



Research paper

Pyrolysis behavior of raw/torrefied rice straw after different demineralization processes



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ABSTRACT

This study aims to evaluate the effects of different demineralization processes on the pyrolysis behavior and pyrolysis product properties of raw/torrefied rice straw. To achieve this target, different demineralization pretreatment processes with deionized water, acetic acid and hydrochloric acid solutions of rice straw were carried out, and the detailed information of fuel characteristics, alkali and alkaline earth metals (AAEMs) concentration, thermal degradation behavior and pyrolysis product properties were figured out. The results indicated that demineralization processes improved the fuel characteristics. The removal efficiencies of AAEMs increased in the order hydrochloric acid > acetic acid > deionized water. Torrefied samples exhibited lower removal efficiencies of AAEMs than that of raw samples because of the speciation transformations of AAEMs during torrefaction. More obvious effect of alkali metals on the pyrolysis process can also be obtained than that of alkaline earth metals. Compared with raw rice straw, the effects of demineralization processes on the changes of cellulose crystallinity of torrefied rice straw can be ignored. All the demineralization processes enhanced the bio-oil yield at the expense of biochar and non-condensable gases for raw/torrefied samples. They also have important promoting influence on the properties of bio-oil and biochar by enhancing the sugars formation and improving the fuel characteristics of biochar. The obtained results can be helpful for understanding the pyrolysis behavior of raw/torrefied rice straw after different demineralization processes and for further utilization of biomass resources with high contents of silica and potassium.

1. Introduction

With the rapid increase in energy consumption, the widespread use of fossil fuels has brought about serious energy crisis and environmental issues. In recent years, biomass resource has been considered as promising alternatives to fossil fuels due to its abundant availability at low-costs and carbon-neutral nature. Rice straw is considered to be the main agricultural residue of rice crops that are left over as waste products on the field. The annual production of rice straw is about 731 million tons, which is mainly from Africa, Asia, Europe, America and Oceania as 20.9, 667.6, 3.9, 37.2 and 1.7 million tons, respectively [1]. Until today, the most common practice for handling rice straw after harvesting season is open burning in many countries [2]. This disposal way of rice straw gives rise to the energy waste and adversely affects environment (CO, SO₂, NO_x, particulate matters and dioxins) and human health (cancer and asthma) [3,4]. Therefore, new methods to dispose

rice straw have shifted towards the “waste to resource”, and rice straw also has the potential to be used as alternatives to fossil fuels for production of renewable energy and high value-added products.

Rice straw has particularly high contents of silica and potassium and is a very challenging feedstock for thermochemical conversion to produce of renewable energy. Among biomass conversion technologies, pyrolysis is an attractive way to facilitate the transformation of biomass into solid (biochar), liquid (bio-oil) and gaseous (non-condensable gases) products. However, the drawbacks of rice straw, including the hydrophilic character, low energy density and high moisture content, limited its large-scale application. Furthermore, the relatively high amount of alkali and alkaline earth metals (AAEMs) found in rice straw adversely affects the pyrolysis behavior and pyrolysis product properties, especially the yield and quality of bio-oil [5–8]. In order to overcoming these adverse impacts of AAEMs during pyrolysis process, demineralization pretreatment by leaching with water or acidic solutions

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of rice straw has been investigated. Shi et al. found that water washing of rice straw removed most of alkali metals and acid washing removed almost all AAEMs [9]. Eom et al. compared the pyrolysis product properties from raw and demineralized rice straw in a fluidized bed pyrolyzer, and the results found that demineralization affected the distribution of pyrolysis products [10].

Torrefaction has been known as a thermochemical pretreatment process of biomass feedstock in the absence of oxygen under the temperatures ranging from 200 to 300 °C [11–13]. Previous studies have indicated that torrefaction process had the obvious effect on improving the fuel characteristics of biomass with high energy density and low oxygen content [14–17]. The adverse effects of AAEMs on pyrolysis behavior became more serious due to the higher relative content of AAEMs in torrefied biomass sample [14,18]. Furthermore, in addition to the changes on the organic composition and structure of biomass, torrefaction also led to the change in the chemical association of AAEMs. Khazraie Shoulaifar et al. found that torrefaction resulted in the transformation of AAEMs from a water-soluble form to an ion-exchangeable form, and at high torrefaction condition, a small amount of water-soluble or ion-exchangeable AAEMs could transform to acid-soluble and stable forms [19]. Similar results of the transformation of inherent K and Na during torrefaction process were also obtained by other researchers [20–22]. However, the investigation on demineralization process from torrefied biomass and its effects on subsequent pyrolysis behavior are rarely reported.

The present study aims to comparatively evaluate the effects of different demineralization processes on the pyrolysis behavior and pyrolysis product properties of raw/torrefied rice straw. To achieve this target, different demineralization pretreatment processes with deionized water, acetic acid and hydrochloric acid solutions of raw/torrefied rice straw samples were carried out, and the detailed information of fuel characteristics and AAEMs concentration was clearly figured out. Finally, the effects of different demineralization processes on thermal degradation behavior and pyrolysis product properties of raw/torrefied rice straw sample were also investigated. The obtained results can be helpful for understanding the pyrolysis behavior of raw/torrefied rice straw after different demineralization processes and for further utilization of biomass resources with high contents of silica and potassium.

2. Materials and methods

2.1. Raw/torrefied materials

Rice straw (RS), a kind of agricultural residue, was selected to evaluate the effects of different demineralization processes on the pyrolysis behavior in this study. The as-received samples were first milled to a particle size ranging from 60 to 125 µm, and then dried at 105 °C for 12 h. Torrefied rice straw sample (TS) was obtained by torrefaction of raw rice straw at 240 °C for 1 h in a tubular furnace reactor under the N₂ atmosphere with a rate of 200 mL/min. The detailed description of torrefaction process was presented in our previous studies [18,23].

2.2. Demineralization pretreatment processes

In this study, three different leaching solutions were used (deionized water, acetic acid and hydrochloric acid) for demineralization of raw/torrefied rice straw samples. Specifically, 20 g of raw/torrefied rice straw samples were demineralized by leaching and stirring for 2 h with 500 mL leaching solutions at the temperature of 30 °C. For leaching solutions of acetic acid and hydrochloric acid, the pH was kept at about 2. After leaching, the wet samples were vacuum filtered and further rinsed with deionized water to neutral. Finally, the samples were dried at 105 °C to remove residual moisture. The rice straw samples after demineralization with different leaching solutions were labeled as RS-

H₂O, RS-C₂H₄O₂, RS-HCl for raw rice straw and TS-H₂O, TS-C₂H₄O₂, TS-HCl for torrefied rice straw, respectively. Proximate analysis 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). The changes on crystallinity of raw/torrefied rice straw samples during different demineralization processes were analyzed by a Bruker D2 Phaser X-ray diffractometer (XRD) where the diffraction angle (2θ) between 5 and 40° with a step size of 0.05°. The crystallinity of rice straw samples was obtained by crystalline index (CrI) according to Eq. (1).

$$\text{CrI}(\%) = \left(\frac{I_{002} - I_{\text{am}}}{I_{002}} \right) \times 100 \quad (1)$$

Where I_{002} is the maximum intensity of the (002) lattice diffraction, and I_{am} is the maximum intensity diffraction at $2\theta = \sim 18^\circ$.

2.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed by a Q5000IR Thermogravimetric analyzer. About 5 mg of sample was heated at 20 °C/min from room temperature to 600 °C. During each run, high purity N₂ was passed through the TGA at a constant flow rate of 100 mL/min to provide the inert gas environment for pyrolysis and to sweep away the volatile released.

2.4. Pyrolysis experiment

Pyrolysis experiments of the raw/torrefied rice straw samples were carried out in a vertical drop fixed-bed reactor, and the schematic diagram for experiment system is presented in our previous study [24]. The reactor is made of a quartz tube with a length of 350 mm and an inner diameter of 32 mm. In a typical experiment, 5 g of samples were placed into the sample feeder in advance and then quickly added to the reactor when reaching the desired pyrolysis temperature of 550 °C. During the whole reaction process, high purity N₂ at a constant flow rate of 200 mL/min to provide the inert gas environment for pyrolysis and to sweep away the volatile released. The pyrolysis volatile was passed through three condensers maintained at 0 °C to collect the bio-oil. After about 5 min under the reaction condition, the pyrolysis reaction was completed, and then the reactor was moved out from the furnace to cool down for collecting biochar.

2.5. Characterization of pyrolysis products

The chemical composition in bio-oil was analyzed using gas chromatography/mass spectrometry (GC/MS, Agilent 7890A/5975C). A Varian Cp-sil 8 cb capillary column (30 m × 0.25 mm × 0.25 µm) was used for product separation. Column max temperature: 280 °C. Carrier gas: He. Injection mode: split ratio of 80. Temperature program: initial temperature 40 °C, then heat up to 180 °C at 5 °C/min, then heat up to 280 °C at 20 °C/min and hold for 10 min. The number of scans per second for MS was 35–550 amu at the ionization energy of 70 eV. For the identification of the chemical composition in bio-oil, the NIST 05 spectral library was used.

The fuel characteristics of biochar including proximate analysis, ultimate analysis and higher heating values (HHVs) were determined as the method mentioned above. The pore structure of biochar was performed by nitrogen adsorption at 77 K with the ASAP 2020 M physical adsorption instrument. The ash compositions of biochar were detected by the ARL-9800 X-ray fluorescence spectrometer.

All the experiments and analyses were repeated at least three times to guarantee the repeatability, and the standard deviation values were calculated.

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