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Fuel properties and combustion kinetics of hydrochar prepared by hydrothermal carbonization of bamboo



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HIGHLIGHTS

- Hydrothermal carbonization was employed to pretreat bamboo for hydrochar preparation.
- Hydrothermal carbonization could elevate the fuel properties of bamboo.
- Combustion kinetics of hydrochars could be expressed by a simple Arrhenius equation.
- Hydrothermal carbonization affected the combustion kinetic parameters of bamboo.

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ABSTRACT

Hydrothermal carbonization, an environmental friendly treatment method was employed to pretreat bamboo for hydrochar preparation in the present study. Hydrothermal carbonization could elevate the fuel properties and combustion behavior of bamboo. The combustion kinetic parameters of raw bamboo and hydrochars were calculated by a simple Arrhenius equation based on the thermogravimetric curves. Two distinct zones were observed for raw bamboo and hydrochars. The activation energies of raw bamboo in zone 1 and zone 2 were 109.5 kJ/mol and 46.6 kJ/mol, respectively, in the heating rate of 20 °C/min. The activation energy of hydrochar in zone 1 increased at the hydrothermal carbonization temperature under 220 °C and then decreased at higher hydrothermal carbonization temperature, due to the decomposition of relative reactive compounds in bamboo, and destruction of cellulose and hemicellulose structures, respectively. The activation energies of hydrochars in zone 2 were among 52.3–57.5 kJ/mol, lower than that of lignin extracted from bamboo.

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1. Introduction

Hydrochar is a kind of charcoal prepared through hydrothermal carbonization (subcritical water treatment) of biomass. Compared with raw biomass, the hydrochar showed higher fuel properties, such as higher carbon content, lower oxygen content, higher hydrophobicity, higher heating value (HHV), higher energy density and lower emission of greenhouse gases (Kang et al., 2012; Yang et al., 2015a; Ben and Ragauskas, 2012). Therefore, hydrochar application to renewable energy has been put forward as a tool to relieve energy crisis and mitigate global warming in recent years.

Up to now, much information could be obtained about hydrothermal carbonization of biomass for hydrochar preparation that was applied as biofuel (Kang et al., 2012; Yang et al., 2015a;

Ben and Ragauskas, 2012; Chen et al., 2012; Liu et al., 2013; Lyman et al., 2011; Reza et al., 2014; Funke and Ziegler, 2010). For example, Liu et al. (2013) and Chen et al. (2012) pretreated waste biomass by hydrothermal carbonization process to improve their fuel properties. Lyman et al. (2011) and Yan et al. (2009, 2010) hydrothermal carbonized loblolly pine at the temperature range from 200 °C to 260 °C. They demonstrated that the HHV of hydrochar increased with increasing of hydrothermal carbonization temperature, whereas the mass yield reduced at higher hydrothermal carbonization temperature. They also found that addition of acetic acid lithium chloride to subcritical water could elevate the energy density of hydrochar. However, this result was different from our previous research during hydrothermal carbonization of husks of nuts from Carya cathayensis Sarg by acid and alkali modified subcritical water (Yang et al., 2015b). In our previous researches, we also hydrothermal carbonized various biomasses by subcritical water in various conditions (Yang et al., 2015a, 2015b). We found that (i) the prepared hydrochar had high

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caloric value and hydrophobicity, (ii) the fuel properties of hydrochar were affected by the component weight ratios of biomass, and (iii) high pH value was not appropriate for hydrothermal carbonization of biomass. Most of the researchers described above characterized the standard fuel properties of hydrochar, such as element content, HHV, mass and energy yield, but only few researches paid attention on the combustion behavior and kinetic parameters of hydrochar, since the hydrochar was prepared to combust in a boiler. Some researchers (Mansaray and Ghaly, 1999; Parthasaeathy and Narayanan, 2014) investigated the kinetic parameters of biomass by thermogravimetric analysis (TGA), but the biomass should be converted to biochar or hydrochar before it was suitable for combustion with fossil fuel, because of its natural drawbacks (high hydrophilicity, high volatile material content and low energy density). Thus, determination of the combustion kinetics of hydrochar was critical for predicting the hydrochar combustion behaviors and applying biomass as biofuel. Meanwhile, TGA is a common method employed to examine the combustion behavior and kinetics of solid materials (Ahmadipour et al., 2012; Vyazovkin et al., 2011). Therefore, TGA was applied to evaluate the combustion behavior and combustion kinetics of hydrochar prepared by hydrothermal carbonization. The aim of this study was to investigate the fuel properties and combustion kinetic parameters of hydrochar.

2. Methods

2.1. Materials

Bamboo, one of the fastest-growing plants worldwide, was selected as a model of biomass. The bamboo planted in China was 4 million hectares, and it was widely used as instant chopstick and feedstock for construction (Tan et al., 2011). However, large quantities of used bamboo were abandoned, and an effective treatment for the used bamboo was anticipated. The bamboo powder with the cellulose, hemicellulose and lignin contents of 34.9%, 16.2% and 28.3%, respectively, was obtained from a bamboo-processing factory in Huzhou city, Zhejiang Province, China. The bamboo powder was screened to get the particles with the diameter under 3 mm. The obtained particles were further dried at 100 °C for one night.

2.2. Hydrochar preparation

Hydrothermal carbonization of bamboo was carried out in a stainless steel batch reactor (Taiatsu Technology Corp., Osaka, Japan) with a working volume of 10 mL. The detailed description of the experimental setups was described in our previous researches (Yang et al., 2015b, 2014). Actually, a weight of 300 mg of bamboo combined with 7 mL deioned water was charged into the batch reactor, and the reactor was tightly closed. The closed reactor was then set into a ceramic furnace (ARF-40K, Asahi-Rika, Chiba, Japan) with a digital temperature controller (TP1000C, Chino, Tokyo, Japan). The reactor was held at the desired temperature range from 180 °C to 260 °C for 10 min. The temperature inside the reactor was measured by a thermocouple inserted into a tube installed in the middle of the reactor. The treatment time was calculated after the temperature inside the reactor reached to the desired level. After the specified reaction time, the reactor was immersed into an iced bath as soon as possible to stop the reaction. The mixture inside the reactor was filtered by a preweighted G-4 sand-core funnel. The solid product (hydrochar) was dried at 105 °C until its weight reached to a constant value.

2.3. Characterization of bamboo and hydrochar

The elemental contents of bamboo and hydrochar were determined by a vario Mircro cube elemental analyzer (Elementar, Germany). The HHVs were calculated from their elemental contents by the following equation (Friedl et al., 2005):

$$HHV = 3.55C^2 - 232C - 2230H + 51.2CH + 131N + 20,600$$
 (1)

where C, H and N were the carbon, hydrogen and nitrogen contents of bamboo or hydrochar expressed on a dry mass percentage, respectively. The energy yields were calculated by Eq. (2) expressed as follows:

Energy yield (%) =
$$HHV_{hydrochar}/HHV_{bamboo}$$

 \times hydrochar mass yield (2)

The combustion behaviors were evaluated by a Mettler-toledo thermogravimetric analysis (TGA/DSC LF1600, Switzerland) at the temperature range from room temperature to 800 °C with the heating rate of 20 °C/min under atmosphere pressure and air atmosphere. The flow rate of air was 100 mL/min. For the samples of raw bamboo and hydrochar prepared at 260 °C, multiple temperature programs (heating rate: 10, 20 and 30 °C/min) were used to evaluate their combustion behaviors.

2.4. Determination of the kinetic parameters of bamboo and hydrochar during combustion

The kinetic parameters of bamboo and hydrochar during combustion in TGA were determined based on a global kinetic equation for devolatilization reaction and a modified form of Arrhenius equation expressed in Eqs. (3) and (4), respectively (Mansaray and Ghaly, 1999; Parthasaeathy and Narayanan, 2014; Yang et al., 2014).

$$-dX/dt = kX^n \tag{3}$$

$$k = Ae^{-E/RT} \tag{4}$$

Substituting the value of k in Eq. (3) by Arrhenius equation (Eq. (4)) and taking Napierian logarithm (In) on both sides, the Eq. (3) could be expressed in the form as

$$\ln(-dX/dt) = \ln A - E/RT + n \ln X \tag{5}$$

The X in Eq. (5) can be written as

$$X = (w_t - w_f)/(w_0 - w_f)$$
 (6)

Substituting the value of X in Eq. (5) and it can be converted to

$$\ln[-1/(w_0 - w_f)dw_t/dt] = \ln A - (E/RT) + n\ln[(w_t - w_f)/(w_0 - w_f)]$$
(7)

Eq. (7) is in the form of

$$y = B + Cx + Dz \tag{8}$$

where y, x, z, B, C and D in Eq. (8) are defined as follows:

$$y = \ln[-1/(w_0 - w_f) dw_t/dt]$$

x = 1/RT

$$z = \ln[(w_t - w_f)/(w_0 - w_f)]$$

 $B = \ln A$

$$C = -E$$

D = n

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