SPONTANEOUS COMBUSTION OF COAL (II)

(STUDYING THE EFFECTS OF OXYGEN CONCENTRATION IN THE METHOD OF THERMOGRAVIMETRIC ANALYSIS)

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ABSTRACT

Thermogravimetry of coal has been carried out by changing the oxygen concentration of the heating atmosphere, and the effect of oxygen in the concentration of 1-60% flow gas has been discussed based on the thermogravimetric curves. The kinetic parameters of exothermic oxidizing reaction of coal in the thermogravimetric, which has one of the critical effects on the spontaneous combustion of coal storage have been discussed, and also the available parameters have been evaluated.

INTRODUCTION

Many works [1] [2] have been reported on the spontaneous combustion of coal, and this reaction has been thought to be an exothermic oxidizing reaction of coal. The phenomenon of spontaneous combustion of coal storage is dominated by several thermophysical and thermochemical parameters such as the rate of reaction, calorific value, etc. and the storage environment. Handa et al [3] have derived a reasonable kinetic parameters from the analysis of oxygen consumption in the oxygen atmosphere but kinetic parameters in various oxygen concentration have not reported. The actual phenomenon of spontaneous combustion of coal storage takes place in the

low oxygen concentration. The investigation of the reaction of oxygen-coal in low oxygen atmosphere is required and the analysis of these kinetic parameters to dominate the spontaneous combustion becomes more important. In this paper, the relationship between the kinetic parameters of oxygen-coal reaction and the oxygen concentration have been analysed and discussed based on the TG curve profiles in the different oxygen concentrations. These parameters will be useful values to predict the actual spontaneous combustion of coal in the large scale coal storage.

EXPERIMENTAL

The coal analysis of the sample used in

Table 1. Coal analysis

Proximate Analysis (%)		Elementary Analysis (%)	
Moisture	3.0	Carbon (C)	69.3
Ash	16.1	Hydrogen (H)	3.9
Volatile Matter	25.1	Oxygen (O)	8.7
Fixed Carbon	55.8	Nitrogen (N)	1.5
		Sulfur (S)	0.55

this study is shown in Table 1. Every sample was crushed into the mesh size (Tyler mesh) 9-16 and stored in a vacuum desiccator over phosphorus pentoxide. The outline of the apparatus is shown in Figure 1. Sample was placed in the sample crucible (C) which was connected to a thermobalance (A) and monitored by the strain gage (S). The temperature was measured by the chromel-alumel type thermocouples (T) which are immediately adjacent to the sample and all the measurements of the temperature of the sample were

carried out in this manner for each run. The temperature was not the actual temperature of the oxidizing coal sample, but the temperature within the crucible was monitored and the heating of the furnace was controlled by monitoring the thermocouple within the crucible. The furnace (B) was heated at a constant heating rate of $5.0^{\circ}\text{C}/\text{min}$. The desired oxygen concentration of the flow gas ($2\text{ l}/\text{min}$) was controlled by the flowmeter (F) in the range of 1-60%. In the bottom part of the furnace, glass beads of $5\text{ mm } \phi$ are placed in 5 cm thick layer to produce a uniform gas flow in the furnace. The size of the furnace is 10 cm in diameter and 30 cm in height. Every run was heated from room temperature up to where there is no further weight change was to be observed, or 900°C at the highest.

Figure 1: Outline of the apparatus.

RESULTS & DISCUSSIONS

The thermogravimetric curves for the oxygen concentration in the range 1-60% are shown in Figure 2. In this figure threshold temperature for the weight loss is shifted toward the low temperature side as the oxygen concentration of the flow gas increases. Look-

ing over the curves they are found to behave approximately the same in the oxygen concentration range of 20-60%, although each of the curve is showing a little different behavior at the point where the weight changes begin. On the other hand, for the oxygen concentration for 1-15% the same behavior of the

Figure 2: Thermogravimetric curves for the oxygen concentration flow gas of 1, 5, 10, 15, 20, 30, 40, 50, and 60%.

curves is not recognized. Especially for the oxygen concentration of 1% the thermogravimetric curve is different from those in other oxygen concentrations. In general, in the TG of coal it is often described that the components after the loss of moisture are to be volatiles, fixed carbon and ash [4] [5]. But in the case of the 1% oxygen concentration the weight loss was about 25% including its moisture content. The volatiles have the great effect on the oxidizing reaction of coal and it is said that a coal of 38% volatiles oxidized three times faster than the coal of 18% one [6]. Taking the idea of the volatile content into consideration, the reaction of coal in the 1% oxygen concentration is different from those of the 20-60%. From the TG curves for 5, 10 and 15% oxygen concentration, they are also seen to show a different behavior from

those in the 20-60%. To consider the reactivity of coal in the present method more accurately and also to obtain the kinetic parameters from the TG curves, the exothermic oxidizing reaction of coal is assumed to obey a first order reaction as follows.

$$-\frac{dW}{dt} = kW \quad (1)$$

where the rate constant k follows the Arrhenius formula

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

where:

W : residual coal sample weight (g)

k : rate constant (1/min)

A^* : apparent frequency factor as (1/min)
function of oxygen concentration

Figure 3: The relationship between $-\ln(-1/W \cdot dW/dt)$ and $1/T$.

R : gas constant (cal/deg/mol)

T : absolute temperature (deg)

E : apparent activation energy (cal/mol)

From equations (1) and (2) the following equation is obtained.

$$\ln \left(-\frac{1}{W} \frac{dW}{dt} \right) = \ln A^* - \frac{E}{RT} \quad (3)$$

Relationships between $\ln(-1/W \cdot dW/dt)$ and $1/T$ are shown in Figure 3 and the value of E was obtained as about 14.7 kcal/mol. As shown in Figure 4, the relationship between the oxygen concentration and the frequency factor from Eq. (3) is recognized as linear in the whole oxygen concentration range been studied. From the relation in Figure 4, the following formula has been derived.

$$\ln A^* = \ln A + \alpha [O_2] \quad (4)$$

then $A^* = A e^{\alpha [O_2]}$

where:

A : frequency factor in 0% oxygen (1/min)

$[O_2]$: oxygen concentration

The values of A and α from Figure 4 are about 14.8 (1/min) and 0.7 respectively. Handa et al [7] reported that the apparent frequency factor was defined as a linear combination of an effective factor and oxygen concentration. However, the apparent frequency factor in the present analysis is considered to be more practical.

The oxygen-coal reaction has been considered to proceed along the following path [8].

The reaction of path (I) is reported as a very rapid reaction [8], which is considered as the adsorption of oxygen taking place due to

Figure 4: The relationship between the frequency factor A^* and the oxygen concentration of the flow gas.

the exposure of the surface in the underground zone. And the used coal sample are considered to be the state just after path (I). In Figure 3, each plot in the oxygen concentration of range 20-60% follows a straight line behavior respectively. Here, the reaction of path (II) and (III) are considered to occur simultaneously. On the other hand, the corresponding behavior feature in 1-15% is recognized to be broken off at the temperature about 500°C. From the plots in Figure 3 and the thermogravimetric curves in Figure 2, it is considered that [COAL-O₂-COMPLEX] in the oxygen concentration lower than 15% is unstable or differently formed from those in the higher concentration. However, ultimate char structure at the end of the reaction in this system seems to be the same as those in 20-60% range, and the charring process is conjectured to be different. In 1-15%, the reactions of path (II) is considered to occur below 500°C, because this reaction is fully concerned in the presence of oxygen. And in above 500°C the coal reaction of 1-15% has been considered as a coking process because of oxygen starvation, which is well described in the curves in Figure 2 and from the plots in Figure 3. It is well recognized that the slope of the plots in Figure 3 decreases with the decrease in oxygen concentration. Finally, the coal-oxygen reaction in the below atmospheric oxygen concentration is well explained by the present TG method and this method will be an useful tool to study

the spontaneous combustion of coal, because the actual spontaneous combustion of coal in the large scale coal storage is considered to take place in the low oxygen concentration.

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