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Research Paper

Co-combustion characteristics and kinetic study of anthracite coal and palm kernel shell char

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HIGHLIGHTS

- The combustion behavior of coal can be improved effectively by mixing with biochar.
- The physical and chemical properties of coal and biochar were studied systematically.
- A complex synergistic effect existed during co-combustion process of the blends.
- The performance of the RPM model is slightly better than that of the VM model.

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ABSTRACT

The non-isothermal thermogravimetric analysis was conducted to evaluate the combustion characteristics of Yangquan anthracite coal (YQ), palm kernel shell char (PC) and their blends with different mass ratios. The physical and chemical characteristics of YQ and PC were also studied systematically. The investigation shows that, compared to YQ, PC was more reactive due to the higher content of the alkali metal oxides, lower ordering degree and more developed porous structures. The combustion reactivity of YQ can be improved effectively by mixing with PC, and a synergetic effect between YQ and PC can be observed. The experimental results of the thermal degradation experiments were represented with both the random pore model (RPM) and the volume model (VM), and the activation energies and pre-exponential factors were further determined. The performance of the RPM model is slightly better than that of the VM model. The activation energies of all samples are in the range of 90.2–121.8 kJ/mol, where the lowest value of 90.2 kJ/mol is for the sample of PC at 60% mass ratio.

1. Introduction

Rapid development of the steel industry has brought a lot of environmental pollutions, and CO_2 emissions is one of the biggest issues [1–3]. Blast furnace is still a dominated facility to produce the hot metal in steel industry due to the high production efficiency and high heat-utilization rate [4,5]. Coal is one important and commonly-used fuel in the blast furnace (BF) process [6] and results in enormous CO_2 emissions during the production. Biomass is considered as one of the most important environmental-friendly carbon-neutral renewable energy sources, and it can also be used as a fuel in the BF process. The substitution of coal by biomass can be an effective way to reduce the CO_2 emission in the BF.

However, both the composition and structure of biomass is different from those of coal, making it a challenge to replace coal with biomass. Compared with coal, the calorific value, the fixed carbon content, the grindability and the energy density are lower, while the bulk volume, and the moisture and volatile contents are higher. All these differences limit a direct and efficient usage of the raw biomass to a large extent in the BF [7,8]. Meanwhile, for the biochar, an upgraded product from the raw biomass, it has a lower moisture content, higher carbon content, higher heating value and higher energy density, compared with the raw biomass [9–11]. Such comparable properties to coal makes biochar possible to be used in the BF process to partially replace the pulverized

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coal in order to mitigate the CO_2 emission [12–14].

To promote the utilization of biochar in the BF, the properties and kinetics need to be determined, and the biochar from different kinds of biomass can be very different. Thermogravimetric analysis (TGA) has been extensively employed to investigate the reaction characteristics and kinetics of the solid fuels [15–18], and it can also be used to assess the reaction behaviors on a large scale [19–21]. A lot of work has been carried out with the focus on thermochemical characteristics for the co-combustion of coal and biomass [22–27], and it is found that the coal and biomass blends can achieve a lower ignition index, burnout temperature and activation energy during the combustion. This observation implies that the ignition performance, the thermal reactivity and the kinetic behavior can be improved by blending biomass with coal. However, the work on the co-combustion of biochar and coal is still scare [28–30]. Kastanaki et al. [28] reported that the biomass-chars are generally more reactive compared with the chars from the hard-coal and lignite. The limited investigation shows that the combustion behaviors of blends are extremely influenced by the proportion of each component in the blend. For example, in the work of Sahu et al. [29], the combustion characteristics for the blends of a typical Indian coal and low temperature sawdust and rice husk chars (300 and 450 °C) were studied with DSC–TGA apparatus, the reduction of the activation energy and the increase of the reactivity were observed in the coal/biochar blends, and the blends with less than 50% biochar performed better than the blends with higher biochar contents. Yousaf et al. [30] investigated the combustion characteristics of the biochars that are produced from the peanut shell and wheat straw at 300, 500 and 700 °C, respectively, as well as the blends with coal at mass ratios of 20 and 50%, respectively. Their investigation shows that the biochar-coal blends with an equal proportion can achieve steady-state combustion over a broad temperature range, increasing the combustion efficiency and improving the thermal characteristics. Therefore, an enhanced combustion performance can be achieved by adjusting the ratios of blends. While different kinds of coal and biochar can lead to different results. Meanwhile, the synergistic effect of coal and biochar during co-combustion can be an important factor, however, the corresponding study has not been available. Therefore, more work on the co-combustion of the selected coal and biochar needs to be carried out in order to provide theoretical guideline for their practical applications, e.g. in the BF processes.

The goal of this work was to investigate the combustion characteristics for the blends of coal and biochar combined with synergetic effect. In this work, the palm kernel shell char (PC) was chosen as the biochar considering that the annual production of palm kernel shell as wastes and the great potential to be used as fuel [31]. The Yangquan anthracite coal (YQ) was chosen because it is a typical high-quality coal and usually used for BF injection in the Huabei area of China. To achieve the goal, the research work was conducted on (1) physical and chemical properties of YQ and PC by proximate analysis, elemental analysis, scanning electron microscopy (SEM), N_2 adsorption technique, X-ray diffraction (XRD) and Raman analyses, (2) the thermochemical characteristics of YQ, PC and their blends at different ratios with different heating rates via thermogravimetric analysis (TGA), (3) the synergistic effects between YQ and PC, (4) the kinetic parameters during the co-combustion process in two typical models.

2. Materials and methods

2.1. Materials

In this study, the palm kernel shell (PKS) was chosen for biochar preparation. The PKS was devolatilized for 60 min using a tube furnace under a continuous nitrogen atmosphere at the temperature of 600 °C. The yield of palm kernel shell char (PC) is 31.93%. The experimental apparatus have been described in detail in our previous work [32].

YQ and PC were dried at 105 °C for 12 h and then grounded and sieved to obtain the samples with a size smaller than 74 μm. YQ and PC blends were prepared with 4 different PC ratios, (i.e. 20 wt.%, 40 wt.%, 60 wt.% and 80 wt.%) and named as 20PC80YQ, 40PC60YQ, 60PC40YQ and 80PC20YQ, respectively.

2.2. Analysis methods

The proximate analysis of each sample was performed under the Chinese standard of GB/T 212-2001. The elemental composition (C/H/N/S) was measured using an elemental analyzer (Vario EL), and the oxygen content was further calculated by difference. The ash content was determined by the X-ray fluorescence spectrometer (XRF).

The different analytical techniques were used to detect the physicochemical characteristics of YQ and PC samples. The carbon crystallite structures of YQ and PC were determined by the X-ray diffraction (XRD, Rigaku SmartLab, Japan) using Cu Kα radiation source (λ = 0.1541 nm). Each sample was scanned in the angular range of 10–90° with a scan rate of 0.3°/min. The inter layer spacing (d_{002}) and the stacking height (L_c) were calculated with the Bragg formula (Eq. (1)) and the Scherrer formula (Eq. (2)), respectively [33]. The crystalline stacking layer number n was estimated from the d_{002} and L_c according to Eq. (3):

$$d = \frac{\lambda}{2\sin\theta(002)} \tag{1}$$

$$Lc = \frac{0.94\lambda}{\beta(002)\cos\theta(002)} \tag{2}$$

$$n = \frac{L_c}{d_{002}} \tag{3}$$

The structure morphologies of YQ and PC were observed with the scanning electron microscopy (SEM) analysis (FEI Quanta-450) performed under 15 kV voltage. The surface area and the pore volume of the YQ and PC were characterized via N_2 adsorption using a Quadrasorb SI instrument at 77 K. Before measurements, all samples were degassed at least 12 h in vacuum at the temperature of 573 K. The N_2 adsorption isotherms were measured at 77 K. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas. The intrinsic carbonaceous structures of YQ and PC were determined using the Raman spectrometer (Jobin Yvon Labram HR800, French) with a 532 nm wavelength. The recorded spectral range was 800–2000 cm^{-1}.

The non-isothermal combustion experiments for each samples were carried out with the thermogravimetric analyzer (WCT-2C, China). The sample (about 5 mg) was spread uniformly in a 3 mm × 1.5 mm alumina crucible and then burned under air atmosphere from room temperature to 900 °C with a rate of 5 °C/min, 10 °C/min, 15 °C/min or 20 °C/min. The values of the TG and the DTG curves can be obtained from the original TGA data with Eqs. (4) and (5):

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \tag{4}$$

$$DTG = \frac{d\alpha}{dT} \tag{5}$$

where DTG is the first derivative of the TG values, m_t is the sample weight at time t in the TGA experiment, m_0 is the initial weight of the sample, m_∞ is the final weight of the sample at the end of the reaction, and α is the combustion conversion rate of the sample.

To evaluate the reactivity quantitatively during the co-combustion of different blends, the reactivity index $R_{0.5}$, proposed by Takayuki et al. [34] was used in this work:

$$R_{0.5} = \frac{0.5}{t_{0.5}} \tag{6}$$

where $t_{0.5}$ is the time when the α reaches 0.5. The higher the $R_{0.5}$, the