Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 447-453

STUDY OF THE KINETICS OF THE COMBUSTION REACTION ON SHUANGYA MOUNTAIN COAL DUST BY TG

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Abstract

The combustion behavior of Shuangya Mountain (SYM) coal dust has been investigated by means of TG in this paper. The reaction fraction α can be obtained from isothermal TG data. The regressions of $g(\alpha)$, an integral function of α *vs.* t for different reaction mechanisms were performed. The mechanism of nucleation and nuclei growth is determined as the controlling step of the coal dust combustion reaction by the correlation coefficient of the regression, and the kinetic equation of the SYM coal dust combustion reaction has been established.

Keywords: coal, combustion reaction, kinetics, TG

Introduction

The energy resources in China are mainly composed of coal, some of which is used in chemical industries, while a great deal of them is burnt up as fuel. In addition, often detonation occurs during mining, transporting and storing of coal dust. In order to make full use of coal and to prevent the detonation of it, it is important to study the combustion reaction of coal dust.

Many studies on the combustion characteristics of coal dust have been published [1, 2], however, most of them focus on their ignition and combustibility and few on the kinetics of the combustion reaction. In this paper, a study of the combustion reaction kinetics of SYM coal dust by TG has been done. First, the combustion behavior of the coal dust in air has been investigated. From the isothermal TG data, the reaction fraction α has been obtained. Second, a possible reaction mechanism is determined according to the correlation coefficient, as a criterion, of the linear regression of $g(\alpha)$ *vs.* t, and a further proof has been given in a non-isothermal method simultaneously. As a result, a kinetic equation for the combustion of the coal dust has been established according to the correlation between the actual measured values of reaction rate and the calculated values at a given reaction mechanism. Some useful information is provided for the combustion design and detonation of the coal dust.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

The sample was SYM coal dust, made in Heilongjiang Province, China. Measurements were carried out by a Shimadzu DT-20B thermal analyzer. Experimental conditions were: sample mass, about 20 mg; chart speed, 5 mm min^{-1}; atmosphere, flowing air; measuring range, 20 mg.

Results and discussion

Thermal behavior of SYM coal dust in air

In order to investigate the combustion behavior of SYM coal dust in air, TG was used to follow its thermal behavior in air. Figure 1 shows the combustion TG curves of SYM coal dust at various different temperatures. Data from these curves are summarized in Table 1.

The combustion reaction of SYM coal dust started at 310°C in air, and finished at 710°C in a temperature-programmed mode by a heating rate of 10 K min^{-1}. The mass loss is about 87% in the whole combustion process. At constant temperature-programmed mode, the loss of mass varies from 76 to 80% in the temperature range from 430 to 500°C. A good linear relationship between combustion rate and temperature can be obtained. From the colour of the remains, we can conclude that the most complete combustion reaction is at 500°C.

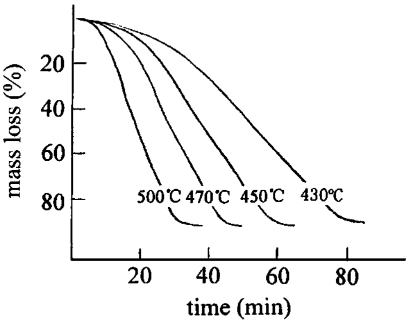

Fig. 1 Isothermal combustion TG curves of SYM coal dust in air at different temperatures

Table 1 TG results of SYM coal dust under different temperatures

Temperature/ °C	Sample mass/ mg	Mass loss/ mg	Combustion time/ min	Combustion rate/ g min^{-1}
430	17.8	13.6	80	$9.550\cdot10^{-3}$
450	17.2	13.4	56	$13.911\cdot10^{-3}$
470	15.6	12.2	42	$18.620\cdot10^{-3}$
500	14.0	11.1	28	$28.316\cdot10^{-3}$

Distinguishment of the combustion reaction mechanism of SYM coal dust

We can designate the isothermal rate equation of combustion reaction as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \qquad (1)$$

where α is the reaction fraction, t the time, $f(\alpha)$ a function of α, related to the reaction mechanism, k the reaction rate constant, expressed by the Arrhenius equation

$$k = A\mathrm{e}^{-E/RT} \qquad (2)$$

where A is the frequency factor, E the activation energy, R the gas constant and T the absolute temperature. Thus the isothermal rate equation can be expressed as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\mathrm{e}^{-E/RT}f(\alpha) \qquad (3)$$

Suppose $g(\alpha)$ is $\int \mathrm{d}\alpha/f(\alpha)$, the following equation can be obtained from Eq. (1)

$$g(\alpha) = \int k\mathrm{d}t = kt \qquad (4)$$

When $f(\alpha)$ or $g(\alpha)$ is properly chosen the plot of $g(\alpha)$ *vs.* t would be linear and the reaction mechanism can be confirmed from $g(\alpha)$ [3], assuming that only one combustion reaction mechanism $f(\alpha)$ is valid in the investigated $\alpha–t–T$ range.

For this reason, the isothermal TG curves of the coal dust combustion and some values of α from these curves were obtained at 430, 450, 470 and 500°C in flowing air.

According to the values of $g(\alpha)$ derived by Šesták [4] for the nine kinds of reaction mechanisms in Table 2, the regressions of $g(\alpha)$ at various temperatures *vs.* t were performed in the least square method. Using the values of the correlation coefficient as a criterion, the reaction mechanism would be determined. Table 3 shows the calculated correlation coefficient results of the regressions of $g(\alpha)$ *vs.* t.

It can be seem from Table 3 that the values of correlation coefficient of F_1 model are the highest of all the models at four different temperatures, followed by D_3 and D_2 . It shows that it is well possible that the combustion reaction mechanism of SYM coal dust corresponds to the F_1 model, that is, nucleation is the rate controlling step, followed by fast nuclei growth.

In order to confirm this, a simple and convenient non-isothermal method, derived by Phadnis [5], was used.

The non-isothermal form of Eq. (3) can be expressed as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\Phi}\mathrm{e}^{-E/RT}f(\alpha) \qquad (5)$$

then

Table 2 Values of $g(\alpha)$ for different solid state reaction mechanisms

Model	$g(\alpha)$	Reaction mechanism
R_1	$1-(1-\alpha)^{1/2}$	contracting sphere
R_2	$1-(1-\alpha)^{1/3}$	contracting cylinder
D_1	α^2	power law, one-dimensional diffusion
D_2	$\alpha+(1-\alpha)\ln(1-\alpha)$	Valensi, two-dimensional diffusion
D_3	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	Brounshtein-Ginsing, three-dimensional diffusion
F_1	$-\ln(1-\alpha)$	Mampel unimolecular law
F_2	$[-\ln(1-\alpha)]^{1/2}$	Avrami-Erofeev, two-dimensional nuclei growth
F_3	$[-\ln(1-\alpha)]^{2/3}$	Avrami-Erofeev, three-dimensional nuclei growth
F_4	α	power law

Table 3 The values of the regression correlation coefficient of $g(\alpha)$ *vs. t*

Model	430°C	450°C	470°C	500°C
R_1	0.9900	0.9845	0.9821	0.9875
R_2	0.9956	0.9909	0.9917	0.9937
D_1	0.9913	0.9879	0.9767	0.9624
D_2	0.9985	0.9965	0.9950	0.9880
D_3	0.9981	0.9977	0.9986	0.9958
F_1	0.9998	0.9983	0.9990	0.9975
F_2	0.9895	0.9825	0.9874	0.9956
F_3	0.9805	0.9717	0.9769	0.9892
F_4	0.9620	0.9566	0.9365	0.9288

$$g(\alpha)=\int\frac{A}{\Phi}\,\mathrm{e}^{-E/RT}\mathrm{d}T=\frac{ART^2}{\Phi E}\left(1-\frac{2RT}{E}\right)\mathrm{e}^{-E/RT} \tag{6}$$

from Eqs (5) and (6), we obtain

$$f(\alpha)g(\alpha)=\frac{RT^2}{E}\left(1-\frac{2RT}{E}\right)\frac{\mathrm{d}\alpha}{\mathrm{d}T} \tag{7}$$

neglecting the value of $2R^2T^3/E^2$, then Eq. (7) can be simplified as

$$f(\alpha)g(\alpha)=\frac{RT^2}{E}\frac{\mathrm{d}\alpha}{\mathrm{d}T} \tag{8}$$

so

$$g'(\alpha)=\int\frac{\mathrm{d}\alpha}{f(\alpha)g(\alpha)}=\int\frac{E}{RT^2}\mathrm{d}T=-\frac{1}{RT} \qquad (9)$$

then we can determine the reaction mechanism according to the fact whether the plot of $g'(\alpha)$ *vs.* $1/T$ is linearity or not.

Figure 2 shows the plot of $g'(\alpha)$ *vs.* $1/T$ for the F_1, D_3 and D_2 model, for which the regression correlation coefficients of $g(\alpha)$ *vs.* $1/T$ are the highest at constant temperature.

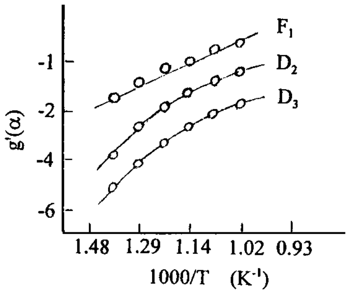

Fig. 2 The relationship of $g'(\alpha)$ *vs.* $1/T$

It can be found from Fig. 2 that the plot of $g'(\alpha)$ *vs.* $1/T$ is linear for the F_1 model, so the combustion reaction mechanism of SYM coal dust is determined as nucleation and nuclei growth in Phadnis method.

Parameters of combustion reaction kinetics of SYM coal dust and reaction rate equation

In order to calculate the parameters of the combustion kinetics of the coal dust, a set of values of α corresponding to the F_1 model at various temperatures were substituted to Eq. (4), and the average values of the rate constant $\bar{k}$ were obtained.

Taking the natural logarithm of both sides of Eq. (2) gives

$$\ln K=\ln A-\frac{E}{R}\frac{1}{T} \qquad (10)$$

The Eq. (10) can be used to determine the parameters of combustion reaction kinetics of the coal dust. That is, the plot of $\ln k$ *vs.* $1/T$ should be linear, and the activation energy can be obtained from the slope of the plot, the frequency factor from the intercept of the plot.

Table 4 shows the measured results of the average reaction rate constant $\bar{k}$ at various temperatures and Fig. 3 shows the plot of $\ln\bar{k}$ *vs.* $1/T$.

Table 4 The calculated results of average reaction rate constant, $\bar{k}$ at various temperatures

Temperature/°C	$1/T \cdot 10^{-3}$ K^{-1}	$\bar{k}$	ln$\bar{k}$
430	1.4227	0.0411	–3.1915
450	1.3831	0.0584	–2.8400
470	1.3458	0.0915	–2.3913
500	1.2936	0.1218	–2.1051

A good linearity of the plot is shown in Fig. 3. The slope value of the line is $-8.6329 \cdot 10^{-3}$ in the least square method, and the intercept is 9.12. Then we can calculate that the activation energy is 71773.93 J mol^{-1}, and the frequency factor is 9136.2.

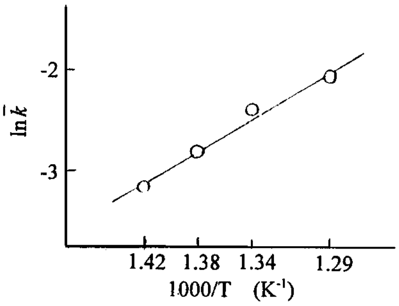

Fig. 3 The relationship of ln$\bar{k}$ *vs.* $1/T$

From these data, the rate constant and the rate equation of the combustion reaction can be expressed respectively, as follows:

$$k = 9136.2e^{-71773.9/RT} \tag{11}$$

$$d\alpha/dt = 9136.2e^{-71773.9/RT}(1-\alpha) \tag{12}$$

where R is 8.314 J mol^{-1} K^{-1}.

Table 5 shows the comparison between the actual measured values and the calculated values of reaction rate constant k according to Eq. (11) at various temperatures.

The results indicate that the calculated values of the reaction rate constant k basically coincide with the measured ones. That the difference between the calculated values and the measured ones is higher at 470°C may be due to variation in the temperature control. Table 6 shows the comparison between the calculated values of the combustion reaction rate according to Eq. (12) using the average values of α at 500°C ($\bar{\alpha}$=0.7679), and the actual measured ones.

One can see that the values of combustion reaction rate calculated by Eq. (12) are basically in agreement with the values measured by TG experimentally, the error is

Table 5 Comparison of values of rate constant *k*

Temperature/ °C	*E*/*RT*	Rate constant, *k*		Error/ %
		calculated	measured	
430	12.2820	0.0423	0.0411	2.8
450	11.9401	0.0596	0.0584	2.0
470	11.6181	0.0822	0.0915	11.3
500	11.1675	0.1290	0.1218	5.5

Table 6 Comparison of values of combustion reaction rate

Temperature/		Calculated/ g min^{-1}	Measured/ g min^{-1}	Error/ %
°C	K			
430	703	$9.873 \cdot 10^{-3}$	$9.550 \cdot 10^{-3}$	0.9
450	723	$13.883 \cdot 10^{-3}$	$13.911 \cdot 10^{-3}$	0.6
470	743	$19.087 \cdot 10^{-3}$	$18.620 \cdot 10^{-3}$	2.4
500	773	$29.954 \cdot 10^{-3}$	$28.316 \cdot 10^{-3}$	5.4

less than 5.4%. Therefore, the rate equation of combustion reaction of SYM coal dust can be expressed by Eq. (12).

Conclusions

1. In air, the combustion reaction of SYM coal dust started at 310 and 710°C when temperature-programmed by a heating rate 10 K min^{-1}. The mass loss in the whole process is about 87%. At constant temperatures, the mass loss is between 76 and 80% in temperature range 430–500°C.

2. From isothermal TG data, the F_1 model is determined as the combustion reaction mechanism of SYM coal dust because the regression correlation coefficient of $g(\alpha)$ *vs.* t is maximal, must like the value of the correlation coefficient of $g'(\alpha)$ *vs.* $1/T$ from TG data in the temperature-programmed mode. This indicates that nucleation is the controlling step of the combustion reaction of SYM coal dust, and on this basis the kinetic equation of the combustion reaction has been established.

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