H).

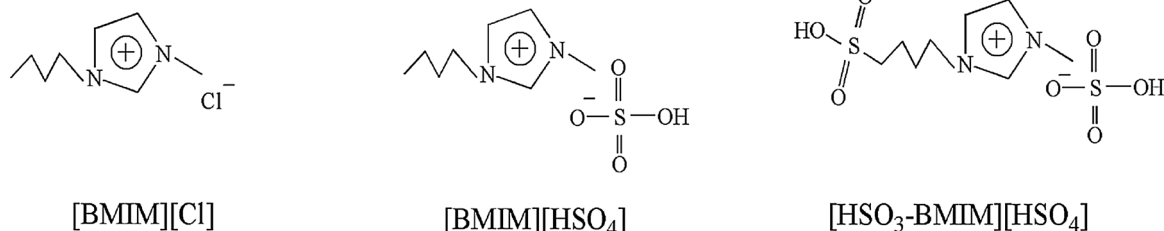


Fig. 1. Chemical structures of ionic liquids.

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