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Pyrolysis characteristics of bituminous coal

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Pyrolysis characteristics of Shenmu bituminous coal and its pyrolysates were investigated in this paper. The results show that Shenmu bituminous coal is a kind of valuable resource. The semi-coke, tar and pyrolysis gas are useful material for industrial production. Friedman method was used to describe Shenmu bituminous coal pyrolysis. By using this model, the kinetic parameters were detemined based on TGA data. The pyrolysis process of bituminous coal involves the rupture of different types of chemical bonds with different energies.

1. Introduction

Shenmu belongs to Dongsheng-Shenfu coalfield, which is the largest coalfield in the world. Shenmu bituminous coal has the following properties: good thermal stability, high volatile matter and low ash, strong chemical activity, low phosphorus, low sulfur and high calorific value. Shenmu bituminous coal is a kind of high quality steam coal and can be used for chemical industry, so, it has important scientific and realistic significance for studying of Shenmu bituminous coal.

So far, many investigations have been performed on the pyrolysis kinetics of coal. Experimental methods used include differential thermal method, thermogravimetric method, Rock-Eval method, etc. Thermogravimetric analysis (TGA) is a thermal analysis technique which measures the weight change in a material as a function of temperature and time, in a controlled environment. The weight loss information can be used to develop kinetic models of the decomposition process. Thermogravimetric analysis (TGA) was extensively used to determine the kinetic parameters of pyrolysis [1–6]. Because of the complexity of coal pyrolysis, so far, a satisfactory kinetic model that really reflecting the process of coal pyrolysis can not be developed [7–9]. However, some kinetic models are practical and have been widely used by many researchers, such as Integral method [10], Differential method [2] and distributed activation energy model [11,12]. Like Integral method and Differential method, Friedman method derives from overall kinetic model, but the calculated kinetic parameters by Friedman method are instantaneous values corresponding with the fractional conversion at a certain time, so Friedman method can better reflect the pyrolysis process. Friedman method has been used to describe the pyrolysis kinetics of oil shale [3,13], but it is rarely used for the pyrolysis kinetics of coal.

In this paper, the pyrolysis characteristics of Shenmu bituminous coal were investigated. Friedman method was used to obtain the kinetic parameters on the basis of TGA weight loss data.

2. Experimental

2.1. Sample

Bituminous coal was obtained from Sanjiang Coal Chemical Company, Shenmu, Shanxi province, China. It was crushed and sieved to corresponding sizes for different uses.

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2.2. Methods

The Fischer assay, proximate analysis and property analysis of tar were performed according to the universal standards. Heat value was determined by oxygen bomb method. Ultimate analysis was determined by LECO CHN-2000 (LECO, USA) and LECO S-144DR analyzer (LECO, USA). Gas composition was analyzed by Agilent 6890 gas chromatograph. Simulated distillation of tar was analyzed by Agilent 6890 simulated distillation chromatography, complied with ASTM D2887 standard.

Pyrolysis experiments were carried out with the aid of a TGA (NETZSCH STA409PC) at different heating rates of 10, 20, 30 and 40 °C/min from ambient temperature to 600 °C. During the experiments, to eliminate effects of heat transfer and mass transfer on coal pyrolysis, all samples were ground and sieved. We took fine coal particle with a size of less than 200 meshes. The weight of the sample was about 15 mg, the flow rate of carrier gas was 60 ml/min of high-purity nitrogen with the purity of 99.99%.

2.3. Mathematical model

2.3.1. Regression function

The 3-spline interpolation equation can be used to calculate pyrolysis rate of coal samples:

$$\frac{dx}{dT}(T) = \frac{6}{h_j^2}\left[\frac{1}{h_j}(T_{j+1}-T)^2-(T_{j+1}-T)\right]x_j + \frac{6}{h_j^2}\left[(T-T_j)-\frac{1}{h_j}(T-T_j)^2\right]x_{j+1} + \frac{1}{h_j}\left[\frac{3}{h_j}(T_{j+1}-T)^2-2(T_{j+1}-T)\right]m_j - \frac{1}{h_j}\left[2(T-T_j)-\frac{3}{h_j}(T-T_j)^2\right]m_{j+1} \tag{1}$$

where T is the pyrolysis temperature, x is the fractional conversion, m = dx/dT is the pyrolysis reaction rate, $h = T_{j+1} - T_j$ is the temperature interval, and j represents the point numbers for numerical derivatives.

When solving equation, the boundary conditions are as follows:

$$\left.\frac{d^2x}{dT^2}\right|_{x\to 0} = \left.\frac{d^2x}{dT^2}\right|_{x\to 1} = 0 \tag{2}$$

2.3.2. Friedman method

It is assumed that coal pyrolysis was a series of first order reaction, so the kinetic equation of oil shale pyrolysis can be described with the following equation:

$$\frac{dx}{dt} = A\exp\left(-\frac{E}{RT}\right)(1-x) \tag{3}$$

Taken the logarithm of Eq. (1), it will give following equation:

$$\ln\frac{dx}{dt} = \ln[A(1-x)] - \frac{E}{RT} \tag{4}$$

The specific temperatures T and the instantaneous reaction rate dx/dt of coal samples are various when reaching the same conversion in different heating rates. There are four different x-T curves corresponding to four different heating rate values. Set a series of different values of fractional conversion $x(x_1, x_2, x_3 \ldots)$ as constants. According to Eq. (4), the linear regression of ln(dx/dt) vs. 1/T will determine the apparent activation energy E and frequency factor A for each x.

3. Results and discussion

3.1. Pyrolysis of bituminous coal

Table 1 shows the Fischer Assay analysis result of the shenmu bituminous coal sample. The oil yield of the sample is 9.24 wt%, higher than that of Dongsheng lignite (6.31 wt %) [2] and Huolinhe lignite (5.48 wt %) [14] (China) and lower than that of Huainan bituminous coal (10 wt %) [15] (China).

Fig. 1 illustrates that the oil yield and retorting gas increase with the rise of temperature. When the temperature reaches 520 °C, the oil yield has stopped increasing. So the optimum retorting temperature of Shenmu bituminous coal can be determined as 520 °C.

The proximate analysis results were shown in Table 2. As seen from Table 1, the ash content of Shenmu bituminous coal is lower than that of Huolinhe lignite and Huainan bituminous coal, while the content of fixed carbon is higher than that of Huolinhe lignite and Huainan bituminous coal. Table 2 also shows that the fixed carbon and ash contents of bituminous coal are lower than those of semi-coke, because of the complete combustion of combustible material and the decomposition of minerals of bituminous coal.

Table 1
Analyzed results of Fischer assay at 520 °C (received basis, %).

Tar	Water	Semi-coke	Gas
9.24	8.74	76.78	5.24

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