ARTICLE IN PRESS

Journal of Analytical and Applied Pyrolysis xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Catalytic fast pyrolysis of rice husk: Effect of coupling leaching with torrefaction pretreatment

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ARTICLE INFO

Keywords:
Catalytic fast pyrolysis
Bio-oil
Leaching
Torrefaction
Rice husk

ABSTRACT

The effect of coupling leaching with torrefaction pretreatment process on bio-oil production from catalytic fast pyrolysis using ZSM-5 zeolite catalyst was evaluated by Py-GC/MS. During coupling leaching with torrefaction pretreatment, the fuel characteristics and structural characteristics of rice husk samples were changed, which were evaluated using proximate, ultimate, and calorific analyses, Fourier transform infrared spectroscopy (FTIR) and X-ray diffractometer (XRD) techniques. The experimental results of catalytic fast pyrolysis indicated that coupling leaching with torrefaction pretreatment further improved the relative contents of BTX (benzene, toluene and xylene) compounds in bio-oil compared to that of raw rice husk sample. It was mainly ascribed to the effective removal of metallic species during leaching process. In addition, the selective removal of hemicellulose fraction and the increasing lignin fraction and changes in the structure of lignin (cleavage of ether linkages and demethoxylation) during torrefaction process also plays positive roles. Severe torrefaction process resulted in the cross-linking and charring of sample, thus reducing the formation of BTX compounds. Thus, coupling leaching with middle torrefaction pretreatment process was the optimum pretreatment conditions for catalytic fast pyrolysis of rice husk samples.

1. Introduction

Biomass, as an alternative energy resource, is abundant worldwide and can potentially produce liquid transportation fuels and mitigate environmental impacts caused by the utilization of fossil fuels. Furthermore, using of biomass for energy could contribute to mitigating the effects of the global warming due to its carbon neutrality. Compared to other methods of producing biobased products from biomass, fast pyrolysis is a promising thermochemical technology for converting biomass into liquid product known as bio-oil. Bio-oil can be either combusted as a fuel in various applications, or served as a platform for synthesis of transportation fuels and various commodity chemicals [1–4]. However, some negative attributes of bio-oil, including high moisture content, high oxygen content, high acidity, poor volatility and high viscosity, and low heating value, limit its final application in chemicals production and fuel applications. Catalytic fast pyrolysis (CFP) technology, which is based on the use of acidic catalyst in pyrolysis process, has been reported to have the effect on improvement of the bio-oil quality [5–7]. In addition, biomass pretreatment prior to pyrolysis, such as torrefaction, is also gaining a lot of attention for improvement of bio-oil quality since the oxygen in raw biomass can be partially removed prior to pyrolysis [8–11].

Torrefaction is a mild pyrolysis process operated at low temperature under oxygen-deficient conditions [12–14]. It was found that torrefaction improved fuel properties of biomass with lower atomic H/C and O/C ratios compared to raw biomass [15,16]. Chen et al. [17] defined decarbonization, dehydrogenation, and deoxygenation indices to identify the mass losses of C, H, and O in biomass from torrefaction, and the results indicated that torrefaction has a larger influence on removal of oxygen compared to that of carbon and hydrogen. Recently, several studies suggest that torrefaction pretreatment could improve the selectivity for formation of hydrocarbons over zeolite catalysts during catalytic fast pyrolysis [18–21]. Torrefaction process caused the chemical and structural changes of biomass constituents of hemicellulose, cellulose and lignin, all of which affected the hydrocarbons production from catalytic fast pyrolysis [22,23]. Besides the three major constituents of hemicellulose, cellulose and lignin, biomass naturally contains minor amounts of inorganic minerals. Considering most inorganic minerals still remaining in the torrefied biomass, the deleterious effect of biomass originated metallic species on hydrocarbon yields from

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https://doi.org/10.1016/j.jaap.2018.04.016
Received 30 March 2017; Received in revised form 11 April 2018; Accepted 23 April 2018

Please cite this article as: Zhang, S., Journal of Analytical and Applied Pyrolysis (2018), https://doi.org/10.1016/j.jaap.2018.04.016

catalytic fast pyrolysis of biomass has been investigated [24,25]. On the one hand, the metallic species contained in the biomass structure, especially alkali and alkaline earth metals (AAEMs), are known to catalyze cracking and fragmentation of primary pyrolysis volatiles, which change the distribution of primary pyrolysis products and favor the formation of char and gas products [26–28]. On the other hand, accumulation of metallic species on zeolite catalyst is responsible for catalyst deactivation, affecting the volatiles conversion and resulting in a reduction in the selectivity of hydrocarbons from catalytic fast pyrolysis [29,30]. To alleviate the deleterious catalytic effects of biomass originated metallic species, acid leaching pretreatment for removal of AAEMs prior to catalytic fast pyrolysis is also an effective method for improvement of bio-oil quality [25]. Remarkable advances in understanding separate leaching or torrefaction pretreatment have been achieved. However, effect of coupling leaching with torrefaction pretreatment on catalytic fast pyrolysis for bio-oil production remains relatively obscure.

In this work, the fuel characteristics and structural characteristics of rice husk samples under different pretreatment processes, such as acid leaching for removal of AAEMs and the coupling leaching with torrefaction pretreatment under different torrefaction severity, were characterized using proximate, ultimate, and calorific analyses, Fourier transform infrared spectroscopy (FTIR) and X-ray diffractometer (XRD) techniques. The effect of coupling leaching with torrefaction pretreatment process on bio-oil production from catalytic fast pyrolysis using ZSM-5 zeolite catalyst was evaluated using Py-GC/MS. It is believed that the obtained results of these experiments could provide a comprehensive insight into catalytic fast pyrolysis of biomass.

2. Materials and methods

2.1. Materials and pretreatment process

The rice husk was collected from a rice milling factory (supplied by JiangXi Jinkang Advanced Material Sci-Tech Co., Ltd), which was dried in a laboratory oven before storage in sampling bags for subsequent pretreatment process and ensuring the accuracy of experimental results. ZSM-5 zeolite catalyst ($SiO_2/Al_2O_3 = 30$, $S_{BET} = 425\ m^2/g$) with the particle diameter of 2–5 μm was purchased from the Catalyst Plant of Nankai University. Prior to experiment, the ZSM-5 zeolite catalyst was calcined in air at 550 °C for 4 h in a furnace.

Pretreatment process of coupling leaching with torrefaction was carried out by acid leaching for removal of AAEMs followed by torrefaction, which was similar to our previous studies [9,31]. Specifically, 20 g of RH were leached and stirring for 2 h with 200 mL leaching solution at 30 °C in a water bath. Aqueous solution of acetic acid (pH = 2.0) was used as leaching solution in this study for avoiding modifications in biomass polymer composition. After leaching, the samples were rinsed with deionized water, and the leached RH was then oven-dried at 105 °C overnight to remove residual moisture.

A lab-scale vertical drop fixed-bed reactor as described in our previous study was used for torrefaction experiments [32]. In each run, prior to torrefaction, approximately 10 g of raw/leached rice husk was loaded in the reactor and inserted into the furnace. A continual high purity N_2 with a constant flow rate of 200 mL/min was admitted to the reactor. Subsequently, the furnace was programmed to ramp from room temperature to the target temperatures of 210, 240 and 270 °C corresponding to light, mild, and severe torrefaction conditions at 10 °C/min, and then holds for 60 min and cooling to room temperature. After cooling of solid product from torrefaction process under the N_2 atmosphere, the solid product was collected from reactor.

Raw rice husk, leached rice husk and rice husk samples after coupling leaching with torrefaction process were labeled as RH, W-RH, LW-RH, MW-RH, and SW-RH corresponding to different torrefaction severity, respectively. Mass and energy yields of rice husk samples during pretreatment were calculated according to the equations as mentioned in our previous study [31].

2.2. Physical and chemical characterization

Proximate analysis of solid product was carried out based on ASTM standard. A vario EL-III elemental analyzer was performed for elemental composition analysis. A SDACM3000 bomb calorimeter was performed for determining higher heating values (HHVs). Prior to performing these analyses, sample was dried in a drying oven at 105 °C for 24 h. Thus, these results were obtained in terms of dry basis. As reported by Chen et al. [17], decarbonization, dehydrogenation and deoxygenation indices resulting from pretreatment process can be used to account for mass losses of carbon, hydrogen, and oxygen, which were defined as:

$$\text{Decarbonization}(\%) = \left(1 - \frac{Y_m \times Y_{C,p}}{Y_{C,r}}\right) \times 100 \tag{1}$$

$$\text{Dehydrogenation}(\%) = \left(1 - \frac{Y_m \times Y_{H,p}}{Y_{H,r}}\right) \times 100 \tag{2}$$

$$\text{Deoxygenation}(\%) = \left(1 - \frac{Y_m \times Y_{O,p}}{Y_{O,r}}\right) \times 100 \tag{3}$$

where Y_m is the mass yield of pretreatment process; Y_C, Y_H, and Y_O denote the C content, H content and O content obtained from ultimate analysis, respectively, and the subscript r and p stand for raw and pretreated samples.

Inductively coupled plasma optical emission spectrometry (ICP-OES, Leeman Laboratories, Inc., Hudson, NH) analysis was carried out to measure the changes of metallic species concentration in rice husk sample after pretreatment [9]. Fourier transform infrared spectroscopy (FTIR) analyzer (Bruker Vector 22) was used to characterize the functional groups changes of rice husk samples after pretreatment. A Bruker D2 Phaser X-ray diffractometer (XRD) where the diffraction angle (2θ) was between 5 and 40° was used to characterize the crystallinity changes of sample after pretreatment. The crystallinity index (CrI) of sample was calculated according to the equations below:

$$\text{CrI} = \left(\frac{I_{002} - I_{am}}{I_{002}}\right) \times 100 \tag{4}$$

where I_{002} is the peak intensity at $2\theta = \sim 22.5^\circ$, while I_{am} is the peak intensity at $2\theta = \sim 18.5^\circ$.

The analysis experiments were replicated three times, and the averaged data were used.

2.3. Py-GC/MS

Catalytic fast pyrolysis experiments were performed in a commercialized pyrolyzer (model no. 5200, CDS Analytics Inc.), which was connected to an Agilent gas chromatograph/mass spectrometer (7890GC/5975MS). As shown in Fig. 1, 0.50 ± 0.01 mg rice husk sample placed in the middle of a quartz tube (20 mm long, 2 mm inner diameter). Two equally weighed catalyst layers were placed at both sides of rice husk sample. The total catalyst to biomass sample ratio was 10 for all catalytic fast pyrolysis experiments. In each run, the rice husk sample and catalyst layers were separated by quartz wool so that only the primary pyrolysis volatiles could be upgraded when they passed through the catalyst layers. The pyrolysis experiments were carried out at 550 °C with a heating rate of 20000 °C/s and held at the final temperature for 20 s. The pyrolysis volatiles were then carried by helium to GC/MS for analysis immediately, and the injector temperature was kept at 300 °C. The GC separation was performed using a HP-5MS capillary column (0.25 mm × 0.25 μm × 30 m). Helium (purity: 99.99%) was used as the carrier gas at a flow rate of 1 mL/min and the split ratio was set to 1:80. Other parameters for GC/MS operation can be seen in our