Bioresource Technology 146 (2013) 355–362

Contents lists available at ScienceDirect

Bioresource Technology

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

Influence of ultrasonic pretreatment on the yield of bio-oil prepared by thermo-chemical conversion of rice husk in hot-compressed water

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HIGHLIGHTS

- Ultrasonic pretreatment significantly changes the structure of the rice husk.
- The pretreated rice husks have higher conversion and bio-oil yield.
- Ultrasonic pretreatment changes the chemical composition of the bio-oil.

ARTICLE INFO

Article history:
Received 23 May 2013
Received in revised form 15 July 2013
Accepted 20 July 2013
Available online 26 July 2013

Keywords:
Ultrasonic pretreatment
Thermo-chemical conversion
Rice husk
Hot-compressed water
Bio-oil

ABSTRACT

The aim of the current study is to investigate the feasibility of thermo-chemical conversion of rice husk in hot-compressed water via ultrasonic pretreatment to increase the bio-oil yield. The results show that ultrasonic pretreatment remarkably changes the structures of the rice husk, such as enhancing swelling and surface area, eroding lignin structure, and resulting in more exposure of the cellulose and hemicellulose. The highest bio-oil yield of 42.8% was obtained from the thermo-chemical conversion at 300 °C and 0 min of the residence time for the 1 h pretreated rice husk. GC–MS analysis indicates that the relative contents of phenols, 5-Hydroxymethylfurfural, and lactic acid are higher in bio-oils obtained from the pretreated rice husks than that from the raw rice husk.

1. Introduction

As the by-product in rice processing plant, rice husk has a huge production of approximate 140 million tons annually worldwide (Chen et al., 2011). However, rice husk does not attract enough attention due to the properties of high ash and lignin contents, thus it is usually utilized as a low-value energy resource (Lu et al., 2012). Actually, rice husk contains relative high cellulose content, and it can be used as available biomass feedstock for bio-oil preparation via thermo-chemical conversion in hot-compressed water. However, limited attempts have been implemented to prepare bio-oil from rice husk to our best knowledge. This may because the recalcitrant nature of rice husk leads to the low bio-oil yield (Huang et al., 2013). Therefore, it is necessary to break down the resistance of lignin and enhancing accessibility of cellulose and hemicellulose with pretreatment route.

Prevailing pretreatment approaches include alkali pretreatment (Lin et al., 2013), organic/inorganic acid pretreatment (Gholizadeh et al., 2013; Manzoor et al., 2013), ozonolysis (Garcia-Cubero et al., 2009), organosolv (Koo et al., 2012), and ionic liquids pretreatment (Mora-Pale et al., 2011), etc. However, these methods usually use large amount of alkalis, acids, organic solvents and expensive ionic liquids, which increase the cost of recycling and disposal. Ultrasonic pretreatment is a new green method because no acids, alkalis or organic solvents are used, and it may be a promising alternative to the conventional chemical pretreatments (Wong et al., 2009).

Ultrasound is an oscillating sound pressure wave with frequency above the hearing range of humans, and its delivery in water will lead to the erosion of the biomass surface (Yang et al., 2012a). Ultrasonic pretreatment has been extensively investigated in many fields such as bio-ethanol preparation (Sasmal et al., 2012), sludge disposal (Yang et al., 2012b), and bio-hydrogen production (Leaño and Babel, 2012). In previous report, ultrasonic pretreatment was used to enhance the yield of bio-oil from the liquefaction of the pure cellulose in hot-compressed water (Shi et al., 2013). The results show that ultrasonic pretreatment significantly increase the yield of bio-oil. The enhanced bio-oil yield is attributed to the structural changes of cellulose caused by ultrasonic pretreatment, such as increasing surface area and decreasing crystallinity. Compared to the pure cellulose, rice husk have more complex structure and components (cellulose, hemicellulose, and

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http://dx.doi.org/10.1016/j.biortech.2013.07.094

lignin). In order to further expand the application range of this method, this work investigated the influences of ultrasonic pretreatment on the bio-oil yield from the liquefaction of rice husk. The influences of the ultrasonic pretreatment on the physicochemical property of rice husk, the yield of bio-oil, and chemical composition of bio-oil were studied, respectively. The carbon and energy balances were estimated.

2. Methods

2.1. Rice husk and ultrasonic pretreatment

The raw material, rice husk with a particle size below 100 mesh, was obtained from a rice processing plant in Jiangsu province, China. The characterization of rice husk has been reported in our previous literature (Shi et al., 2012). The rice husk contains 22.6% of cellulose, 33.7% of hemicellulose, 19.5% of lignin, 9.0% of extractives, and 11.95% of ash. The elemental analysis (on ash-free basis) shows that the rice husk consists of 45.22% of carbon, 6.48% of hydrogen, 46.75% of oxygen (by difference), and 1.55% of nitrogen.

The ultrasonic pretreatment of rice husk was performed on a 60 mL glass beaker equipped with a water bath to keep a constant temperature of 30 °C. Ultrasound generation system (1200Y, Bi Long Inc., China) is composed of an ultrasonic generator of 20 kHz frequency and a Ti-6 Al-4 V (titanium alloy) cylindrical horn with a probe (Φ = 15 mm). In the pretreatment, the rice husk and deionized water were added into the glass beaker according to the mixture ratio of 5 g sample/50 mL water. The maximum power output of the ultrasonic generator is 1200 W, and the power used was set at 5% (60 W) in all the pretreated experiments. The actual power output, 9.29 W, was determined based on calorimetry method and the assumption that all the power entering the water medium is dissipated as heat. (Hagenson and Doraiswamy, 1998; Inoue et al., 2006; Lorimer et al., 1991; Sasmal et al., 2012).

2.2. Liquefaction and separation procedure

The liquefaction experiments of rice husks were performed in a 450 mL stainless steel reactor equipped with a mechanical agitator (Nantong Huaxing Petroleum Instrument Co., Ltd., China). A temperature sensor is placed inside the reactor and a pressure transmitter is connected with the reactor. The maximum working temperature and pressure of this reactor are 400 °C and 35 MPa, respectively. In a typical run, the pretreated rice husk slurry containing 5.0 g sample and 50 mL water was directly loaded into the reactor without filtration and separation. The reactor was sealed, and then evacuated using a vacuum pump to get rid of the oxygen. The mechanical agitator was opened, and then the reactor was heated by an electric heating jacket to the set-point temperature at the average heating rates of 8 °C/min, and the set-point temperature was maintained for a desired residence time. Once the reaction was completed, the reactor was cooled rapidly by tap water until the reactor temperature decreased to 25 °C. The cooling rate was calculated at about 40 °C/min. After waiting for a period of time, the reactor was opened, and the liquefied products were separated according to the procedure described in Fig. 1. The separated procedure is identical with the previous literature (Shi et al., 2013). Firstly, the gas was vented and not collected because this work mainly focuses on the liquid products, but the effects of ultrasonic pretreatment on the yield and carbon balance of gas were also considered by differences. The liquid and solid products in the reactor were transferred into a beaker together, and then they were separated by reduced filtration. The water in the filtrate was removed by a rotary evaporator at 40 °C and the water soluble oil (WSO) was obtained. The water insoluble fraction and interior wall of the reactor were washed three times with acetone, and finally, they were collected together. The mixtures were separated by filtration. The acetone in the extract liquor was removed by blowing nitrogen method at the ambient temperature and the leftover was designated as heavy oil (HO). Both the HO and WSO are known as the bio-oil. The acetone-insoluble phase was dried in oven at 105 °C for 2 h, and designated as solid residue (SR).

The yields of HO, WSO, and SR are calculated by dividing the mass of products by the mass of dry rice husk. The raw rice husk was also liquefied under the identical operating conditions as that of the pretreated rice husk (such as the heating rates, loading, temperature, and residence time) as control groups. All experiments were performed three times and the relative errors were less than 5%.

2.3. Characterization of raw and pretreated rice husks

Before characterization, the pretreated rice husk slurries were dried on a freezer dryer (FreeZone Stoppering Tray Dryer, Labconco) to preserve their original structures as much as possible. After that, the dried pretreated samples were stored in desiccators at room temperature. The surface structures of the raw and pretreated rice husks were observed on a Hitachi S-4800 scanning electron microscope (SEM). The BET surface Area Analyses of raw and pretreated rice husks were performed on a NOVA2200e surface area analyzer (Quanta chrome, USA). The infrared signatures of the raw and pretreated rice husks were analyzed by a Spectrum 100 Fourier transform infrared spectrophotometer (FT-IR, Perkin Elmer Inc., USA) using KBr tablet containing 1% of samples.

2.4. Analysis of products

The elemental analyses of HO, WSO and SR were carried out on an Elementar Vario EL III analyzer. The high heat values (HHVs) were calculated according to the Dulong's equation (Theegala and Midgett, 2012; Zhuang et al., 2012):

$$\text{HHV (MJ/kg)} = 0.3383\text{C} + 1.422\ (\text{H-O}/8) \quad (1)$$

GC–MS (gas chromatography–mass spectrometry) analysis was carried out to identify the chemical compositions of the bio-oils (HO and WSO) on Agilent 7890A/5975C (USA). The column used is HP-5MS (5% Phenyl Methyl Siloxane, 30 m × 0.25 mm × 0.25 μm), and the carrier gas is helium with 99.999% purity. The column temperature was set programmatically from 60 °C to 300 °C: isothermal at 60 °C for 4 min, then temperature rise at a rate of 5 °C/min to 300 °C and a hold for 8 min at the final temperature. The compounds were identified with the help of NIST11 Mass Spectral Database.

3. Results and discussion

3.1. Effect of ultrasonic pretreatment on the structures of the rice husks

Fig. A1A shows that the difference of the rice husk slurries before and after ultrasonic pretreatment. Ultrasonic pretreatment increases the volumes of rice husks in the water causing the enhancement of dispersion and swelling. The influences of ultrasonic pretreatment on the rice husk structures were further investigated by SEM. Fig. A1(B–D) shows that the surface morphologies of the pretreated rice husks are significantly different with that of the raw rice husk. Compared to the smooth surface of raw rice husk, the surfaces of pretreated rice husks were seriously destroyed. The longer pretreated time results in the more serious surface corrosion. Ultrasonic pretreatment results in the loose