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Characterisation and model fitting kinetic analysis of coal/biomass co-combustion

Guangwei Wang [a], Jianliang Zhang [a,*], Jiugang Shao [a], Shan Ren [b]

[a] School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, PR China
[b] College of Materials Science and Engineering, Chongqing University, Chongqing 400044, PR China

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ABSTRACT

The combustion behaviors of biomass, coal and their blends were studied by thermogravimetric analysis. Combustion parameters such as ignition, burnout, peak rate, ignition index, and combustibility index were analyzed. The kinetic parameters were optimized based on experimental results by a double parallel reactions random pore model (DRPM) proposed in this paper. The results show that the combustion characteristic temperature of the biomass is lower and maximum rate of combustion is higher than that of anthracite coal. With the increase of biomass content, ignition temperature and burnout temperature of blends tended to decrease, while the ignition index and combustibility index increased. Compared with the original RPM model, the DRPM model could not only describe the combustion process with a single peak rate, but also the combustion of biomass-coal blends with two rate peaks. The combustion activation energies of blends were extracted by DRPM model in the present study.

1. Introduction

With the increase of steel production, metallurgical coke resource is becoming scarce, and it is very urgent to develop new resources [1,2]. As a renewable resource, biomass has advantages of high yield, wide spread range and low emission of pollutant. Compared with traditional fossil fuel, great economic, environmental advantages and social benefits could be obtained [3–5]. Right now the utilization of biomass as energy resource is limited, especially for the ironmaking process in blast furnace. Based on these facts, the development of biomass resource in blast furnace smelting has significant meanings. Due to its low energy density, it is difficult to use biomass alone in blast furnace which has a high energy density requirement. Right now the main way to use biomass is to mix it with pulverized coal together for combustion [6,7].

The fundamental information on co-combustion process of biomass and coal blends are important for the proper design of combustion device with high efficiency. The most popular and simplest technique to study the combustion kinetics is method of thermogravimetric analysis (TGA) [8–10]. In the present work, this method will be used to investigate the combustion kinetics of biomass, coal and their mixtures to provide theoretical basis in optimizing the process of biomass injection in blast furnace.

2. Experimental

2.1. Experimental apparatus

Experiments were carried out on a thermogravimetric analyzer (HCT-3, Henven Scientific Instrument Factory, Beijing) at atmospheric pressure. Gas mixing device is consisted of a gas mixing cylinder and two digital mass flow controllers which are used to control oxygen and nitrogen gas flow, respectively. The volume fraction of oxygen is 21 vol% in gas mixture with the rest as nitrogen. Both gases flow through the gas mixing cylinder, and then enter into thermogravimetric analyzer to react with sample.

2.2. Raw materials

Pulverized coal named Haolin anthracite (HL) was offered by a domestic steel corporation and biomass (BI) was come from a lumber mill as a pine wood. HL and BI samples were dried in a drying oven under 378 K for two hours, and then grinded and sieved. BI and HL particles with the size smaller than 0.074 mm were selected for test. The proximate and ultimate analysis results of BI and HL were shown in Table 1; they were based on ASTM

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[*] Corresponding author. Tel.: +86 10 62332550; fax: +86 10 62332265.
E-mail address: zhang.jianliang@hotmail.com (J. Zhang).

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Table 1
Proximate and ultimate analysis of BI and HL.

Sample	Proximate analysis (% by wt)				Ultimate analysis (% by wt)			
	FC_d[a]	A_d	V_d	C_d	H_d	O_d[a]	N_d	S_d
BI	16.39	0.45	83.16	48.04	5.06	39.77	0.37	0.06
HL	79.20	10.61	10.19	81.50	3.12	2.10	1.02	0.54

FC, fixed carbon; A, ash; V, volatile matter; d, dry basis.
[a] Calculated by difference.

D5373 criterion and GB212-91/GB212-84 criterion, respectively. The BI and HL powder were mixed by blending together in a mortar for 10 min, with the mixing ratios of BI 0%/HL 100%, BI 25%/HL 75%, BI 50%/HL 50%, BI 75%/HL 25% and BI 100%/HL 0%, respectively.

2.3. Combustion experiments

Thermogravimetry (TG) experiments were carried out on a HCT-3 simultaneous thermogravimetric analyzer. About 5.0 mg sample was used and placed in a 3mm × 1.5 mm alumina crucible. The sample in the reactor was heated up from room temperature to 1073 K at different heating rates of 2.5, 5, 10 and 20 K/min. The flow rate of reaction gas is controlled to be 60 ml/min. It was important to ensure that the good reproducibility of the experiment, so each test was repeated at least three times before a final result was ascertained.

Thermogravimetry (TG) and derivative thermogravimetry (DTG) curves for combustion reactions were recorded by a computer. The reacted fraction of the sample was calculated by following equation:

$$\alpha = \frac{(M - m_t)}{(M - m_\infty)} \tag{1}$$

where M is the initial mass of the sample; m_t is the mass of the sample at time t; m_∞ is the residual mass of the sample at the end of the reaction.

3. Results and discussion

3.1. Kinetics model description

In this work, combustion of sample is assumed to contain two parallel reactions which occur simultaneously as indicated by Font et al. [11]. The overall reaction and the two individual reactions are expressed by Eqs. (2), (3) and (4), respectively. And each component decomposes simultaneously at different rates and temperatures, producing gaseous products and ash. In the Eqs. (3) and (4), Material 1 is considered as the volatile matter in sample and Material 2 considered as the carbon residue combined with oxygen to produce water vapor, carbon dioxide and ash. Both the two processes can be described by the Random Pore Model (RPM) [12,13]. In addition, it is further assumed that two competing reactions are both controlled by the chemical reaction step.

$$\text{Raw material} + O_2 \rightarrow H_2O + CO_2 + \text{Ash} \tag{2}$$

$$\text{Material 1} + O_2 \rightarrow H_2O + CO_2 \tag{3}$$

$$\text{Material 2} + O_2 \rightarrow CO_2 + \text{Ash} \tag{4}$$

The reacted mass fractions of sample are defined as follows:

$$\alpha_1 = \frac{M' - m'_t}{M - m_\infty} \quad \alpha_2 = \frac{M'' - m''_t}{M - m_\infty} \tag{5}$$

where M' and M'' are mass of Material 1 and Material 2, respectively. $m_t{}'$ and $m_t{}''$ are mass of Material 1 and Material 2 at time t, respectively. The relationship among M, M', M'', m_t, $m_t{}'$ and $m_t{}''$ is as follows:

$$M = M' + M'' \tag{6}$$

$$m_t = m_t{}' + m_t{}'' \tag{7}$$

RPM model developed by Bhatia and Perlmutter [12,13] took into account the pore structure and its evolution during the reaction. This model could predict the maximum in reaction rate, because the influences of pore growth during initial stage of combustion and destruction due to the coalescence of neighboring pores are considered. When chemical reaction is the control step, combustion rate can be written as:

$$\frac{d\alpha}{dt} = A \cdot \exp\left(\frac{-E}{RT}\right) \cdot (1-\alpha)\sqrt{1 - \psi \ln(1-\alpha)} \tag{8}$$

where A is the pre-exponential factor; E is apparent activation energy, kJ/mol; R is the universal gas constant, 8.314 J/(mol/K); T is the absolute temperature, K; ψ is parameter of particle structure, expressed as $(4\pi L_0(1-\varepsilon_0))/(S_0^2)$, where S_0, L_0 and ε_0 are the pore surface area, pore length, and solid porosity, respectively; t is the reaction time, s.

In the non-isothermal thermogravimetric method the heating rate β is expressed as the differential operation of temperature T by time t:

$$\frac{dT}{dt} = \beta \tag{9}$$

Inserting Eq. (9) into Eq. (8), the kinetic equation at non-isothermal condition can be obtained as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot \exp\left(\frac{-E}{RT}\right) \cdot (1-\alpha)\sqrt{1 - \psi \ln(1-\alpha)} \tag{10}$$

Integrating and rearranging Eq. (10),

$$\alpha = 1 - \exp\left(-A \cdot \exp\left(-\frac{E}{RT}\right) \cdot \left(\frac{T-T_0}{\beta}\right) \cdot \left(1 + \frac{A \cdot \exp\left(-\frac{E}{RT}\right)}{4 \cdot \psi} \cdot \left(\frac{T-T_0}{\beta}\right)\right)\right) \tag{11}$$

Eq. (11) is the integral form of RPM model used in non-isothermal condition, where T_0 is initial reaction temperature (which is equal to 298 K in the present study). For reactions (3) and (4), RPM model was used to describe the relation of conversion rate with time for Material 1 and Material 2, and following equations were obtained:

$$\alpha_1 = 1 - \exp\left(-A_1 \cdot \exp\left(-\frac{E_1}{RT}\right) \cdot \left(\frac{T-T_0}{\beta}\right) \cdot \left(1 + \frac{A_1 \cdot \exp\left(-\frac{E_1}{RT}\right)}{4 \cdot \psi} \cdot \left(\frac{T-T_0}{\beta}\right)\right)\right) \tag{12}$$

$$\alpha_2 = 1 - \exp\left(-A_2 \cdot \exp\left(-\frac{E_2}{RT}\right) \cdot \left(\frac{T-T_0}{\beta}\right) \cdot \left(1 + \frac{A_2 \cdot \exp\left(-\frac{E_2}{RT}\right)}{4 \cdot \psi} \cdot \left(\frac{T-T_0}{\beta}\right)\right)\right) \tag{13}$$

The overall reaction extent can be expressed as a linear addition function of the α_1 with α_2,

$$\alpha = \varepsilon_1\alpha_1 + \varepsilon_2\alpha_2 \tag{14}$$

where ε_1 and ε_2 are initial values of α_1 and α_2, respectively, and they indicate the initial weight fractions of component Material 1 and Material 2 in the starting raw material. The relationship between ε_1 and ε_2 is expressed as:

$$\varepsilon_1 + \varepsilon_2 = 1 \tag{15}$$