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Effect of inorganic species on torrefaction process and product properties of rice husk

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ABSTRACT

The objective of this study was to evaluate the effect of inorganic species on torrefaction process and product properties. Torrefaction process of raw and leached rice husk was performed at different temperatures between 210 and 270 °C. Inorganic species have significant effect on the torrefaction process and properties of torrefaction products. The results indicated that solid yield increased, gas yield decreased and liquid yield remained unchanged for leached rice husk when compared to raw rice husk. Gas products from torrefaction process mainly contained CO_2 and CO, and leaching process slightly reduced the volume concentration of CO_2. Removal of inorganic species slightly decreased water content and increased organic component content in liquid products. Acetic acid, furfural, 2,3-dihydrobenzofuran and levoglucosan were the dominant components in liquid product. Inorganic species enhanced the effect of deoxygenation and dehydrogenation during torrefaction process, resulting in the enrichment of C component in solid products.

1. Introduction

Torrefaction is a thermo-chemical process that subjects the biomass feedstock to thermal treatment at mild reaction temperatures typically between 200 and 300 °C in the absence or presence of oxygen (Chen et al., 2015a,b; Chew and Doshi, 2011). In recent years, various sources of biomass feedstock, such as wood (Nachenius et al., 2015), bamboo (Li et al., 2015), agricultural residues (Chen et al., 2018, 2014), municipal solid waste (Poudel et al., 2015), and microalgae (Chen et al., 2015a,b, 2016a,b), were investigated through the torrefaction process. The benefits of torrefaction process for solid products including improvement in energy density and grindability, decrease in hygroscopicity and biological degradation tendency, have been widely reported in previous studies (Chen and Kuo, 2011; Chen et al., 2015a,b). Additionally, the enhancement of resulting products of the final transformation process such as combustion, gasification and pyrolysis processes can also be obtained when torrefied feedstock is used as a fuel. Panahi et al. assessed that the torrefied biomass had high fuel characteristics, which was suitable for co-firing with coal (Panahi et al., 2018). Recari et al. found that torrefaction process improved the gasification parameters of solid recovered fuel (SRF) with lower tar yield and higher H_2/CO ratio (Recari et al., 2017). Chen et al. also evaluated the influence of torrefaction pretreatment on improving the syngas quality and cold gas efficiency during gasification process with a bench-scale laminar entrained-flow gasifier (Chen et al., 2011). Furthermore, some researchers concluded that the changes in physicochemical properties during torrefaction process improved the bio-oil properties by reduction of water and oxy-compound contents from pyrolysis or catalytic pyrolysis (Zeng et al., 2018; Chen et al., 2016a,b; Ren et al., 2013). Hence, in-depth study on the influence factors of torrefaction process was inevitable.

In addition to the reaction conditions such as temperature and time, torrefaction behavior was also significantly dependent on the biomass compositions (cellulose, hemicellulose, lignin and inorganic species). The decomposition of hemicellulose is the dominant reaction at the temperature ranges of 200–300 °C when compared to the organic compositions of cellulose and lignin (Ru et al., 2015). Thus, torrefaction process has more remarkable influence on the biomass feedstock with high fraction of hemicellulose. Large amounts of previous studies have achieved remarkable advances in the influences of organic species on torrefaction process by different analytical methods (Ben and Ragauskas, 2012; Chen et al., 2018; Wang et al., 2017a,b; Wen et al.,

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2014). Additionally, it has been known that inorganic species contained in biomass feedstock (especially agricultural residues) have significant influences on its thermo-chemical conversion behavior (Eom et al., 2012). However, limited studies have focused on the effect of inorganic species on the torrefaction process. Previous studies of our group found that removal of alkali and alkaline earth metals (AAEMs) prior to torrefaction reduced the mass loss of torrefaction process under the same reaction conditions (Zhang et al., 2016, 2018a,b,c,d). Khazraie Shoulaifar et al. also showed that organically bonded K and Na significantly increased the mass loss during torrefaction for a fixed time and temperature (Khazraie Shoulaifar et al., 2016). However, to the best of our knowledge, in-depth study on the effect of inorganic species on the properties of torrefaction products (solid, liquid and gas products) has not been reported.

A type of agricultural residue of rice husk (RH) was used as feedstock for torrefaction in this study. Approximately 670 million tonnes of paddy residues are produced annually in the world, of which 91% is harvested in Asia, resulting in large quantities of rice husk available as waste by-product for energy recovery (Quispe et al., 2017). Organic acid was used as leaching solution for removal of inorganic species. The basic properties of raw and leached rice husk were analyzed. Torrefaction process was performed at the temperatures between 210 and 270 °C by a lab-scale fixed-bed reactor. We have compared the different torrefaction behavior of raw and leached rice husk samples to evaluate the effect of inorganic species on the torrefaction process and product properties.

2. Materials and methods

2.1. Materials

Biomass feedstocks of rice husk (RH) used in this study was collected from Jiangxi Province, China. The rice husk was screened using standard sieves ranging from 2 to 5 mm, and then dried in an oven at 105 °C overnight before storage. The results of proximate and ultimate analyses of rice husk were listed in Table 1.

2.2. Experimental method and process

Leaching of rice husk with organic acid for removal of inorganic species was conducted in accordance with the procedure described by our previous studies (Zhang et al., 2016, 2018a,b,c,d). Specifically, rice husk was leached in a beaker for 2 h at room temperature using 25 mL of acetic acid solution (pH = 2.0) per gram of dry rice husk. After leaching, we rinsed it with deionized water, and then we placed the wet samples in the oven at 105 °C overnight to re-dry. The surface morphology was analyzed by scanning electron microscopy (SEM, LEO1530VP LEO, Germany). The contents of inorganic species of raw and leached rice husk samples were determined using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) as our previous study (Zhang et al., 2015).

A lab-scale fixed-bed reactor with 450 mm in length and 38 mm in inner diameter was used for torrefaction. The fixed-bed reactor is illustrated schematically in Fig. 1. Approximately 10 g of rice husk samples were put into the reactor. N_2 with a flow rate of 200 mL/min was admitted to the reactor to provide an inert atmosphere. Subsequently, the reactor was heated to the target temperatures at 10 °C/min, and then hold there for 60 min. The target torrefaction temperatures were selected as 210, 240, and 270 °C corresponding to light, mild, and severe torrefaction conditions in this study (Chen et al., 2015a,b). After torrefaction was completed, solid product from torrefaction process was cooled under the N_2 atmosphere. In addition, the solid, liquid and gas products were collected in the reactor, condensing system and gas sampling bags during torrefaction process, respectively.

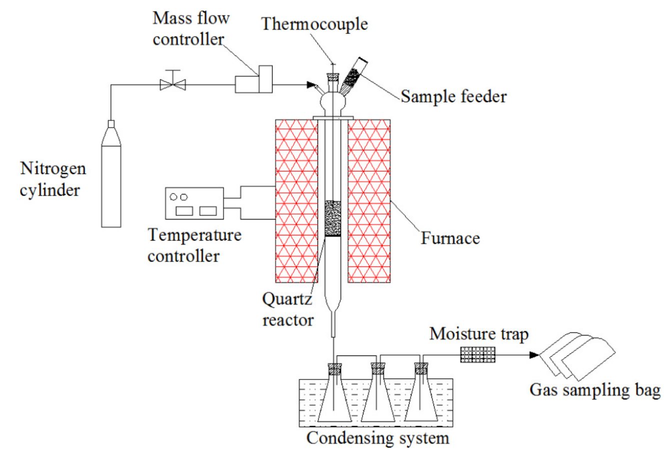

Fig. 1. Schematic diagram of lab-scale fixed-bed reactor for torrefaction.

Table 1
Basic properties of raw and leached rice husk samples.

Items		RH	WRH
Proximate analysis (wt%, db)	A_d	11.8	11.3
	V_d	73.5	75.5
	FC_d	14.7	13.2
Ultimate analysis (wt%, db)	C	40.8	41.1
	H	5.7	5.7
	O	40.3	40.7
	N	1.2	1.1
	S	0.2	0.1
HHV (MJ/kg)		16.25	16.27
Inorganic species concentration (wt%)	Si	47,970	45,040
	K	4582	103
	Ca	1003	489
	Mg	361	27
	Fe	83	60
	Al	149	85
	P	391	98
	S	528	135
	Cl	122	7

2.3. Characterization of torrefaction products

Proximate analysis of solid product from torrefaction process was performed to determine the ash, volatile matter and fixed carbon contents based on ASTM standard. Ultimate analysis of solid product was determined by a vario EL-III elemental analyzer. The higher heating value (HHV) of solid product was obtained by a SDACM3000 bomb calorimeter.

Water content of liquid product was measured by Karl Fischer titrimetric method. The chemical composition of liquid product was analyzed using gas chromatography/mass spectrometry (GC/MS, Agilent 7890A/5975C). A Varian Cp-sil 8cb 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 chemical composition in bio-oil, the NIST 05 spectral library was used. The volume concentrations of gas product were determined by an Agilent 6890N GC equipped with TCD and FID detectors.