



Physicochemical pretreatments and hydrolysis of furfural residues via carbon-based sulfonated solid acid



Bao Jun Ma^{*}, Yuan Sun, Ke Ying Lin, Bing Li, Wan Yi Liu^{*}

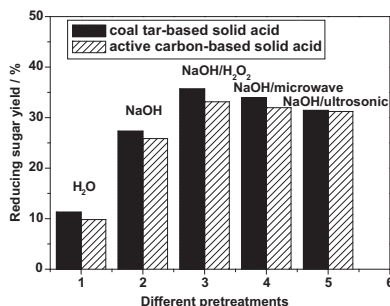
State Key Laboratory Cultivation Base of Natural Gas Conversion, College of Chemistry, Ningxia University, Yinchuan 750021, China

HIGHLIGHTS

- Furfural residues conversion into reducing sugars was researched.
- Potential commercial physicochemical pretreatment methods are developed.
- Carbon-based sulfonated solid acid catalysts were applied.
- The catalysts are green, efficient, and low cost.

GRAPHICAL ABSTRACT

The reducing sugar yields are related to the pretreatment methods.



ARTICLE INFO

Article history:

Received 18 November 2013
 Received in revised form 13 January 2014
 Accepted 15 January 2014
 Available online 27 January 2014

Keywords:

Furfural residues
 Physicochemical pretreatment
 Solid acid
 Reducing sugars

ABSTRACT

Potential commercial physicochemical pretreatment methods, NaOH/microwave and NaOH/ultrasound were developed, and the carbon-based sulfonated solid acid catalysts were prepared for furfural residues conversion into reducing sugars. After the two optimum pretreatments, both the content of cellulose increased (74.03%, 72.28%, respectively) and the content of hemicellulose (94.11%, 94.17% of removal rate, respectively) and lignin (91.75%, 92.09% of removal rate, respectively) decreased in furfural residues. The reducing sugar yields of furfural residues with the two physicochemical pretreatments on coal tar-based solid acid reached 33.94% and 33.13%, respectively, higher than that pretreated via NaOH alone (27%) and comparable to that pretreated via NaOH/H₂O₂ (35.67%). The XRD patterns, IR spectra and SEM images show microwave and ultrasound improve the pretreatment effect. The results demonstrate the carbon-based sulfonated solid acids and the physicochemical pretreatments are green, effective, low-cost for furfural residues conversion.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The worldwide depleting fossil energy and the environmental pollution are the two important questions threatening the development of human society. In the long run, the exploiting and using of clean and recycling energy is the inexorable trend. Now, the bio-energy has attracted much interest in the world as one of efficient

way to solve the energy and environment questions (Kempainen et al., 2012; Tang et al., 2011; Nakagame et al., 2011).

The furfural residues are biomass wastes for the furfural production. They are produced by hydrolysis from agricultural products, such as corncob, vegetable fibre. Furfural residues are converted easily into reduced sugar because of their low hemicellulose content. In China, there are large numbers of furfural residues. From the economical and environmental points of view, it has the important practical significance to reuse this kind of low cost, extensive, renewable biomass sources (Yu et al., 2013; Mao et al., 2012; Wang et al., 2013).

^{*} Corresponding authors. Tel.: +86 951 206 2061.

E-mail addresses: bjma@nxu.edu.cn (B.J. Ma), liuwy@nxu.edu.cn (W.Y. Liu).

The hydrolysis of the raw material of lignocellulose including furfural residues is to convert the lignocellulose and hemicellulose into reducing sugars. Generally, the hydrolysis of the biomass includes enzymatic hydrolysis (Nakagame et al., 2011; Yu et al., 2013; Wang et al., 2013) and acidic hydrolysis (Mao et al., 2012; Irmahboob et al., 2002). The enzymatic hydrolysis is expensive and the liquid acidic hydrolysis can corrode the reaction equipment and pollute the environment. One of the promising way is to use solid acidic hydrolysis which is low cost, environmentally friendly and has been attracted much attention. For example, Ji et al. reported WC catalyst for cellulose conversion into ethylene glycol (Ji et al., 2008). Onda et al. reported molecular sieve with different Si/Al ratio for cellulose conversion into reducing sugar and obtained 25% of the yield of the reducing sugar under optimum reaction condition (Onda et al., 2008). Shimizu et al. reported cellulose conversion into reducing sugar with heteropolyacid catalyst and obtained 23% of the yield of the reducing sugar (Shimizu et al., 2009). Carbon-based sulfonated solid acid catalyst with strong acid is low cost, environmentally friendly and has been used for cellulose hydrolysis (Onda et al., 2008; Suganuma et al., 2008). However, the carbon-based sulfonated solid acid catalyst for furfural residues hydrolysis into reducing sugar has not been reported as far as we know.

Researches have demonstrated that the lignin in biomass could inhibit hydrolysis (Kumar et al., 2012; Yu et al., 2011; Berlin et al., 2006). Pretreatment separating the lignin from the substrate is a necessary step in bioconversion of lignocellulose to fuels and chemicals, and furfural residue is no exception. Many pretreatment methods had been reported for lignocellulose residue pretreatment (Karagoz et al., 2012; García-Cubero et al., 2009; Wang et al., 2009; Antoni et al., 2007; Asada et al., 2011). Among the pretreatment methods, NaOH delignification is a simple and low cost method which can open the chemical ester bonds formed unstably among cellulose, hemicellulose and lignin. However, NaOH delignification is not an effective method to remove lignin from furfural residue owing to the condensed structure of lignin (Bu et al., 2011). Some researchers have reported NaOH/H₂O₂ pretreatment can effectively degrade the lignin from furfural residue (Xing et al., 2012; Wang et al., 2013; Yu et al., 2013). These indicate there are great spaces to improve the NaOH pretreatment method. Microwave and ultrasound with specific functions (such as heating, dispersion and cavitation) can give extra energy and had been effectively used in biomass pretreatment (Azuma et al., 1984; Ooshima et al., 1984; Kitchaiya and Intanakul, 2003; Svetlana et al., 2010, 2011). It is anticipated to adopt physicochemical pretreatment methods (such as NaOH/microwave, NaOH/ultrasound) for improved furfural residues conversion.

Here, we reported carbon-based sulfonated solid acid catalysts for furfural residues conversion into reducing sugars. Also, we developed two physicochemical pretreatment methods, NaOH/microwave and NaOH/ultrasound. The catalysts and pretreatment techniques are effective, low cost, environmental friendly and thus have potential commercial value for the furfural residue recycle.

2. Methods

2.1. Raw materials and chemicals

All chemicals are of analytical grade without further purification. Furfural residue was kindly provided by Gongxiang chemical Company (Ningxia Province, China). The main components were determined as: cellulose 39.1%, hemicellulose 3.9% and lignin 28.6% (absolute wt.% of starting material). The raw furfural residue, with an initial pH of 2–3, were immersed in fresh water and then

rinsed until a neutral pH was reached. The residues were screened with 40 meshes after be dried at 60 °C for 24 h. The furfural residue was filtered through the 40 meshes and then collected as the experimental samples. The average contents of cellulose, hemicellulose and lignin were 50.3%, 3.1% and 37.2%, respectively.

2.2. Pretreatments with NaOH/microwave or NaOH/ultrasound

For the pretreatments with NaOH/microwave, the furfural residue and NaOH with the weight ratio of 5% were mixed in the distilled water with furfural residue to water ratio of 0.1 g/mL, and stirred for 24 h at the room temperature. Then, a microwave oven (WD900, Grante, China) was used for further treatment of the furfural residue at different power and for different time. Last, the furfural residue was rinsed until neutral pH and being dried at 120 °C for the further hydrolysis. The pretreatment with NaOH/ultrasound was almost same as the NaOH/microwave except ultrasound generator (KQ500DE, Kunshan, China) with a water bath instead of microwave.

The NaOH/H₂O₂ pretreatments were also performed for the comparison. The furfural residue, 5% NaOH and 2.5% H₂O₂ (weight ratio) were mixed in the distilled water with furfural residue to water ratio of 0.1 g/mL, and stirred for 24 h at the room temperature. The furfural residue was rinsed until neutral pH and being dried at 120 °C for the further hydrolysis.

2.3. Chemicophysical characterization of furfural residues

The compositions of the cellulose, hemicellulose and lignin were determined using Van Soest method (Van Soest et al., 1963, 1967, 1968) on FIWE3 fiber analyzer (VELP, Italy). The FT-IR spectra were obtained on a Shimadza-8400S FT-IR spectrophotometer (Shimadza, Japan) using KBr discs containing 1% finely ground samples in the range of 4000–500 cm⁻¹. The crystal structure was examined by X-ray diffraction on D/MAX220 instrument (Rigaku, Japan) using a Cu K α radiation source at a voltage of 40 kV and a current of 40 mA at the room temperature. Diffraction patterns were collected from 5° to 60° at a rate of 5° min⁻¹. The scanning electron microscopy (SEM) images were obtained on a KYKY 2800 B scanning electron microscope (KYKY, China).

2.4. Preparation of carbon-based sulfonated solid acid catalysts

For the preparation of active carbon-based solid acid, 5.5 mL concentrated sulfuric acid was added dropwise to 5.0 g active carbon (Ningxia coal industry, China) with stirring. Then the sample was static adsorbed for 12 h, then dried at 120 °C. Last, washing the sample by absolute ethyl alcohol and drying at 120 °C.

For the preparation of coal tar based solid acid, coal tar, benzaldehyde and p-toluenesulfonic acid were mixed with the weight ratio of 1:1:0.05 and reacted at 150 °C for 16 h under N₂ atmosphere, then, the same amount of benzaldehyde and p-toluenesulfonic acid were added and reacted at 250 °C for 7 h and at 350 °C for 1 h under N₂ atmosphere. The reaction product was pulverized and washed by distilled water at 80 °C, and then, dried at 120 °C. Last, the reaction product and concentrated sulfuric acid was mixed and sulfonated at 150 °C for 8 h. The sample was washed by water at 80 °C and dried at 120 °C. The amount of acid was determined by acid–base titration method. In a typical experiment, 0.2 g of catalyst was added to 40 mL of NaCl aqueous solution (0.3 mol/L). The resulting suspension was allowed to equilibrate after magnetic stirring 24 h, and then filtrated. The filtrate was titrated by dropwise addition of 0.006 M NaOH solution using phenolphthalein as the indicator agent. The acidities of the two catalysts were 2.3 mmol/g and 2.8 mmol/g, respectively.

Download English Version:

<https://daneshyari.com/en/article/7079002>

Download Persian Version:

<https://daneshyari.com/article/7079002>

[Daneshyari.com](https://daneshyari.com)