SPONTANEOUS COMBUSTION OF COAL (I) (METHOD OF OXYGEN CONSUMPTION)

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(Received, June 28, 1985)

ABSTRACT

The spontaneous combustion of coal is a typical reaction of exothermic oxidizing reaction. The rate of oxygen consumption of coal has been measured as a function of temperature from 80°C to 380°C. The kinetic parameters of the exothermic oxidizing reaction of coal in oxygen have been determined and the reaction was found to act the three stage reactions in the temperature range of 80-380°C.

INTRODUCTION

The problems of spontaneous combustion of coal are very well recognized in the mining industry particularly in coal storage¹⁾. Many investigations have been conducted for prevention of the spontaneous combustion. The spontaneous combustion is considered as the exothermic oxidizing reac-

tion of coal for it is mainly the reaction of coal and oxygen. The exothermic oxidizing reaction of coal involves several reactions of an extremely complex and variable chemical nature. The exothermic oxidation reaction of coal is considered to proceed along the following path²⁾.

Path (I) is the adsorption of oxygen which is considered to take place due to the exposure of the surface in the underground zone. Path (II) is

the reaction which lowers the quality of the coal. Path (III) is the exothermic oxidizing reaction which takes place in the high temperature range

and is the combustion process. Many experiments have been done on the oxidation of various coals³⁾⁴⁾ However, virtually no works have been done to determine the kinetic parameters of the exothermic oxidizing reaction of coal in a pure oxygen atmosphere. In this study, we have obtained the kinetic parameters of the oxygen consumption in the temperature range of 80°C to 380 °C.

EXPERIMENTAL

The coal sample been used was Russain G. S. S. H. coal and the coal analysis is shown in Table 1. Every sample were seived to mesh size of 9–16 (JIS mesh) and stored

in a vacuum desiccator over phosphorus pentoxide. The initial amount of sample was approximatly 0.5g for all the runs. The volume of the oxygen consumption of coal was measured by the aparatus shown in Figure 1. The sample was placed in the bottom of the sample tube (S), together with Molecular sieve 5A 1/16 which was used as an adsorbent for gases generated from the exothermic oxidizing reaction of coal. The size of the outer part of the sample tube (the bigger tube) was 27.5 (mm) in diameter and 206.5 (mm) in height and the inner (the smaller) was 12.9 (mm) in diameter and 39.2 (mm) in height. To maintain the pressure of the system to

Table 1. Coal Analysis

Proximate Analysis (%)		Elementary Analysis (%)	
Moisture	3.1	Carbon (C)	83.14
Ash	10.1	Hydrogen (H)	5.17
Volatile Matter	34.8	Oxygen (O)	8.18
Fixed Carbon	52.0	Nitrogen (N)	2.69
		Sulphur (S)	0.28

Figure 1 Out line of apparatus

be at 101.3kPa. the system was controlled by the manometer (M), the volume of the oxygen consumption was measured by the buret (B) and converted into terms of oxygen consumption value per gram of sample and has been denoted as (g/g sample). An electric furnace (F) has been applied to heat the sample tube and the temperature was measured by the chromel-alumel type thermocouple (T). The temperature of the sample reaches the thermal equilibrium with the electric furnace within about 7 minutes after the sample tube is placed into the electric furnace. Therefore, the temperature of the sample was assumed to that of the furnace and each runs were carried out in this manner. The oxygen consumption value has been measured at a constant temperature of 80, 160, 200, 220, 300, 340, 360 and 380°C. Also the weight of final residue was weighed.

RESULTS AND DISCUSSIONS

Figures 2 -(a), (b), (c) and (d) show the value of oxygen consumption as a time history at the temperature of 80, 160, 200, 300, 340, 360, and 380 °C respectively. Looking over the oxygen consumption value at 80°C, it exhibits the value of 0.110 (g/g sample) which is the value that no further change in oxygen consumption is to occur after 1100 hr. So this value seems to be the final value of oxygen consumption at 80°C. Comparing the value derived by Swann and

Evans¹⁾ which was 0.108 (g/g sample) at 70°C (1080hr), there is no doubt to consider the value of 80°C as the final oxygen consumption value at 80°C. And this idea has been applied for the oxygen consumption value and this value is denoted as $[O_2]_{\infty}$. The plots of the final value $[O_2]_{\infty}$ versus temperature and the relationship between final residue (the weight percentage of sample after the measurements of oxygen consumption) and the temperature are shown in Figure 3. The plots in Figure 3 are the experimental data and the curve of $d[O_2]_{\infty}$ versus dT is calculated from the curve of the final oxygen consumption value versus temperature. Also curve of $d[W^{\infty}]$ versus dT is from the residue versus temperature. From Figures 2-(a), (b), (c) and (d) the reaction of oxygen consumption at each temperature can be fitted into a nth-order reaction and the following equation is applied.

$$-\frac{d[O_2]}{dt} = k[O_2]^n \quad (1)$$

where : $[O_2] = [O_2]_{\infty} - [O_2]_t$

k : reaction rate constant

$[O_2]_{\infty}$: final oxygen consumption value

$[O_2]_t$: oxygen consumption value at time t

To obtain the value of n in the nth-order reaction, equation (1) can be written as (2)

$$\ln \left\{ -\frac{d[O_2]}{dt} \right\} = \ln k + n \ln [O_2] \quad (2)$$

Figure 2 (a) The value of oxygen consumption as a function of time at 80°C.

(b) The value of oxygen consumption as a function of time at 160 and 220°C.

(c) The value of oxygen consumption as a function of time at 200°C.

(d) The value of oxygen consumption as a function of time at 300, 340, 360 and 380°C.

Figure 3 The plots of final oxygen consumption value versus temperature, residual amount versus temperature, oxygen consumption rate versus temperature and residual loss rate versus temperature.

In Figure 4 the relationship between $\ln\{-d[O_2]/dt\}$ and $\ln[O_2]$ is shown. At each temperature the plots of $\ln\{-d[O_2]/dt\}$ against $\ln[O_2]$ were found to be linear. And the value of n in equation (2) was proved to be $n \approx 1$ from the slopes of the plots, this agrees with the value in literature⁵. According to the value of n , the reaction of oxygen consumption of coal could be considered as a first-order reaction and equation (1) will be written as (3).

$$-\frac{d[O_2]}{dt} = k[O_2] \quad (3)$$

Figure 4 The plots of $\{-\ln [O_2]\}$ versus $-\ln \{-d[O_2]/dt\}$ at 80, 160, 200, 220, 300, 340, 360 and 380°C.

The solution of equation (3) with the initial condition

$$[O_2] = [O_2] \exp(-kt) \quad (4)$$

From equation (4) and assuming the reaction rate constant k to follow the Arrhenius equation $k = A \exp(-E/RT)$, equation (3) will be (5)

$$\ln\left\{-\frac{d\ln[O_2]}{dt}\right\} = \ln A - \frac{E}{RT} \quad (5)$$

where:

A : apparent frequency factor
(min^{-1})

R : gas constance
($\text{cal mol}^{-1} \text{K}^{-1}$)

E : apparent activation energy
(cal mol^{-1})

T : absolute temperature (K)

The right hand side of equation (5) corresponds to $\ln k$ in equation (2). As the value of $\ln k$ obtained from Figure 4 shows a low accuracy, E and A are obtained more accurately by equation (5). Figure 5 shows the

Figure 5 The plots of $-\ln \{-d\ln [O_2]_{\infty}/dt\}$ versus $1/T$.

relationship between $\ln \{-d\ln [O_2]_{\infty}/dt\}$ and $1/T$ from equation (5). And the values for E and A are $E = 7.55(\text{kcal/mol})$ and $A = 2.22(\text{min}^{-1})$. From the curves in Figure 3, in the temperature range of $80-200^{\circ}\text{C}$, the increase in the final oxygen consumption value seems to be larger than in the other temperature range, which could be seen from the steepness of the slope. On the other hand, from the plots of final residual amount against temperature, the final residual amount decreased largely above 200°C , but the final value of oxygen consumption did not increase corresponding to the change of the final residue. This indicates that the change of oxygen consumption value does not correspond to the residue change of the sample, so the following idea is to be brought up. The moisture usually starts to vaporize around 80°C , so that the final residue amount

at $80-160^{\circ}\text{C}$ should have decreased if only moisture vaporizing was to occur. But in the measurements of the oxygen consumption, despite of the moisture content of coal shown in Table 1 (3.1%), the final residual amounts for 80°C and 160°C were 100.92% and 99.36%. This shows there is an increase in the final residual amount at $80-160^{\circ}\text{C}$ which could be thought there must have been a reaction that resulted in residual increase. At above 200°C the final residue value decreased largely and finally reached the value where no further change in the final residual amount to occur. In general, the exothermic change of coal is thought to act the three stage reactions at 450°C ^{5)~8)}. The change at around 100°C is due to the loss of the inherent moisture, at $270-310^{\circ}\text{C}$ it is due to the solid state oxidation of organic matter, and over 450°C the volatile material begins to lose and a large proportion of the volatile material is to be removed. From the peaks in Figure 3, the peak in the final oxygen consumption $[O_2]_{\infty}$ with the temperature is at about 160°C and that for the final residual amount is at about 220°C , so it is clear that the final oxygen consumption $[O_2]_{\infty}$ changes very rapidly at about 160°C and the changes in the final residual amount is the largest at about 220°C . Taking the above three stage concept into consideration, the reaction of oxygen consumption at about 160°C is inferred

to be the path (II), and path (III) to be the reaction over 220°C. On the other hand the oxygen consumption reaction at 80–160°C can be considered as path (I) and path (II), because though the final residual change at this temperature range should be decreasing due to the loss of inherent moisture, the final residual change is actually increasing. Therefore, the reaction of the oxygen consumption is to act three stage reactions.

As the value of oxygen consumption is described as a function of time and temperature, the following relation can be written.

$$[O_2] = [O_2](t, T) \quad (6)$$

and we obtain,

$$\frac{d[O_2]}{dt} = \frac{\partial[O_2]}{\partial t} + \frac{\partial[O_2]dT}{\partial T dt} \quad (7)$$

From equation (3) and (7),

$$\begin{aligned} -\frac{d[O_2]}{dt} &= -\left(\frac{\partial[O_2]}{\partial t} + \frac{\partial[O_2]}{\partial T} \frac{dT}{dt}\right) \\ &= k[O_2] \end{aligned} \quad (8)$$

When T is constant, the relationship between the final oxygen consumption value and temperature in Figure 3 can be described as the following equation.

$$-\frac{d[O_2]}{dt} = -\frac{\partial[O_2]}{\partial t} = k[O_2]$$

and from equation (3),

$$\begin{aligned} -\frac{d[O_2]}{dt} \frac{dt}{dT} &= -\left(\frac{\partial[O_2]}{\partial t} \frac{dt}{dT} + \frac{\partial[O_2]}{\partial T}\right) \\ &= \frac{dt}{dT} k[O_2] \end{aligned} \quad (9)$$

When $[O_2]$ is defined as $[O_2]_\infty$ where

no further change in the value of oxygen consumption is to occur, the following expression can be applied for Figure 3.

$$\frac{\partial[O_2]}{\partial t} = 0$$

and equation (9) will be

$$-\frac{d[O_2]}{dT} = -\frac{\partial[O_2]}{\partial T} = \frac{dt}{dT} k[O_2] \quad (10)$$

Hence, dt/dT is unknown, k^* is denoted as $k^* = dt/dT k$, the above equation will be written as follows when time t is ∞ .

$$-\frac{d[O_2]_\infty}{dT} = -\frac{\partial[O_2]_\infty}{\partial T} = k^*[O_2]_\infty$$

this would express the relationship between the final oxygen consumption value and temperature.

And substituting $k^* = A^* \exp(-E/RT)$,

$$-\frac{d[O_2]_\infty}{dT} = A^* e^{(-E/RT)} [O_2]_\infty \quad (11)$$

furthermore equation (11) will be (12)

$$\ln -\frac{d[O_2]_\infty}{dT} = \ln A^* - \frac{E}{RT} \quad (12)$$

The relationship between $\ln\{-d[O_2]_\infty/dT\}$ and $1/T$ is shown in Figure 6 which were described by using the curve in Figure 3. The values of E and A^* are $E = 7.55 \text{ kcal/mol}$ and $A^* = 4.03 \times 10^2 \text{ K}^{-1}$. The values of E obtained from both method; equations (5) and (12), were the same. In the latter method (equation 12), the value E was obtained from the value $[O_2]_\infty$ when $d[O_2]/dt = 0$. On the other hand, in the former method (equation 5) the value

Figure 6 The plots of $-\ln\{-d\ln[O_2]_{\infty}/dT\}$ versus $1/T$.

of E was to be obtained even if it is not $d[O_2]/dt=0$. Therefore, considering from Figure 5, when the accurate value of E is obtained in Figure 5, making the experimental time more shorter would be possible. And also applying the Coats method⁹⁾ the value E was about the same as the value given above. The activation energy value in literature was nearly around 2.6 to 5.7 kcal/mol⁵⁾, and that of this study was 7.55 kcal/mol.

The elemental analysis for the coal in the above literature were: C (72.9%), H (4.64%) and O (20.2%); and for this study they were; C (83.14%), H (5.17%) and O (8.18%). And the volatile matter was approximately the same. It is difficult to indicate the difference of the reaction between the high carbon content coal and low one, but the low one are to react in the lower temperature than the high

one¹⁰⁾. From the content of oxygen it is clear that the high oxygen content coal is to react more quickly than the low one and this would effect in the value of activation energy. Considering from the activation energy the value derived in this study is an agreeable value compared from the values of Merrill⁵⁾. Therefore, it can be said the approach in this study is a reasonable method. And finally the measurements of oxygen consumption will be a useful tool when considering the problems of spontaneous combustion of coal.

ACKNOWLEDGMENT

This work has been supported by the Takenaka Kohmuten Co. Ltd. Japan. And the authors wish to express their hearty thanks to Mr. Motoki Kondou the director and executive of the Takenaka Technical Research Laboratory and also to the chief research engineer Mr. Takehiko Ohsawa.

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