Industrial Crops and Products 70 (2015) 266–271

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Conversion of bamboo fiber into 5-hydroxymethylfurfural catalyzed by sulfamic acid with microwave assistance in biphasic system

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ARTICLE INFO

Article history:
Received 29 December 2014
Received in revised form 10 February 2015
Accepted 15 March 2015
Available online 27 March 2015

Keywords:
Bamboo fiber
Sulfamic acid
5-Hydroxymethylfurfural
Biphasic system

ABSTRACT

The present work reports the conversion of lignocellulosic biomass into 5-hydroxymethylfurfural (HMF) catalyzed by solid organic acid catalyst with microwave heating in H_2O/THF biphasic system. The 52.2% yield of HMF was achieved from the bamboo fiber degradation using NH_2SO_3H as catalyst at 180 °C for 40 min with 500 Hz microwave heating. The results showed that HMF yield increased significantly with adding NaCl, which not only could effectively increase the HMF distribution coefficient between organic phase and water phase, but also can separate HMF from water phase to organic phase continuously. Moreover, the catalytic system also showed effectiveness to convert other raw lignocellulosic variants to HMF, including softwood, hardwood, and cotton in the optimal biphasic system.

1. Introduction

In the pace of global modernization, the shortage of fossil fuels is leading to the potential energy crisis. With the development of renewable biomass, the biorefinery has become one of the most important alternative to relieve the global climate change, and the rapid consumption of fossil fuels (Klass, 1998). With the right technology, abundant biomass resources can be converted into a variety of valuable bio-products (Bozell and Petersen, 2010; Gallezot, 2012).

Among various chemicals that can be synthesized from biomass, 5-hydroxymethylfurfural (HMF) is one of the high potential and versatile biomass-derived chemicals platform compounds, because of its rich chemistry and potential availability from carbohydrates such as monosaccharide, disaccharide, and cellulose (Fan et al., 2011; Okano et al., 2013; Simeonov and Afonso, 2013; van Putten et al., 2013; Wu et al., 2014). Based on the hydroxylmethyl and aldehyde groups in its molecule, HMF can be used in the synthesis of many useful compounds such as *N*, *N*-dimethylformamide (Chatterjee et al., 2014), 2, 5-furandicarboxylic acid (Hu et al., 2012; Teong et al., 2014), levulinic acid (Holladay et al., 2007), etc., and new polymer materials through hydrogenation, halogenation, polymerization and other chemical reactions. Due to rich raw material source and low price, considerable efforts have been made on the transformation of carbohydrates into HMF (Dutta et al., 2012; Liu and Chen, 2013; Rosatella et al., 2011; Yi et al., 2012).

So far, a great deal of scientific effort has been put into the HMF production derived from lignocellulosic biomass and carbohydrate compounds (Ngee et al., 2014; Nie et al., 2014). Very recently, metal salts were shown to be highly efficient in the conversion of biomass with excellent selectivity toward platform compounds (Moliner et al., 2010; Nikolla et al., 2011). A HMF yield of 62.0% was achieved by using $CrCl_2$ in low melting mixtures (Ilgen et al., 2009). Wang et al. (2008) provided a catalytic conversion of chitin using $ZnCl_2$, in which HMF yield was obtained in 21.9%. Especially, metal chlorides are particularly efficient catalysts for the dehydration of monosaccharide (Yan et al., 2013) and the hydrolysis of cellulose to HMF in different media. Nevertheless, until now the occurrence of mild conditions is only related to the use of rather toxic heavy metal and expensive noble metal reagents, which led to the problems of the equipment corrosion and environmental pollution. On

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http://dx.doi.org/10.1016/j.indcrop.2015.03.044
0926-6690/

these basis, some solid acid catalysts including ion-exchange resin (Perez-Maqueda et al., 2014), H-type zeolite (Hu et al., 2014), metal oxide (McNeff et al., 2010), heteropolyacid (Zhao et al., 2011), etc., were tried and several interesting variants were developed. However, the lower density of catalytic active sites, and the easier to activity losing still cannot be eliminated.

Knowing the above disadvantages of the methods, the development of the homogeneous conversion of cellulose into glucose and further dehydration to HMF was studied widely. Zhou et al. (2013) achieved 63.0% yield of HMF from cellulose catalyzed by ionic liquid. Hu et al. (2013) studied the dehydration of carbohydrates to HMF in ionic liquid, which resulted in 46.4% HMF yield. In further, Hu et al. (2014) have improved the HMF yield to 50.3% using zeolite in ionic liquid at 150 °C. Metal chorides are particularly efficient catalysts for hydrolysis of cellulose in [EMIM]Cl and [BMIM]Cl ionic liquids (Su et al., 2011). In addition, acidic ionic liquid [HSO_3BMIM]HSO_4 and [BMIM]HSO_4 in [BMIM]Cl also efficiently catalyzed the hydrolysis of corn stalk (Jiang et al., 2011). Although ionic liquids possess favorable properties, such as nonvolatility, acid-base controllability and chemical stability, but they are expensive for practical production. New types of microwave have mushroomed and developed in recent years, Liu et al. (2013) used microwave-assisted catalytic in ionic liquid, HMF was obtained in a high yield of 51.4% from cellulose with $ZrCl_4$. Even though, these catalytic systems showed good performance, it was lacked for demand for practical application.

Sulfamic acid (NH_2SO_3H, SA) is a dry, nonvolatile, nonhygroscopic, odorless, uncorrodible crystalline solid with outstanding physical stability. It is cheap and commercially available. SA is recyclable and easy to handle as a catalyst owing to its immiscibility with common organic solvents, and the unique catalytic features and intrinsic zwitterionic property. Recently, it is shown that SA has the prospect to be used as a substitute for conventional acidic catalytic materials (Rostami and Yari, 2012; Wang et al., 2004). SA is very different from the conventional acidic catalyst, which prompted us to explore further applications of other reaction process.

On the other hand, the problem, which is almost common to all conventional catalytic systems, is that it is very difficult to separate the product from the solution containing catalyst, because there exists on the inevitable interaction of catalyst with product. Yang et al. (2012a) obtained a high HMF yield of 61.0% from lignocellulosic biomass in a biphasic solvent system at 160 °C with $AlCl_3{\cdot}6H_2O$ as catalyst. Likewise, Shen et al. (2014b) showed that the HMF yield of 39.7% was obtained in a H_2O/THF biphasic system promoted by adding NaCl. In the present study, therefore, we investigated the conversion of monosaccharide and lignocellulosic biomass including softwood, hardwood, cotton, and bamboo into HMF using sulfamic acid as catalyst with microwave heating in H_2O/THF biphasic system. In addition, NaCl was used in order to increase the partition coefficient between THF and water.

2. Materials and methods

2.1. Materials

Sulfamic acid (purity ≥ 99.5%) was purchased from XiLong Chemical Co. Ltd., Guang Xi. HMF (98%) and levulinic acid (98%) were supplied by Acros Organics. Glucose (99%), NaCl, THF and concentrated sulfuric acid were purchased from Sinopharm Chemical Reagent Co. Ltd., and used without further purification. The bamboo fiber was separated and obtained from the bamboo (*Neosinocalamusaffinis*) from the experimental farm of North-Western University of Agriculture and Forestry, Yangling, China. Cotton linter fiber (DP = 920) was supplied by Silver Hawk Fiber Corporation, Shandong Province, China. Eucalyptus (*Eucalyptus urophylla*) was obtained from Guangdong Province, China. Tamarix austromongolica was harvested in Inner Mongolia, China.

2.2. Experimental procedure

All reactions were conducted in a microwave-heating reactor (MDS-6G, Sineo Microwave Chemistry Technology Co. Ltd., Shang Hai). The reaction temperature and pressure were measured by thermowell and pressure transducer. In a typical run, a 30 mL plastic reaction container with protective sleeve was filled with bamboo fiber (1.25 mmol/0.2025 g based on monosaccharide units), SA (0.5 mmol), NaCl (1.75 g), deionized water (5 mL) and THF (15 mL) was put in the microwave reactor under irradiation at 500 W. The reaction contained rapid heating, constant temperature and cooling. The dehydration reaction was carried out at 2 MPa and was heated to 180 °C to react for 40 min. When the reaction was completed, the reaction mixture was cooled to room temperature automatically. After reaction, solid residues were collected by filtration with a 0.45 μm membrane and samples were filtered with 0.2 mm syringe filter prior to analysis. The liquid products in both aqueous phase and organic phase were analyzed by UV, GC–MS and HPLC instruments. ^{1}H NMR and ^{13}C NMR spectra of samples were recorded on Bruck Advance 400 Hz spectrometer.

2.3. Analytical methods

HMF and levulinic acid (LA) were analyzed by high-performance liquid chromatography (Agilent-1200) fitted with an aminex HPX-87H column (Bio-Rad) and a refractive index (RI) detector, the column temperature was set at 50 °C, and mobile phase was 5 mmol H_2SO_4 at a flow rate of 0.55 mL/min. LA was also analyzed by gas chromatograph (GC-7890F, Shanghai Tianmei Science and Technology Corporation, China) fitted with a capillary column and a FID detector. Total reducing sugar (TRS, include reducing chemicals produced from degradation of cellulose, such as glucose, fructose, cellobiose, and higher soluble oligodextrins) indicated the rate of cellulose hydrolysis. TRS was measured through DNS method using D-glucose as a standard (Miller, 1959) on an UV spectroradiometer (UV 2300, Shanghai Tianmei Science and Technology Corporation, China) at 520 nm. The mass of TRS, M_{TRS} and the yield of TRS Y_{TRS} were calculated as follows:

$$M_{TRS}(\text{mg}) = \text{TRS concentration (mg/ml)} \times 25(\text{ml}) \times (V_1/1)$$

$$Y_{TRS}(\%) = \frac{M_{TRS} \times 0.9}{M_{\text{cellulose}}} \times 100\%$$

In which, M_{TRS} is the mass of TRS, V_1 is the volume of the sample, and 0.9 is the ratio of glucose unit of cellulose and molecular weight of glucose.

2.4. Separation of the product 5-hydroxymethyfurfural

The separation of HMF is an important process, we can obtain the isolated yield. After the degradation of bamboo fiber, the mixture was added into a saturated sodium bicarbonate solution and stirred with a magnetic stirrer 12 h. The sample was extracted three times with ethyl acetate. The organic layer was collected and dried with anhydrous sodium sulfate. The organic phase was distilled under reduced pressure to obtain pure HMF as a main product (Wang et al., 2014).

HMF: total yield 52.2%, isolated yield = 35.5% (74.6 mg).

^{1}H NMR spectrum (DMSO): 3.38–3.41(d, 1H, J = 12), 4.48 (s, 2H), 6.58–6.59 (d, 1H, J = 4), 7.46–7.47 (d, 1H, J = 4), 9.53 (s, 1H); ^{13}C NMR spectrum (DMSO): 56.39, 110.07, 124.73, 152.20, 162.63 and 178.35.