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Microwave pyrolysis of moso bamboo for syngas production and bio-oil upgrading over bamboo-based biochar catalyst

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ABSTRACT

Microwave pyrolysis of moso bamboo over bamboo-based biochar catalyst was conducted to achieve the bio-oil upgrading and high quality syngas production. The influence of the biochar on bamboo pyrolysis involving the temperature rise, product yield, and bio-oil and gas compositions was studied. The gas production was facilitated by the biochar mainly at the cost of the bio-oil, indicating the biochar had an excellent activity for the bio-oil cracking. The main compositions in bio-oil were acetic acid and phenol with the total contents ranging from 73.145% to 82.84% over the biochar catalysts, suggesting the upgrading of the bio-oil were achieved. The biochar exerted a positive effect on the syngas ($CO + H_2$) production with the maximum content reaching up to 65.13 vol% at the 20 wt% addition amount of biochar under microwave condition. The biochar became more effective on the bio-oil upgrading and syngas production under microwave heating than conventional heating.

1. Introduction

The excessive utilization of fossil fuels and disadvantageous influences of burning fossil fuels on the worldwide environment are forcing researchers to look for and develop the abundant and environment-friendly alternatives to fossil fuels. Biomass has attracted significant attention due to its renewability, carbon neutrality, low emissions of nitrogen oxides (NO_x) and sulphur dioxide (SO_2) (Zhang et al., 2010).

In general, converting biomass into high value-added products can be realized mainly through biochemical and thermochemical conversion technologies. Thermochemical conversion technologies are characterized by the capability to accept a wider range of feedstocks and higher conversion rates compared to biochemical conversion (Chen et al., 2015). Pyrolysis, one of the thermochemical technologies, is recognized to be a promising way to achieve efficiently the production of bio-oil, biochar and gases from biomass. At present, the studies on pyrolysis are mainly focused on optimizing the reaction conditions to obtain the high quality target-products via applying new heating methods and/or the addition of catalysts (Zhao et al., 2013).

Microwave heating can penetrates the feedstock particle and the electromagnetic energy can be directly converted into heat throughout the volume of the irradiated materials (Zhang et al., 2017). Consequently, the temperature distribution for the entire material under microwave condition is more uniform than that under conventional condition where the heat is passed on from the outside to the interior through conduction or convection. This difference in temperature distribution is unescapable to lead to the different pyrolysis characteristics between microwave and conventional conditions. It has been demonstrated that microwave heating was favorable to the heterogeneous reactions due to the generation of its thermal effect (De la Hoz et al., 2005). This advantage over conventional heating could promote the cracking and reforming reactions of the pyrolysis volatiles over catalysts during microwave pyrolysis, which could upgrade the bio-oil and promote the productions of syngas and hydrogen (Bu et al., 2012; Hong et al., 2017).

The application of catalysts, including metallic catalysts (Nordgreen et al., 2006), natural minerals (Rapagnà et al., 2018), mineral-supported catalysts and carbon materials (Shen, 2015), was another approach to obtain the high quality target-products. Among these catalysts, the carbon materials have attracted more and more attentions. Biochar, as the solid product from biomass pyrolysis or gasification, is one of the main carbon materials used as catalyst or catalyst support.

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The analysis of its characteristics showed that biochar has relatively developed pore texture, high contents of minerals, oxygen-containing and acid functional groups on its surface (Abnisa et al., 2013; Feng et al., 2017). Moreover, biochar has the advantageous of the low cost and the ability of being simply gasified to recover the energy from the char, which avoided the frequent catalyst regeneration after deactivation (Shen, 2015). These positive properties make the biochar having the great potentiality as catalyst and catalyst support. It is especially pointed out that biochar is a good microwave absorber. In consequence, pyrolysis of biomass could be accomplished at the lower microwave output power, which is favorable for saving energy consumption due to the poor microwave absorbing capacity of the pure biomass material (Dong et al., 2018).

In the field of biomass pyrolysis, the current studies on the application of biochar were concentrated mainly upon its catalytic effects on the tar removal and biogas reforming under conventional condition (Abu El-Rub et al., 2008; Feng et al., 2018; Li et al., 2016). Although Zhao et al. (2014a) made a study of the effect of the biochar obtained from wheat straw pyrolysis on the biomass pyrolysis under microwave condition, the published report only involved the temperature-rising characteristics and the weight loss process of biomass. The influence of biochar on the product distribution and properties was not involved in the report.

In this work, microwave-assisted pyrolysis of moso bamboo was conducted over bamboo-based biochar catalyst in order to upgrade the bio-oil and obtain high quality syngas. A comparison between conventional and microwave pyrolysis was also made in terms of the product distribution, the properties of the bio-oil and gaseous products.

2. Experimental section

2.1. Materials

Moso bamboo sawdust, which was collected from a bamboo processing plant in Zhejiang Province of China, was used for the present study. The bamboo sample was firstly shattered and then the particles with the size of 20–40 mesh were selected for the experiments after being sieved. Prior to the experiment, the selected samples were dried at 105 °C for 12 h. GB212-91 standard was applied to conduct its proximate analysis. The contents of ash, volatile matter and fixed carbon are 3.4 wt%, 76.5 wt% and 20.1 wt%, respectively. The ultimate analysis was carried out by using a Vario EL-III elementar (ELEMENTAR Analysensysteme GmbH) and the results are presented as follows: C, 43.7 wt%, H, 4.3 wt%, S, 2.94 wt%, N, 2.26 wt% and O, 46.8 wt%, respectively. The thermal properties of the bamboo during pyrolysis was obtained with the help of a differential scanning calorimeter (Pyris 1 DSC, Perkin-Elmer) at 10 °C/min under a nitrogen gas atmosphere at 50 ml/min and the obtained DSC curve was obtained.

2.2. Catalyst preparation

The same moso bamboo was used for the biochar preparation in this study. The raw material was dried at 105 °C for 12 h and then crushed. After being sieved, the particles with sizes less than 200 mesh were used for the biochar production. The description about the experimental apparatus can be found in our previous report (Zhang et al., 2015). The maximum power of the oven was 3.6 kW at the frequency of 2.45 GHz. The pyrolysis of bamboo was conducted under a nitrogen gas atmosphere with a constant flow rate of 0.15 m^3/min. The microwave output power was set as 700 W and the heating time was 20 min. The reactor was cooled down to room temperature under the nitrogen gas atmosphere.

The contents of the metallic element contained in the biochar were obtained by using an ICP-OES (Leeman Labs Inc., USA). The contents of the acid functional groups present in biochar before and after pyrolysis were determined by using Boehm method (Boehm, 1994). The ultimate analysis was carried out by using a Vario EL-III elementar (ELEMENTAR Analysensysteme GmbH). The fresh and used bamboo-based biochar were characterized by using a D/max 2500VL /PC X-ray diffractometer (XRD) using Cu Ka radiation (40 kV, 200 mA) from 10° to 80° with a step of 0.02°/s.

2.3. Experimental apparatus and procedure

The microwave pyrolysis experiments were conducted using a multi-mode microwave oven with four magnetrons. The experimental apparatus and the detailed operation steps have been presented in the previous report (Zhang et al., 2015). About 50 g of the raw material were placed in the quartz reactor put into the microwave oven. The addition amounts of the biochar were 5%,10% and 20% of the raw material mass, respectively. Accordingly, the samples subjected to microwave pyrolysis were labeled as MP-5, MP-10 and MP-20 for the 5%,10% and 20% biochar addition amount, respectively. High-purity nitrogen gas at a flow rate of 0.15 m^3/min was passed through the reactor from the bottom of the reactor before and during the treatments to maintain the inert atmosphere and help to remove the pyrolysis volatiles. The heating time was set as 20 min at the 600 W of the microwave output power.

The conventional pyrolysis of moso bamboo was carried out in an electric furnace. The systematic diagram of the experimental apparatus was presented in Fig. 1. The pyrolysis experiment was performed at 700 °C for 20 min. The raw material mixed with the biochar catalyst was loaded in the quartz glass tube (60 cm long, 3.8 cm inner diameter) until the target temperature was reached inside the electric furnace. The addition amounts of the raw material and biochar catalyst were about 5 g and 1 g, respectively. High-purity nitrogen gas at a flow rate of 100 ml/min was used as the carrier gas. The sample subjected to conventional pyrolysis was marked as CP-20.

The pyrolysis volatiles after the in-situ catalytic reforming under microwave and conventional conditions were passed through the condensate systems. The condensable volatiles adhering to the tube was washed by ethanol. The other bio-oil was recovered from the condensing flask by dissolving it in ethanol. It was then subjected to further evaporation to remove the solvent at 60 °C. The non-condensable gases were collected in gas-collecting bags at the time intervals of 2 min. The pyrolyzed char and bio-oil were weighed and the gas yield was calculated by difference. All the experiments were performed in three runs to confirm the values obtained.

2.4. Pyrolysis products analysis

The organic phase of the bio-oils were determined by using a gas chromatography-mass spectrometry (GC/MS; Agilent 7890A-5975C) equipped with a Varian Cp-sil 8cb capillary column capillary column (30 m length × 0.25 mm ID diameter × 0.25 μm film thickness). Helium gas (99.999% purity) was applied as the carrier gas and the flow rate was set as 3 ml/min. The injection volume was 1 μL and a split of the carrier gas (1:30) was applied. The temperature of the column oven was initially maintained at 40 °C for 3 min, followed by a ramp from 40 °C to 180 °C at 5 °C/min and then from 180 to 280 °C at 20 °C/min, finally held at 280 °C for 2 min. Typical operating conditions were listed as follows: ion source 230 °C, electron energy 70 eV and transfer line 230 °C.

The compositions of the non-condensable gases obtained from bamboo pyrolysis under microwave condition were analyzed off-lined by applying a gas chromatography (6890N, Agilent) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). High-purity argon was applied as the carrier gas.