Bioresource Technology 129 (2013) 616–619

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Short Communication

Selective conversion of cellulose to levulinic acid via microwave-assisted synthesis in ionic liquids

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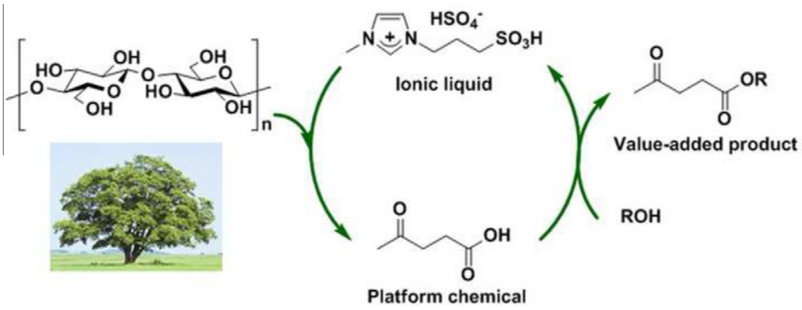
HIGHLIGHTS

- ▶ SO_3H-functionalized ILs selectively catalyzed cellulose conversion to levulinic acid.
- ▶ Microwave irradiation improved production of levulinic acid from cellulose.
- ▶ The highest yield of levulinic acid was 55.0%.
- ▶ Catalytic activities of SFILs depend on anions.
- ▶ Further esterification enabled product separation and SFIL recovery.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 July 2012
Received in revised form 18 December 2012
Accepted 19 December 2012
Available online 26 December 2012

Keywords:
Biomass
Cellulose
Ionic liquids
Levulinic acid
Microwave

ABSTRACT

A highly selective approach to produce levulinic acid from cellulose was developed via microwave-assisted synthesis in SO_3H-functionalized ionic liquids (SFILs). The effects of reaction conditions and ionic liquid structures on the yield of levulinic acid have been investigated, where the highest yield of 55.0% was obtained. The catalytic activities of SFILs depend on the anions and decrease in the order: $HSO_4^- > CH_3SO_3^- > H_2PO_4^-$, which is in good agreement with their acidity order. The SFILs are efficient catalysts for cellulose conversion into levulinic acid and the subsequent esterification, which facilitates the separation of product and reuse of ionic liquids.

1. Introduction

Diminishing fossil resources and increasing concern about sustainable development have prompted the research on production of liquid hydrocarbon fuels and chemicals from biomass, which is the only renewable resource of fixed carbon (Ragauskas et al., 2006). As the most abundant biomass and sustainable raw materials, cellulose (Klemm et al., 2005) can be utilized to produce platform chemicals such as levulinic acid (LA) (Corma et al., 2007; Rackemann and Doherty, 2011), a versatile building block for fuel additives, polymer precursors, herbicides, pharmaceuticals, flavor substances and chemical intermediates. Recent work demonstrated that LA can serve as initial feedstock for existing petrochemical processing operations (Bozell, 2010), thus production of LA from cellulose has attracted considerable attention and become one of the key steps for the biomass refining. However, cellulose is generally regarded as a difficult material to work with due to its densely packed structure and insolubility in water (Jarvis, 2003). Various catalytic systems have been attempted to convert cellulose into LA directly, including mineral acids (Girisuta et al., 2007), metal chlorides (Seri et al., 2002), solid acid catalysts (Zakzeski et al., 2012) and acidic polymers (Vyver et al., 2011), whereas the limiting issues were focused on improving the selectivity of LA and developing efficient strategies for product separation and catalyst recovery.

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http://dx.doi.org/10.1016/j.biortech.2012.12.132

Ionic liquids have been widely recognized as green reaction media due to their negligible volatility and excellent thermal stability (Welton, 1999). Vast combinations of cations and anions could be used to design tailor-made ionic liquids for many different performances. SO_3H-functionalized ionic liquids (SFILs) with strong Brønsted acidity were firstly reported by Davis and co-workers (Cole et al., 2002), which have large potentials in replacing conventional acidic catalysts for they are flexible, recyclable, and could be used as dual solvents and catalysts. Tao et al. (2011) found that $MnCl_2$ in SO_3H-functionalized ionic liquids were effective catalysts for the production of 5-hydroxymethylfurfural (HMF) and furfural from cellulose, whereas levulinic acid was obtained as a side product. Herein for the first time, SO_3H-functionalized ionic liquids such as 1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate ($[C_3SO_3Hmim]HSO_4$) were employed in the selective conversion of cellulose to levulinic acid under microwave (MW) irradiation, whereafter the reaction yield was quantitatively determined by ^1H NMR with ionic liquid as internal standard. The effects of reaction conditions and SFILs structures on the yield of levulinic acid were studied in detail.

2. Methods

Microcrystalline cellulose with an average particle size of 50 μm was purchased from Acros Organics (USA) and used as received. Ethyl levulinate (EL) was obtained from TCI Chemical Co. (Japan). 1,3-Propane sultone, 1,4-butane sultone and 1-methylimidazole were freshly distilled prior to use. The ionic liquids including 1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate ($[C_3SO_3Hmim]HSO_4$), 1-methyl-3-(3-sulfopropyl)imidazolium dihydrogen phosphate ($[C_3SO_3Hmim]H_2PO_4$), 1-methyl-3-(3-sulfopropyl)imidazolium methanesulfonate ($[C_3SO_3Hmim]CH_3SO_3$), 1-methyl-3-(4-sulfobutyl)imidazolium hydrogen sulfate ($[C_4SO_3Hmim]HSO_4$), N-(3-sulfopropyl)pyridinium hydrogen sulfate ($[C_3SO_3HPy]HSO_4$) and N,N,N-trimethyl-N-(3-sulfopropyl)ammonium hydrogen sulfate ($[C_3SO_3HN_{111}]HSO_4$) were synthesized by acidification of the respective zwitterions according to literature (Cole et al., 2002), and characterized by NMR before use (Supplementary data). ^1H NMR and ^{13}C NMR spectra were recorded on Bruker DRX-400 and Avance III 500 MHz spectrometers. Microwave experiments were realized in the MicroSYNTH plus microwave system (Milestone, Italy). UV–vis spectra were recorded on UV-2550 spectrophotometer (Shimadzu, Japan). The gas chromatography analysis was carried on Agilent 7890A with a FID detector and a HP-5 capillary column (30.0 m × 320 μm × 0.25 μm).

In a typical reaction, cellulose (250 mg), ionic liquid (3.3 mmol) and de-ionized water (2.000 g) were mixed in a 50 mL quartz tube and the mixture was heated in MicroSYNTH plus at 800 W, 160 °C for 30 min. After filtration of insolubles and removal of water, the crude products were analyzed by ^1H NMR using ionic liquid as internal standard. The yields of products were calculated from the equation: yield (%) = (mol of the product)/(mol of glucose unit in cellulose) × 100%.

The ionic liquids were reused as following. In the first run, the reaction of cellulose (0.400 g), $[C_3SO_3Hmim]HSO_4$ (1.000 g, 3.3 mmol) and de-ionized water (2.000 g) was heated in MicroSYNTH plus at 800 W, 160 °C for 30 min. After filtration and removal of water, ethanol (1 mL, 17 mmol) was added to the mixture and the esterification reaction was carried out in an oil bath of 100 °C for 1 h. Afterwards, ethyl levulinate (EL) was extracted by n-hexane 5 mL × 4, and then subjected for GC analysis. The lower layer of ionic liquid layer was separated, dried under high vacuum and reused in the second and third run as above. The yields of EL were calculated from the equation: yield (%) = (mol of EL)/(mol of glucose unit in cellulose) × 100%.

Table 1
The effects of reaction time and temperature.[a]

Entry	Time (min)	Temperature (°C)	Yield (%)	
			LA	Glucose
1	5	160	15.7	20.9
2	10	160	21.1	20.5
3	20	160	35.1	0
4	30	160	44.5	0
5	40	160	34.8	0
6	30	80	0	0
7	30	100	0	4.7
8	30	120	0.3	15.6
9	30	140	9.7	22.9
10	30	150	38.2	14.8
11	30	170	43.2	0

[a] Reaction condition: 250 mg cellulose, 1.000 g $[C_3SO_3Hmim]HSO_4$, 2.000 g H_2O, MW.

3. Results and discussion

The selectivity and yield of the products vary during the reaction course (Table 1). The yield of levulinic acid rose up with the reaction time increasing from 5 to 30 min and decreased afterwards. On the other hand, glucose was formed in the yield of 20.9% at 5 min and converted totally after 20 min. Therefore, the optimum reaction time was determined to be 30 min with 44.5% yield of levulinic acid.

The yield of levulinic acid increased at higher temperature. As shown in Table 1, levulinic acid was not formed in the temperature range of 80 to 120 °C, and reached the maximum yield at 160 °C. On the contrary, glucose was formed exclusively below the temperature of 120 °C, but could not be detected above 160 °C. Apparently higher temperature is in favor of levulinic acid rather than glucose.

Fig. 1a shows the effect of ionic liquid dosage on the yield of levulinic acid. Neither levulinic acid nor glucose could be detected in the absence of SFIL, indicating that SFIL acts as essential catalyst in the conversion of cellulose. The yield of levulinic acid increased and finally levelled off when more than 1 g of ionic liquid was added. While glucose reached maximum yield of 34.2% with the addition of 100 mg of ionic liquid and was transformed completely with the addition of more than 1 g of ionic liquid. Fig. 1b shows the effect of water amount on the yield of levulinic acid. In the presence of less than 2 g of water, the yield of levulinic acid increased to 44.5% and no glucose detected. In the presence of more than 2 g of water, the yield of levulinic acid decreased, whereas the yield of glucose rose up. Fig. 1c shows the effect of initial cellulose intake on the yield of levulinic acid. Levulinic acid reached the highest yield of 55.0% at an initial cellulose intake of 50 mg. Only trace amount of glucose could be detected at initial cellulose intake over 400 mg.

In order to establish the relationship between SFILs structures and their catalytic activities, the Brønsted acidities of SFILs were determined by Hammett method (Gu et al., 2005) using UV–vis spectrophotometer with 4-nitroaniline as indicator. The maximal absorbance of the unprotonated form of the indicator was observed at 381 nm in H_2O, which decreased after adding acidic ionic liquid. Under the same concentration of 4-nitroaniline (4 mg/L) and ionic liquids (50 mmol/L) in H_2O, Hammett acidity functions (H_0) of SFILs with different cations and anions were calculated and compared thereafter. As shown in Table 2, for SFILs with the same cationic structure, the acidities of the SFILs depend on the anions and decrease in the order: $HSO_4^- > CH_3SO_3^- > H_2PO_4^-$. Different types of cations (imidazolium, pyridinium and ammonium) have negligible effect on the acidity of SFILs, and no obvious variation could be either observed when the alkyl chain near the sulfonic group elongates from propyl to butyl. The activity order of SFILs to catalyze the conversion of cellulose into LA is in good