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Research article

Simulation of large coal particles pyrolysis by circulating ash heat carrier toward the axial dimension of the moving bed

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ABSTRACT

A heat transfer, reaction, pyrolysis mathematical model for the non-isothermal coal particles by using circulating ash as heat carrier toward the moving bed has been established. Combined with the Thermogravimetry-Mass spectrometry technology and Coats–Redfern integral method, the model has the ability to predict the temperature distribution of pyrolysis gas-coal-ash as well as the evolution characteristics of the main volatile products (such as CH_4, CO_2, H_2, CO, C_2H_4, C_2H_6, C_6H_6, C_7H_8, C_8H_{10}, $C_{10}H_8$). The results show that, the maximum temperature difference between the core and surface of coal (10 mm) has reached 406 K at the bed height of 0.05 m. The layer closer to the coal core has a higher but later peak value of the devolatilization rate. The evolution of the main volatile products is concentrated at the bed height of 0.08–0.24 m. The velocity of the moving bed, blending ratio of ash to coal, coal particle size, preheating temperature of coal and initial temperature of ash have obvious influence on the devolatilization process. Radiation is the most significant factor affecting the devolatilization behavior. The model can be applied to different coal species. This study can provide a theoretic foundation for the amplification design of the moving-bed reactor in the poly-generation system.

1. Introduction

The majority of the raw coal in China is used for direct combustion [1] which is inefficient and serious pollution. Fortunately, the circulating fluidized bed (CFB) combustion technology has been developed greatly for its better fuel flexibility, low pollution and load adjustability in recent years [2,3]. Similarly, the moving-bed pyrolyzer is increasingly valued because of its high adjustment capacity, stable operation and uniform heating [4]. So this provides a base for the poly-generation technology of coal pyrolysis and CFB combustion to achieve the grading conversion of coal. High-temperature ash, which comes from the CFB boiler is used as solid heat carrier, mixed with coal is fed into the pyrolyzer simultaneously. Then, the coal is heated to pyrolysis temperature and produce gas and tar. The char produced in the pyrolyzer is returned to CFB boiler to provide electricity and heat [5]. Thus the utilization of coal with high efficiency and low emissions is realized. Furthermore, since the pyrolysis reactor is independent of the CFB boiler, the CFB boiler can be operated separately when the pyrolysis system is out of work. Therefore, the moving-bed pyrolyzer as the critical equipment in the poly-generation technology [6], its operating state is directly relates to the stability and economy of the whole system.

The coal pyrolysis heated by solid or gas carriers has a higher efficiency of heat transfer than the traditional heating technologies. And compared with coal pyrolysis by gas heat carrier, the solid heat carrier not only provide higher heating rate but also avoid the volatiles dilution by the inert gas [7]. So the experimental works on coal pyrolysis by solid heat carrier have been widely valued in recent years [8–11]. However, the simulation studies are relatively few reported. To enable a better understanding on the poly-generation process, it is necessary to establish a mathematical model for the analysis of coal pyrolysis behavior, especially for the prediction and amplification of industrial processes. Some researchers [12–14] carried out the radial stratification of large particles to investigate the temperature-rise period. The studies showed that the coal particle size has significant influence on the pyrolysis behavior. However, the models are inappropriate for the process of coal pyrolysis by solid heat carrier because the heat transfer mechanism outside the coal surface considered only the heat radiation and heat convection. Higuera [15] reported the devolatilization of a moving coal particle by using a competing reaction pyrolysis reaction model. He pointed out that the relative motion of the particles would improve the heat transfer process between the surrounding gas and the particle. Liang et al. [6] reported a steady state, axial-dimensional, numerical model for coal pyrolysis by solid heat carrier toward the moving-bed. However, the coal particle was assumed as an isothermal body in the above two models, the existence of temperature gradient as a result of internal thermal resistance of coal particles should not be ignored. Therefore, a reasonable pyrolysis model of the non-isothermal coal particles by circulating ash carrier toward the axial dimension of the moving bed should be established.

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In this study, the Thermogravimetry-Mass spectrometry (TG-MS) technology and kinetic study were applied to modeling the non-isothermal coal pyrolysis by circulating ash heat carrier. Based on the heat transfer theory, not only the internal pyrolysis behavior of coal particles but also the temperature distribution of pyrolysis gas-coal-ash toward the pyrolyzer can be predicted. Combined with the multiple-reaction model, the evolution characteristics of the main volatile products is revealed. This work will provide a better understanding on the poly-generation technology of coal pyrolysis combined with CFB combustion.

2. Experimental

As shown in Table 1, Shenmu coal from Shaanxi Province is used in this study. The kinetic parameters for model calculation is obtained in the TG-MS system which is composed of a thermogravimetric analyzer (TG/TGA, Setaram Setsys-Evolution, Caluire, France) and a mass spectrometer (MS, Balzers Omnistar, Brügg, Switzerland). Before the TG-MS experiment is carried out, the coal sample was crushed and sieved to ≤74 μm, then dried at 105 °C for 4 h. The high-purity nitrogen (99.999 vol.%) was introduced into the TG-MS system with a flow rate of 80 mL/min. In the TG analyzer, the Shenmu coal sample (15 mg) was heated from the room temperature to 700 °C at a heating rate of 50 °C/min. The evolution characteristics of the gaseous products were analyzed in the MS with the ionization voltage of 40 eV and detection charge-mass ratio ranging from 0 to 300 amu. The physical characteristics of CFB ash, coal, and pyrolysis gas used in the experiment are shown in Table 2. The composition analysis of the circulating ash is shown in Table 3.

3. Mathematical model

3.1. Analysis and assumptions

As Fig. 1 shows that, the coal coupled with high-temperature circulating ash which comes from the mixing section is added into the reactor. As the mixed material moving downwards, the coal is heated by the surrounding ash and pyrolysis gas released from the under layer. Then the pyrolysis reaction occurs with the increase of coal particle temperature. The pyrolysis gas escapes upward, while the ash and char move downwards and return to the CFB boiler. In the moving-bed reactor, the height is axially divided into *m* layers. At any j^{th} layer in the reactor, the temperature of the pyrolysis gas and ash surrounding the coal particles is respectively $T_{\text{g,j}}$ and $T_{\text{a,j}}$. In the coal particle, the diameter is radially divided into *n* layers. From the core to surface, the internal temperature distribution of the coal particle is respectively $T_{0,\text{j}}$, $T_{1,\text{j}}$, … $T_{\text{n,j}}$. Assumptions of the model simplification are as follows:

(1) The particle sizes of coal and ash remain unchanged.
(2) Ash is assumed as an isothermal, inert, spherical particle.
(3) Spherical coal particle is tightly surrounded by the ash, and the characteristics of a single coal particle can predict the coal cluster in the same bed layer.
(4) The diffusion process of pyrolysis products evolved from the internal to external of coal particles is ignored.
(5) The moving-bed reactor is operated at a steady state.
(6) The calculation time step is small enough to ensure little temperature change of coal-ash-gas three phases in any adjacent iterative computation.

Table 1
The proximate and ultimate analyses of Shenmu coal sample (wt%).

Proximate analysis (ad)				Ultimate analysis (daf)				
M	A	V	FC	C	H	N	S	O[a]
7.21	3.89	31.54	57.36	80.88	5.09	1.08	0.29	12.66

[a] By difference; d, dry; daf, dry ash free; M, moisture; A, ash; V, volatile matter; FC, fixed carbon.

3.2. Mathematical model description of coal pyrolysis by solid heat carrier

3.2.1. Pyrolysis kinetic equation

In this model, the multiple independent parallel first-order reactions are assumed to describe the evolution characteristics of the volatile products. Therefore, the kinetic equation of the main volatile products (such as CH_4, CO_2, H_2, CO, C_2H_4, C_2H_6, C_6H_6, C_7H_8, C_8H_{10}, $C_{10}H_8$) and the total volatile (including but not all of the above main volatile products) can be expressed as

$$\frac{dw_j}{dt} = k_{0j} exp\left(-\frac{E_j}{RT}\right)\left(w_j^{*} - w_j\right) \tag{1}$$

where the final volatile product yields w_j^{*} are obtained from the test of low temperature distillation of coal by aluminum retort (GB/T480-2010), the pre-exponential factor k_{0j} and activation energy E_j are calculated by the TG-MS result. In this study, Coat–Redfern method [16–18] is applied to calculate the k_{0j} and E_j because of its wider applicability and better fitting effect. The equations of Coats-Redfern method can be expressed as.

$$\ln\left[-\frac{\ln(1-w_j)}{T^2}\right] = \ln\frac{k_{0j}R}{\alpha E_j} - \frac{E_j}{RT} \qquad (n = 1) \tag{2}$$

$$\ln\left[\frac{1-(1-w_j)^{1-n}}{T^2(1-n)}\right] = \ln\frac{k_{0j}R}{\alpha E_j} - \frac{E_j}{RT} \qquad (n \neq 1) \tag{3}$$

In Eq. (2) or (3), the left side versus 1/*T* shows a linear relationship. Therefore, the pre-exponential factor k_{0j} and activation energy E_j can be calculated from the intercept and slope of the straight line.

3.2.2. Mass conservation equation

$$\frac{d\left(\frac{\rho_c}{\rho_{c0}}\right)}{dt} = -\frac{dw}{dt} \tag{4}$$

3.2.3. Heat transfer mechanisms in the moving-bed reactor

Five heat transfer mechanisms in the moving-bed reactor are considered as follows:

(a) Thermal conduction between the circulating ash and coal particles.

In the moving-bed reactor, the coal particles are uniformly distributed in the circulating ash which has a relatively small size. In the moving downwards process of the mixed material, a circular contact surface between the coal and ash particle will be produced due to the mutual extrusion. Then the heat can be passed through the contact surface from the circulating ash to the coal surface. A formula has been proposed by Luikov [19] for calculating the size of the contact surface, $d_{ac} = 0.2d_{pa}$. Therefore, taken the volume thickness of *dz.* in the pyrolyzer as the calculational unit, the surface area of coal and ash can be respectively written as $s_c = a_c \frac{1-\varepsilon}{1+\theta} Adz$ and $s_a = a_a \frac{1-\varepsilon}{1+\theta} A\theta dz$. In the above two equations, θ is the volume ratio of ash to coal in the pyrolyzer, a_c and a_a are respectively the specific surface area of coal and ash, $a_c = 6(1-\varepsilon)/d_{pc}$, $a_a = 6(1-\varepsilon)/d_{pa}$. The contact area of coal and ash can be given by the equation $s_{ac} = s_c R_{ac}$, where R_{ac} [6] is the ratio of the contact area to coal surface area. Based on the above analysis, the heat flow of thermal conduction between ash and coal particles is expressed as

$$dq_{cod} = \frac{2\lambda_a\lambda_c}{\lambda_a + \lambda_c} s_{ac} \frac{T_a - T_c}{d_{pa}} \tag{5}$$