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Combustion Property and Kinetic Modeling of Pulverized Coal Based on Non-isothermal Thermogravimetric Analysis

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Abstract: Non-isothermal combustion kinetics of two kinds of low volatile pulverized coals (HL coal and RU coal) were investigated by thermogravimetric analysis. The results show that the combustibility of HL coal was better than that of RU coal, and with increasing heating rate, ignition and burnout characteristics of pulverized coal were improved. The volume model (VM), the random pore model (RPM), and the new model (NEWM) in which the whole combustion process is considered to be the overlapping process of volatile combustion and coal char combustion, were used to fit with the experimental data. The comparison of these three fitted results indicated that the combustion process of coal could be simulated by the NEWM with highest precision. When calculated by the NEWM, the activation energies of volatile combustion and coal char combustion are 130.5 and 95.7 kJ·mol^{-1} for HL coal, respectively, while they are 114.5 and 147.6 kJ·mol^{-1} for RU coal, respectively.

Key words: pulverized coal; combustion; kinetic model; non-isothermal thermogravimetric analysis

Due to the complexity of composition and structure, the pulverized coal combustion is a complicated physical and chemical process. Generally speaking, the combustion process of pulverized coal can be divided into two main parts: pyrolysis and combustion of remaining coal char[1,2]. The mechanism and kinetics of coal pyrolysis and coal char combustion have been studied by many investigators and a number of excellent papers have been published on this subject[3-10]. Griffin et al.[8,9] proposed a mathematical model describing the pyrolysis of bituminous coal with different heating rates (10—20000 K/s), particle sizes, pressures and temperatures. Zhang et al.[10] studied the effects of particle size and heating rate on the pyrolysis characteristics and kinetics through thermogravimetric (TG) analysis and optimization toolbox of MATLAB. However, most of researches were dedicated to individual processes of pyrolysis or coal char combustion, and few researches were done on the whole combustion process, especially for kinetic analysis.

In this study, the combustion process of pulverized coal was investigated by TG method, and the combustion characteristics of different coals were compared. According to practical combustion process of pulverized coal, a new kinetic model of pulverized coal combustion was established, and the new model (NEWM) was validated by fitting with experimental data.

1 Model Description

In this study, it was assumed that pulverized coal combustion involved two kinds of reactions and two reactions occurred simultaneously. The overall reaction and two individual parallel reactions are expressed by Eqs. (1) to (3). In Eq. (2), volatile combusts to produce gaseous products and ash, which can be described by the volume model (VM)[11,12]. In Eq. (3), coal char combines with oxygen to produce carbon dioxide and ash, and in this process, the random pore model (RPM)[13,14] is used. In addition, it is further assumed that two competing reactions are both under the chemical reaction control.

$$\text{Coal}+\text{O}_2\rightarrow\text{H}_2\text{O}+\text{CO}_2+\text{Ash} \quad (1)$$

$$\text{Volatile}+\text{O}_2\rightarrow\text{H}_2\text{O}+\text{CO}_2+\text{Ash} \quad (2)$$

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$$\text{Coal char}+O_2\rightarrow CO_2+\text{Ash} \quad (3)$$

The residual mass fraction of sample is defined as follows:

$$\alpha=\frac{M-m_t}{M-m_\infty},\ \alpha_1=\frac{M'-m_t'}{M-m_\infty},\ \alpha_3=\frac{M''-m_t''}{M-m_\infty} \quad (4)$$

where, α, α_1 and α_2 are conversion rate of coal, volatile and coal char, respectively; M, M' and M'' are the initial mass of pulverized coal sample, volatile and coal char, respectively; m_t, m_t' and m_t'' are the mass of pulverized coal sample, volatile and coal char at reaction time t, respectively; and m_∞ is final yield of sample, which is obtained from the final constant mass of TG curve. The relationship among M, M', M'', m_t, m_t' and m_t'' is as follows:

$$M=M'+M'' \quad (5)$$

$$m_t=m_t'+m_t'' \quad (6)$$

In the VM model[11,12], it is assumed that a homogeneous reaction throughout the particle occurs and there is a linear relation between reaction surface and conversion rate. In the regime of chemical kinetic control and assuming grains with spherical shape, the overall reaction rate is expressed as follows:

$$\frac{d\alpha_1}{dt}=A_1\cdot\exp\left(\frac{-E_1}{RT}\right)\cdot(1-\alpha_1) \quad (7)$$

where, A_1 is the pre-exponential factor for volatile reaction; E_1 is apparent activation energy for volatile reaction, kJ·mol^{-1}; R is the universal gas constant, 8.314 J/(mol·K); and T is the temperature, K.

RPM developed by Bhatia and Perlmutter[13,14] takes into account the pore structure and its evolution in the course of reaction. This model is able to predict a maximum value of reaction rate with reaction proceeding because the pore growth during initial stage of combustion and destruction of the pores due to coalescence of neighboring pores are both considered. When chemical reaction is the control step, combustion rate can be written as:

$$\frac{d\alpha_2}{dt}=A_2\cdot\exp\left(\frac{-E_2}{RT}\right)\cdot(1-\alpha_2)\cdot\sqrt{1-\psi\ln(1-\alpha_2)} \quad (8)$$

where,

$$\psi=\frac{4\pi L_0(1-\varepsilon_0)}{S_0^2} \quad (9)$$

A_2 is the pre-exponential factor for coal char reaction; E is apparent activation energy for coal char reaction, kJ·mol^{-1}; ψ is the parameter of particle structure; S_0 is the pore surface area; L_0 is the pore length; and ε_0 is the particle porosity.

Non-isothermal thermogravimetric method or temperature-programmed reaction technique involves heating the samples with constant rate β. The temperature T is related to time t by

$$T=T_0+\beta t \quad (10)$$

where T_0 is the initial temperature.

Replacing t in Eqs. (7) and (8) by Eq. (10), the rate of combustion reaction can be expressed as a function of temperature as follows:

$$\frac{d\alpha_1}{dT}=\frac{A_1}{\beta}\cdot\exp\left(\frac{-E_1}{RT}\right)\cdot(1-\alpha_1) \quad (11)$$

$$\frac{d\alpha_2}{dT}=\frac{A_2}{\beta}\cdot\exp\left(\frac{-E_2}{RT}\right)\cdot(1-\alpha_2)\cdot\sqrt{1-\psi\ln(1-\alpha_2)} \quad (12)$$

After rearranging Eqs. (11) and (12) and integrating them, following equations can be obtained

$$\alpha_1=1-\exp\left[-\frac{A_1\cdot(T-T_0)}{\beta}\cdot\exp\left(\frac{-E_1}{RT}\right)\right] \quad (13)$$

$$\alpha_2=1-\exp\left\{-A_2\cdot\exp\left(-\frac{E_2}{RT}\right)\cdot\left(\frac{T-T_0}{\beta}\right)-\left[1+\frac{A_2\cdot\exp\left(-\frac{E_2}{RT}\right)}{4\cdot\psi}\cdot\left(\frac{T-T_0}{\beta}\right)\right]\right\} \quad (14)$$

The overall reaction extent can be expressed as a linear addition function of α_1 and α_2

$$\alpha=\varepsilon_1\alpha_1+\varepsilon_2\alpha_2 \quad (15)$$

where,

$$\varepsilon_1=\frac{w_V}{w_V+w_{FC}},\ \varepsilon_2=\frac{w_{FC}}{w_V+w_{FC}} \quad (16)$$

ε_1 and ε_2 are coefficients depending on the content of volatile and fixed carbon in the coal sample; and w_{FC} and w_V are fixed carbon and volatile contents in coal sample, respectively.

Combining Eqs. (13), (14) and (15), following equation can be obtained

$$\alpha=\varepsilon_1\left\{1-\exp\left[-\frac{A_1\cdot(T-T_0)}{\beta}\cdot\exp\left(\frac{-E_1}{RT}\right)\right]\right\}+\varepsilon_2\left\{1-\exp\left[-A_2\cdot\exp\left(-\frac{E_2}{RT}\right)\cdot\left(\frac{T-T_0}{\beta}\right)\right]\cdot\left[1+\frac{A_2\cdot\exp\left(-\frac{E_2}{RT}\right)}{4\cdot\psi}\cdot\left(\frac{T-T_0}{\beta}\right)\right]\right\} \quad (17)$$

Eq. (17) was used to determine the five kinetic parameters (A_1, A_2, E_1, E_2 and ψ) by employing nonlinear least-squares fitting methods, which minimizes the objective function (OF):

$$OF=\sum_{j=1}^{N}\left(\frac{\alpha_{exp,j}-\alpha_{model,j}}{\alpha_{exp,j}}\right)^2 \quad (18)$$

where, $\alpha_{exp,j}$ is the experimental data corresponding to temperature T_j; $\alpha_{model,j}$ is the value calculated at