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Research article

Fast pyrolysis and combustion characteristic of three different brown coals

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ABSTRACT

In this study, brown coals fast pyrolysis/combustion was carried out in a moving furnace coupled with a balance, and the mass change of sample and emission of hydrocarbon components were online recorded. On the basis of the experimental results, the pyrolysis/combustion kinetic parameters were calculated. In the fast pyrolysis process, the apparent activation energy of Loy Yang brown coal, Wara brown coal and Usibelli brown coal was 36.9, 33.1 and 28.1 kJ/mol respectively, which was far lower than that obtained under the slow pyrolysis process. The main light hydrocarbon gases evolved from brow coal fast pyrolysis were CH_4, C_2H_6 and C_3H_8. At the same time, it was found that the reaction rate of brown coal fast pyrolysis was strongly influenced by the oxygen content of the raw coal. The high oxygen content of the raw coal was beneficial to pyrolytic reaction. The combustion process of the brown coal could be divided two stages: in the first stage, the evolution and combustion of volatile matter occurred simultaneously. In the secondary stage, only char combustion occurred. The apparent activation energy of char combustion was 2.3–20.8 kJ/mol.

1. Introduction

In recent years, fossil fuels are being exhausted due to the increasing demand for energy in developing/developed countries. The shortage of fossil fuels causes the high prices and unstable energy supply. Compared to other fossil fuels, brown coal utilization has the highest potential because of the huge quantity of deposit, and the low price. The brown coal has been mined and used extensively in several countries [1–4]. However, its production is only about 15% of the high ranked coals [5]. The brown coal has serious shortcomings such as the high moisture content, low calorific value and spontaneous combustion. If the above weak points are overcome, the demand of brown coal will increase and it will become a major industrial energy source [4,6,7]. One method of overcoming the weaknesses is gasification because brown coal has a high gasification reactivity [8,9]. The understanding of the pyrolysis/combustion characteristic (the kinetic parameters) of brown coal pyrolysis is benefit to model, design and develop suitable gasifier.

The influence of pyrolysis conditions such as the heating rate, atmosphere, catalyst and coal size on brown coal pyrolysis characteristic has been widely studied [10–13]. Meanwhile, the evolution of volatile matters during brown coal pyrolysis was also investigated to understand the chemical pathways of pyrolysis [14]. However, the above kinetic parameters of coal pyrolysis have been done using thermogravimetric analysis (TGA), due its ability of being coupled with gas analyzers and differential scanning calorimeters (DSC) and online recording the mass loss with respect to time [15,16]. The activation energy of coal pyrolysis was dependence with the reaction temperature, and the value was 100–200 kJ/mol [17,18]. At the same time, Du et al. reported that the heating rate had a limited effect on the activation energy of coal pyrolysis [17]. However, Zhang et al. stated that the heating rate had a significant influence on the activation energy of biomass pyrolysis. In the fast biomass pyrolysis (1000 °C/min), the activation energy was 65 kJ/mol, which was higher than that from TGA (59 kJ/mol) [19]. While Aguado et al. obtained the opposite conclusion, Aguado et al. reported that the activation energy of tyre pyrolysis at TGA (5 °C/min) was 168.4 kJ/mol, and the data from a microreactor (the maximum heating rate was 20000 °C/min) was 98.6 kJ/mol [20].

In an industrial gasifier/combustor, the maximum heating rate is usually 10^4–10^5 °C/s, which is far higher than that of TGA (the maximum heating rate is about 100 °C/s) [21]. In this paper, the kinetic parameters of brown coal (Wara brown coal, Usibelli brown coal and Loy Yang brown coal) fast pyrolysis/combustion were investigated in a moving furnace coupled with a balance recording the mass loss. Moreover, the evolution of light hydrocarbon components during brown coal pyrolysis/combustion were also measured.

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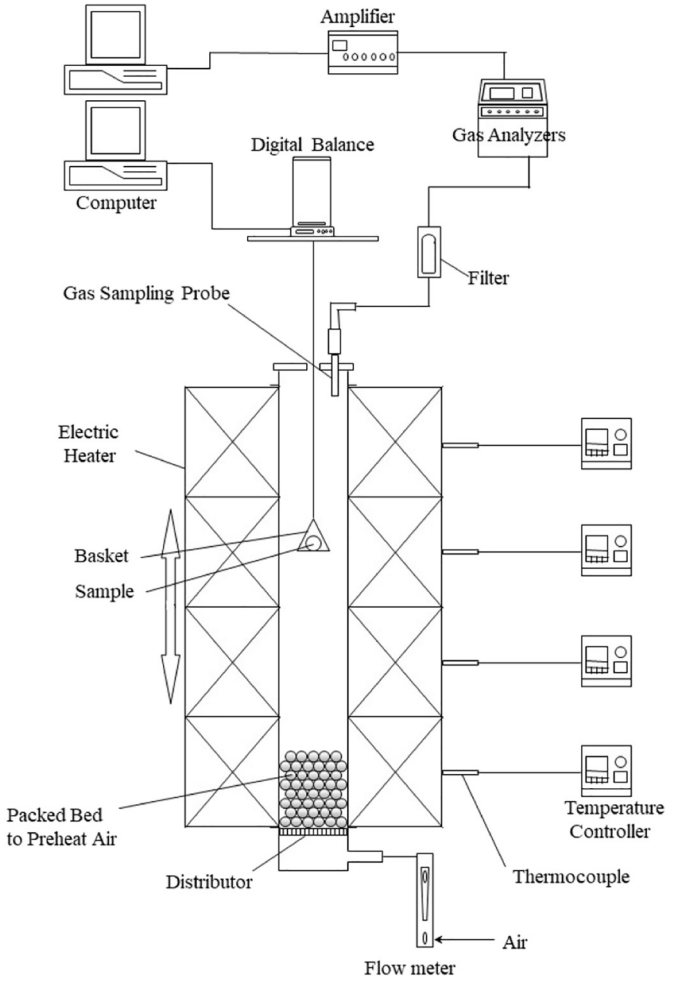

Fig. 1. Scheme of experimental apparatus.

2. Experimental procedure

Experimental methodology was previously discussed [22] and only mentioned briefly here. The experimental apparatus was schematically shown in Fig. 1. It was composed of an electrically heated furnace, temperature controllers, a digital balance, a flue gas analyzing system, and a flow control and gas mixing system. The time histories of mass change were continuously measured during pyrolysis/combustion process by a digital balance. Also, the concentration of SOx, NOx, CO, CO_2 and O_2 in flue gas was continuously measured by a gas analyzer (PG250, Horiba Corp., Japan). The flow gas for coal pyrolysis/combustion was preheated to a predetermined temperature by the packed bed of alumina balls located at the bottom of the furnace. 5 g sample (brown coal) was placed in a basket, which was linked up with the upper digital balance, and positioned in the center of the furnace axis. For fast pyrolysis/combustion of the brown coal, the electrical furnace, which had been heated to the predetermined temperature, was moved upward with a velocity of 5 cm/s. The influence of buoyancy on the indication of the measured mass could be neglected in these experimental conditions. In the experiments, the furnace temperature was set at a given temperature, ranging from 300 to 800 °C, and the heating rate was about 300–100 °C/s. The flow rate of feed gas (O_2/N_2) was fixed at 10 L/min. During fast pyrolysis/combustion process, a part of flue gas was collected by gas bag, and the light hydrogen gases were measured by a gas chromatograph with FID/TCD detector (Agilent 7890, Agilent Corp., USA). The oxygen concentration of feed gas was controlled by changing oxygen/nitrogen flow rate. Oxygen concentration was 0–21%. In this study, three different brown coals were used as samples. Wara brown coal comes from Indonesia, Usibelli brown coal from USA and Loy Yang brown coal from Australia. Usibelli brown coal has a higher oxygen content and a lower carbon content, as compared with Wara brown coal or the Loy Yang brown coal. The Ultimate analysis was measured by a elemental analyzer (Vario ELIII, Elementar Analysensysteme GmbH, German). Oxygen content was obtained by difference method. The ultimate analysis of brown coals was summarized in Table 1.

Table 1
Ultimate analysis results of the samples (moisture and ash free).

Composition (wt%)	Wara brown coal	Usibelli brown coal	Loy Yang brown coal
C	67.91	59.6	69.05
H	5.43	5.06	5.38
N	0.81	0.79	0.47
O	25.59	34.23	24.84
S	0.26	0.32	0.26

In the kinetic study, it is assumed that the overall pyrolysis reaction is pseudo first-order with regards to the mass loss of the sample. The pyrolysis rate (k) could be obtained from the following equations.

$$\frac{dm}{dt} = -km \tag{1}$$

$$\ln(m) = -kt \tag{2}$$

where m is the instantaneous non-conversion fraction of the sample, and t is the time.

The activation energy could be taken from the Arrhenius plot of the pyrolysis rate and reaction temperature by the following equations,

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{3}$$

$$\ln(k) = \ln(k_0) - \left(\frac{E}{R}\right)\frac{1}{T} \tag{4}$$

where, k_0 is the pre-exponential factor, E is activation energy, R is the gas constant, and T is the temperature.

3. Results and discussion

3.1. Pyrolysis process

3.1.1. Apparent activation energy in pyrolysis process

At the different pyrolysis temperature, the time history of non-conversion mass fraction for Loy Yang brown coal is shown in Fig. 2. The results demonstrate that the residue mass fraction is decreased with the enhancement of reaction temperature, and the slope of non-conversion mass fraction curve is sharper under the high reaction temperature. Moreover, the semi-logarithmic plot of the non-conversion mass fraction and time has a linear relationship during Loy Yang brown coal pyrolysis, as presented in Fig. 3. This result means that pyrolytic reaction of brown coal is a first-order reaction. The pyrolysis rate, k, could be obtained from the slope in Fig. 3 according to Eq. (2).

Fig. 4 presents the Arrhenius plot of the pyrolysis of Loy Yang brown coal in the temperature range of 300–800 °C. There are two slopes, that is, Loy Yang brown coal has two decomposition mechanisms. Domazeties et al. reported that the carboxyl groups of three types with small molecules were involved and mass loss reached about 14% during brown coal pyrolysis below 400 °C, and the three carboxyl groups were benzoic acid, tetrahydronaphthoic acid and 4-(phenyl)butanoic acid. In the high temperature decomposition (above 400 °C), carboxyl, carbonyl, ether and phenolic groups gradually decomposed with increasing temperature and mass loss reached 50–60% above 700 °C [23]. The pyrolysis of Loy Yang brown coal can also be explained by the similar thermal decomposition mechanism, because the mass loss is