



Catalytic conversion of duckweed to methyl levulinate in the presence of acidic ionic liquids

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ABSTRACT

In this study, an efficient strategy is proposed for selective methyl levulinate production from duckweed, a typical fast-growing aquatic microalgae in warm and humid regions, in the presence of acidic ionic liquids (ILs). The results show that IL structure has a significant effect on its acidic strength, which finally determines the process efficiency for levulinate methyl generation. With the optimized catalyst of $[\text{C}_3\text{H}_6\text{SO}_3\text{HPy}]\text{HSO}_4$, 88.0% duckweed is consumed, resulting in a comparable methyl levulinate yield of 73.7% and a process efficiency of 81.8% at 170 °C for 5 h. Furthermore, this process is substantially influenced by the reaction condition, particularly, it is significantly temperature-dependent. In addition, solvent has a remarkable intensified effect on the process efficiency, which dramatically decreases from 81.8 to 53.7% when methanol is replaced by water.

1. Introduction

Levulinic acid (LA), one of the twelve key platform chemicals identified by National Renewable Energy Laboratory (Denver, USA), has been recognized as a versatile starting material in manufacturing biodegradable herbicides, solvents, food flavoring agents, fragrance, pharmaceutical compounds and resins (Yu & Tsang, 2017). Alternatively, ester levulinate itself is a novel bio-based diluent for biodiesel as well due to its high saturated fatty acid content (Cirujano et al., 2015). Generally, this compound is originated from petrochemical industry. However, it is well known that fossil fuel is unsustainable. Therefore, the exploration of clean and renewable energy resources becomes inevitable because of the dwindling reserves of fossil hydrocarbons coupled with the serious environmental concerns associated with its excessive use.

Lignocellulosic biomass, which mainly consists of cellulose, hemicellulose and lignin, is the most abundant and widely-distributed renewable resource on the Earth. It is also a promising alternative to fossil fuel for high quality biofuel and biochemical production (Liao et al., 2014; Liu et al., 2015; Zhang et al., 2013). To date, considerable efforts have been devoted to the efficient LA and its ester production from this biopolymer as well (Robertson et al., 2017). For example, Van de Vyver and co-workers found that cellulose could be easily converted to LA with a traditional homogeneous Brønsted acid catalyst (Van de Vyver et al., 2011). A recent work reported by Wang et al. also demonstrated

that 72.5 mol% LA yield could be obtained from the microcrystal cellulose in a H_2SO_4 aqueous solution (Wang et al., 2017). Nevertheless, the post-separation and the corrosivity of protonic acids are inevitable, so lots of attention had been focused on novel materials. As a green and efficient catalyst, acidic ionic liquid (IL) normally shows advantages of both homogenous and heterogeneous catalysts (Zhang et al., 2017), therefore, it had been widely used in small molecule catalysis as well as biomass conversion (Hallett & Welton, 2011; Amarasekara, 2016). Ananda and Bernard claimed that 19.0% ethyl levulinate yield could be obtained from cellulose with IL 1-methyl-3-(3-sulfopropyl) imidazolium chloride in the water-ethanol solvent (Amarasekara & Wiredu, 2014). Shen and the co-workers also found that 39.4% of LA yield was achieved with the acid IL of 1-methyl-3-(3-sulfobutyl) imidazolium hydrogen sulphate (Shen et al., 2015), and this value could be promoted to 55.0% under the assistance of microwave (Ren et al., 2013). Song's study further demonstrated that 71% methyl levulinate yield was achieved from microcrystal cellulose over the heteropolyanion-based IL because of the synergistic effect between acidic catalyzed depolymerization and *in situ* esterification (Song et al., 2016). However, it should be noticed that direct use of crystal cellulose as feedstock for LA production is unrealizable on the industrial scale. In this perspective, LA and its ester produced from native lignocellulosic biomass becomes an attractive concern. Typical cellulose-enriched biomass, such as corncob, bagasse and corn stalk etc., were widely used in this issue with good to excellent process efficiencies in the presence of various acidic

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catalysts (Chen et al., 2011; Dussan et al., 2013; Elumalai et al., 2016; Qing et al., 2018; Zhao et al., 2017). However, an obvious disadvantage is that the cellulose fraction of biomass is tightly connected with other fragments (hemicellulose and lignin) through tightly chemical and hydrogen bonds, making it highly recalcitrant for decomposition (Zabed et al., 2016). In addition, the phenolic oligomer from lignin depolymerization is unsaturated and high thermo-sensitive under an acidic environment (Schutyser et al., 2018; Zhang et al., 2017). Accompanying with the humins formation, the recondensation of phenolic oligomer on the biomass surface would be a big barrier for the native cellulose conversion. Therefore, intensive pretreatments are usually required for the efficient cellulosic biomass conversion (Zabed et al., 2016; Zhang et al., 2017).

Duckweed (*Lemna minor*) is a fast-growing aquatic plant, which can be found in many warm and humid regions. As an energy plant, it is abundant, widely distributed, easily harvested and uncompetitive with most grains and vegetables for arable land (Liu et al., 2018). What's more important is that this nonedible renewable resource contains low lignin but high starch content (it normally is higher than 30 wt% (Soda et al., 2015)). This unique composition of duckweed makes it a good alternative for LA production in industrial biorefinery since many previous studies showed that starch is more flexible for saccharification than cellulose (Tiong et al., 2018). Therefore, in this study, an effective strategy for duckweed conversion to LA and its methyl ester is proposed over the environmental friendly catalyst of acidic ILs. It found that 73.7% methyl levulinate yield and 81.8% process efficiency can be achieved because of the excellent catalytic activity of IL and the promotion effect of *in situ* methyl esterification reaction between generated LA and methanol.

2. Materials and methods

2.1. Material

Imidazole, pyridine, triethylamine, N-methylimidazole, 1,4-buthane sultone, 1,3-propane sultone and 1-chloropropionic acid were purchased from Acros chemical Co., Ltd. (Beijing, China) and used as received. The standard chemicals of levulinic acid, methyl levulinate, ethyl levulinate, propyl levulinate, butyl levulinate and *n*-octanol were provided by J&K chemical Co., Ltd (Beijing, China). Other reagents were supplied by Guanghua Chemical Factory Co., Ltd. (Guangzhou, China) and redistilled before use. All reagents used in these experiments were of analytical grade.

The duckweed was collected from local lakes. It was first thoroughly washed using deionized water and then dried at 120 °C until constant weight. The starch content of this microalgae was determined by Chinese standard method of GB/T 5514-2008. The contents of cellulose, hemicellulose and lignin were measured by National Renewable Energy Laboratory (NREL, USA) method. The ash content was calculated by the weight comparison between the feedstock and the residual solid fraction after aerobic combustion. It was found that the duckweed consists of 30.45% starch, 10.12% cellulose, 37.77% hemicellulose, 1.63% lignin and 0.06% ash.

2.2. IL synthesis, characterization and acid strength determination

The IL catalysts of 1-methyl imidazolium bisulfate ([mim]HSO₄), 1-methyl-3-butyl imidazolium bisulfate ([bmim]HSO₄), 3-(2-carboxyethyl)-1-methyl imidazolium chloride, 1-(4-sulfobutyl)-3-methyl imidazolium bisulfate ([C₄H₈SO₃Hmim]HSO₄), 1-(3-sulfopropyl)-3-methyl imidazolium bisulfate ([C₃H₆SO₃Hmim]HSO₄), 1-(3-sulfopropyl)-3-methyl imidazolium bisulfate ([C₃H₆SO₃Hmim]HSO₄), and N,N,N-triethyl-3-sulfopropan-1-aminium bisulfate ([C₃H₆SO₃HEt₃N] HSO₄) (detailed structures were shown in the Supplementary Data) were prepared according to reported procedures as shown in previous study (Cole et al., 2002). Their structures and purities were determined by the

Fourier transform infrared spectroscopy (FT-IR), electrospray ionization mass spectrometry (ESI-MS), ¹H-nuclear magnetic resonance spectroscopy (¹H-NMR), ¹³C-NMR, ion chromatography and elemental analysis. The results showed that the purities of investigated ILs are greater than 99%. Detailed data about the IL characterization can be found in the Supplementary Data. The acidic strengths of these ILs were determined by pH value measurement and Hammett method with 4-nitroaniline as the indicator, all experiments were conducted on a UV-3010 UV-vis spectrometer in the range from 200 to 800 nm, and the Hammett acidity function (H₀) could be calculated by Eq. (1).

$$H_0 = pK_a + \log [I]/[IH^+] \quad (1)$$

"I" represents the indicator base, [IH⁺] and [I] are the molar concentrations of the protonated and unprotonated forms of the indicator, respectively. The pK(I)aq value of 4-nitroaniline is 0.99.

2.3. Typical procedure for duckweed conversion

The duckweed liquefaction process was carried out in a 50 mL stainless autoclave equipped with a mechanical agitation. In a typical run, 0.5 g duckweed, 2.0 mmol IL catalyst and 20 mL methanol were loaded into the autoclave in sequence. After air displacement using nitrogen for five times, the autoclave was heated to the desired temperature (150–180 °C) and held for a certain time (3–7 h). When the designated time was elapsed, the reactor was cooled to room temperature using flowing water during 30 min. Triplicate experiments were performed to reduce the standard error, and the results listed in this study were the average value with the standard error of less than 3.45%.

2.4. Product separation and analysis

The gaseous fraction from the duckweed depolymerization was collected in an air-bag and identified by gas chromatography with a thermal conductivity detector (GC-TCD). The solid fraction was first separated from the mixture by filtration, and then it was washed thoroughly using deionized water, followed by drying at 120 °C until constant weight. The filtrate and the water soluble fraction were collected in a 50 mL separating funnel. 30 mL chloroform (CHCl₃) was used for organic chemical extraction (10 mL × 3). And the volatile products in the CHCl₃ soluble fraction was qualitatively and quantitatively analyzed using gas chromatography equipped with both a mass and a flame ionization detector (GC-MS-FID). The water phase was analyzed using high performance liquid chromatography (HPLC). The IL catalyst was recovered from the solvent according to following procedure. The water soluble fraction was first submitted to solvent removal under reduced pressure. Then, the remained viscous liquid was extracted by CHCl₃. The CHCl₃ soluble fraction was combined together with that for above product extraction. After further solvent removal under reduced pressure, the obtained liquid (including IL catalyst) was dried in a vacuum oven at 120 °C overnight. The finally achieved IL was then used for the next run to investigate its reusability.

Methyl levulinate and other volatile products were identified on an Agilent 7890/5977A GC-MS-FID based on an Agilent NIST MS library. A HP-INNOWAX column (30 m × 0.25 mm × 0.25 μm) was used for chemicals separation. The initial oven temperature was 50 °C (held for 3 min), and then it was ramped to 250 °C at a speed of 8 °C min⁻¹, and held at this final temperature for another 3 min. The contents of these compounds were measured using an internal standard method with *n*-octanol as the standard compound. The chemicals in the water soluble fraction was identified on an Agilent 1260 HPLC with a refractive index detector via the peak position identification with comparison to the commercial compounds, and the quantitative analysis was conducted using extra standard method. The heteronuclear single quantum correlation (HSQC) spectrum of the residual solid was performed on a Bruker Avance III 600 MHz spectrometer. The comparative

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