

AN ANALYSIS OF COAL PYROLYSIS RATES USING THERMOGRAVIMETRY

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INTRODUCTION

The modeling of coal pyrolysis reactions has been pursued since the initial studies by Gavalas and Howard. Recently, a large number of models has been reported, such as the FG-VDC, CPD, Flashchain and DEAM models. In these models, the activation energy or their distribution plays an important role.

In this study, the weight loss of coals by thermogravimetry (TG) was analyzed to obtain pyrolysis activation energies and frequency factors.

EXPERIMENTAL

Miike, Akabira, and Taiheiyu coals pulverized by a mortar and pestle were used in this study. The results of ultimate and proximate analyses are shown in Table 1.

Pyrolysis was carried out in nitrogen at atmospheric pressure (100 cc/min flow rate) or under vacuum conditions (10-30 Pa total pressure) using a TG to temperatures up to 1073 K at heating rates between 3 K/min and 100 K/min.

RESULTS

Figures 1 and 2 show the weight loss curves for Miike coal at atmospheric pressure and under vacuum, respectively. In both cases, the weight loss curve was moved to the higher temperature zone as the heating rate increases. This phenomenon is also seen in the degradation of synthetic polymers having the simple chemical bonds, such as polyethylene and polypropylene.

The final weight loss of coals heated to 1073 K under vacuum was larger than those under atmospheric pressure, suggesting that mass transfer strongly influences weight loss in experiments under atmospheric pressure.

ANALYSIS

Coal pyrolysis is generally analyzed as a first order reaction of volatile matter in the coal residue. In this study, the final weight loss at 1073 K under vacuum conditions, 0.58, 0.52, and 0.55 for Miike, Akabira, and Taiheiyu coals, respectively, was defined as the quantity of original volatile matter in the raw coals. These values were also used to model the experiments at atmospheric pressure.

Assuming a first order reaction and the Arrhenius Equation for the rate constant, Equation 1 is obtained.

$$(dV/dT)C = (A) \exp(-E/RT)(V^*-V) \quad (1)$$

where, A is frequency factor, E is activation energy, C is the heating rate, T is the temperature, and V* is the original volatile matter in the raw coal.

By integration of Equation 1, Equation 2 is obtained.

$$\ln(C/T^2) = -(E/R)(1/T) + \ln[(AR/E)/\ln[V^*/(V^*-V)]] \quad (2)$$

Assuming that the rate constant, K, of the first order reaction is identical at the same extent of conversion at different heating rates, E at a specific extent of conversion can be obtained by plotting $\ln(C/T^2)$ vs. $(1/T)$, where T is the temperature at which the same conversion is obtained at each heating rate. A is then calculated using Equation 2.

Figure 3 shows the plot of $\ln(C/T^2)$ vs. $(1/T)$ of Miike coal pyrolyzed at atmospheric pressure for conversions from 0.2 to 0.6. Activation energies and frequency factors for the different conversions obtained by the above method are shown in Figures 4 and 5.

Figure 6 shows the relationship between A and E obtained for conversions between 0.2 and 0.6, which can be expressed as a line independent of coal and pressure. The rate constant of the first order reaction is defined by the combination of A and E. This suggests that coal degradation rate constant is the same for the conversions of 0.2 - 0.6 regardless of coals and pressure.

If the frequency factor is assumed to be constant during pyrolysis, a distribution of activation energies is obtained by Equation 3, which is a popular method for the analysis of the first order parallel reactions. In this study, the minimum frequency factors obtained by Figure 5 for the experiments under vacuum condition, which are 1.0×10^{12} , 1.5×10^{12} , 4.0×10^{17} sec⁻¹ for Miike coal, Akabira coal and Taiheiy coal respectively, are used. Figure 7 shows the distribution of the activation energy of each coal.

$$E = (RT) \ln[A(V^* - V)/(dV/dT)] \quad (3)$$

These figures show that activation energies for the experiments at atmospheric pressure and under vacuum are almost identical up to the approximately 0.6 conversion for each coal. On the other hand, activation energies for conversions greater than 0.6 are different at atmospheric pressure and under vacuum conditions. It suggests that the reaction at atmospheric pressure is controlled by mass transfer of the remaining heavy materials produced at conversion below approximately 0.6. It is essential to understand the chemistry of remaining materials in the coals in the experiments at atmospheric pressure.

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Table 1. Analyses of Coals Used

Coal	Ultimate Analysis (daf st%)				Proximate Analysis (dry wt%)			
	C	H	N	S+O(diff.)	V.M.	F.C.	Ash	Water
Taiheiy	74.87	6.55	0.89	17.69	45.87	43.71	10.42	1.24
Akabira	83.32	6.36	1.40	8.92	40.18	52.92	6.90	0.61
Miike	83.78	6.75	1.01	8.46	44.06	47.23	8.71	0.27

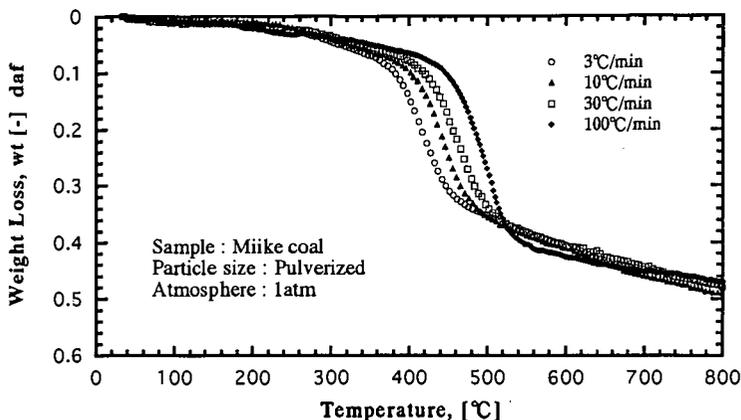


Fig. 1 Weight loss curve of Miike coal at atmospheric pressure

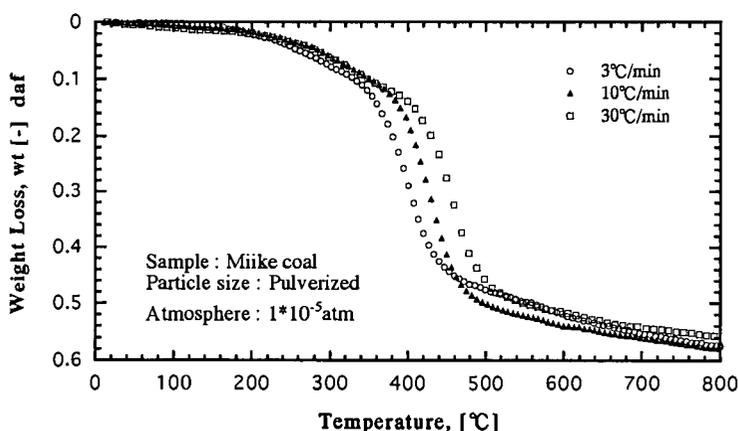


Fig. 2 Weight loss curve of Miike coal under vacuum

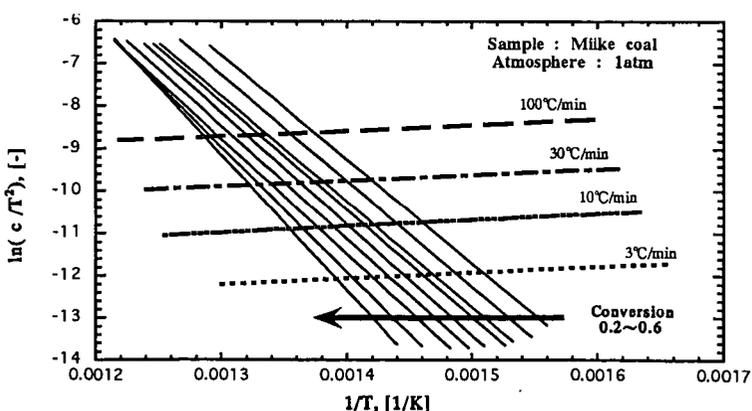


Fig. 3 $\ln(c/T^2)$ vs. $(1/T)$ of Miike coal for conversions between 0.2 and 0.6 at atmospheric pressures

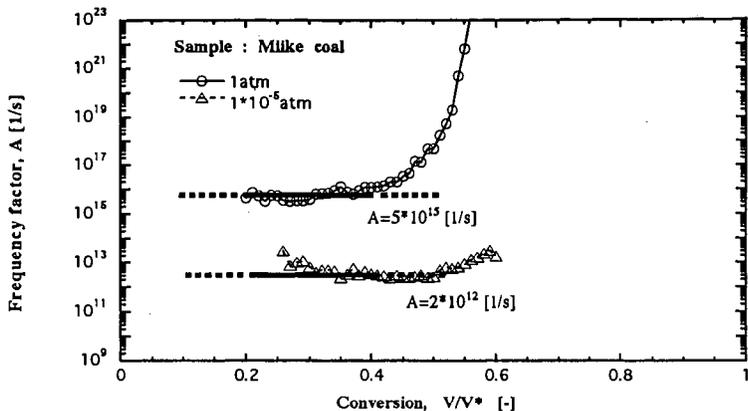


Fig.4 Frequency factor of Miike coal at 0.2-0.6 of the conversion

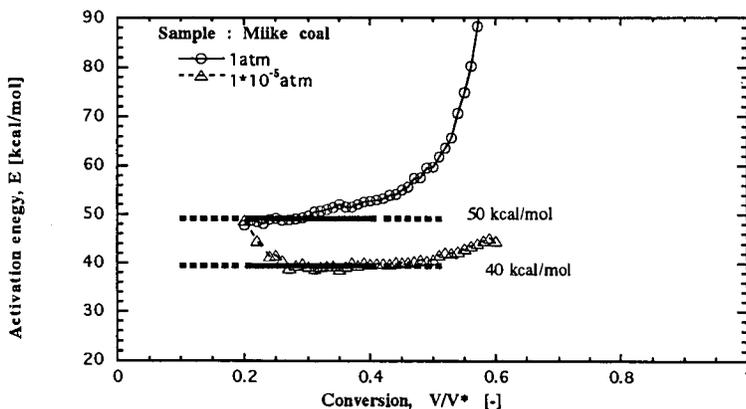


Fig.5 Activation energy of Miike coal at 0.2-0.6 of the conversion

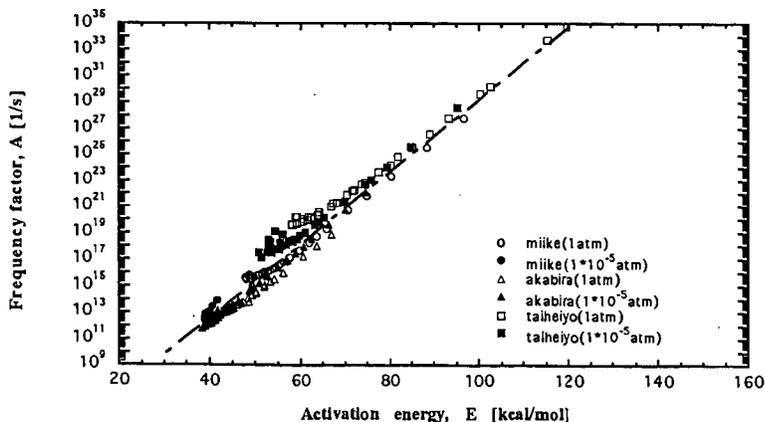


Fig.6 Relationship between frequency factor and activation energy

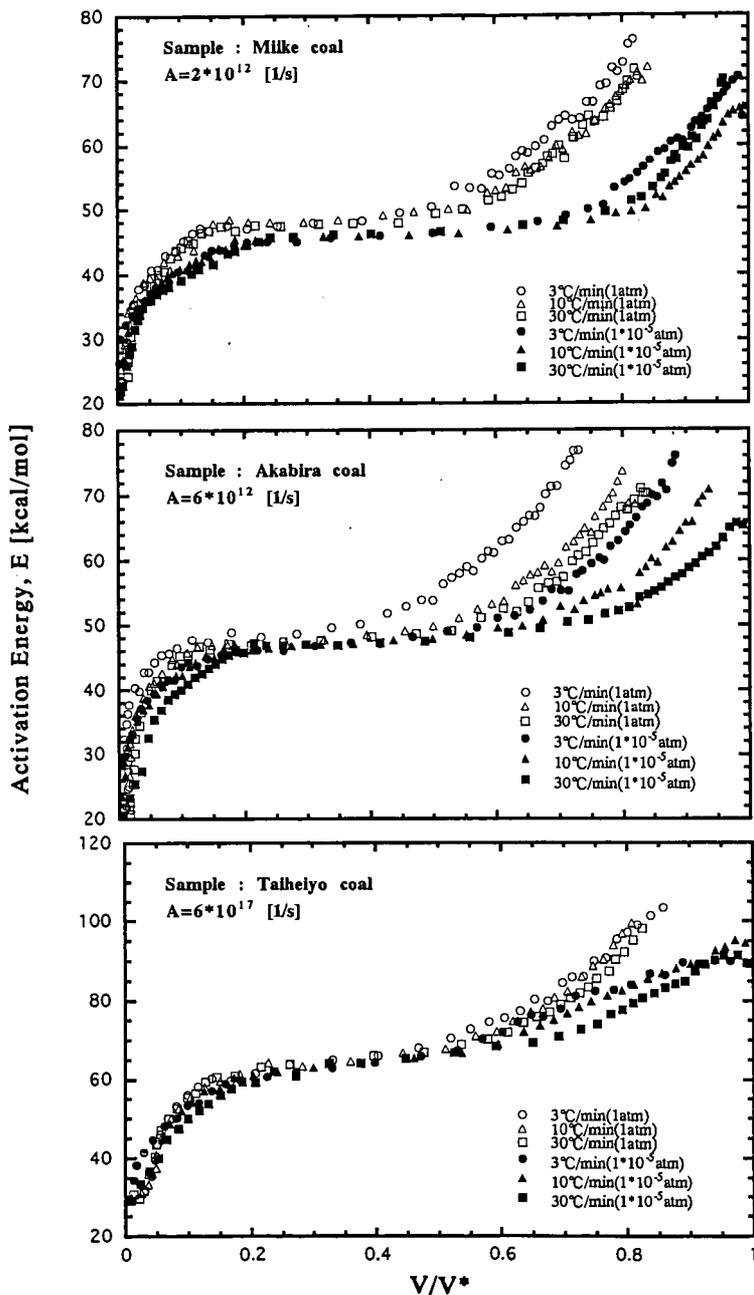


Fig.7 The distribution of activation energy for each coal using a constant frequency factor