

A SIMPLIFIED METHOD TO DETERMINE $f(E)$ AND k_0 IN THE
DISTRIBUTED ACTIVATION ENERGY MODEL FOR COAL PYROLYSIS

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INTRODUCTION

To analyze complex reactions such as pyrolysis of fossil fuels, thermal regeneration reaction of activated carbon *etc.*, the so called distributed activation energy model (DAEM) has been widely utilized. The model has been applied to represent the change in overall conversion¹⁻³ and/or the change in the yield of a given component⁴⁻⁶ during the coal pyrolysis. The model is represented as follows when it is applied to represent the change in total volatiles.

$$1 - V/V^* = \int_0^{\infty} \exp(-k_0 \int_0^t e^{-E/RT} dt) f(E) dE \quad (1)$$

where V is the total volatiles evolved by time t , V^* is the effective volatile content of the coal, $f(E)$ is a distribution curve of the activation energy to represent the differences in the activation energies of many first-order irreversible reactions, and k_0 is the frequency factor corresponding to the E value. The distribution curve $f(E)$ is defined to satisfy

$$\int_0^{\infty} f(E) dE = 1 \quad (2)$$

The focus of the analysis is the estimation of k_0 and $f(E)$. The distribution curve $f(E)$ is generally assumed by a Gaussian distribution with mean activation energy E_0 and standard deviation σ . On the other hand, the frequency factor k_0 is assumed to be a constant in general for all reactions to avoid the complexity of the analysis.

Since k_0 and $f(E)$ are interrelated as clarified by several investigators^{7,8}, k_0 is assigned on some basis first, and $f(E)$, namely E_0 and σ , is determined to fit experimental data. Therefore, eq 1 becomes just a correlation equation when we can not determine k_0 on some sound basis. Even the assumption of a constant k_0 value may not be valid when $f(E)$ spreads over wide range of E values. Furthermore, the assignment of the Gaussian distribution to $f(E)$ does not always reflect real situations.

Recently one of the authors has presented a simple method to estimate both $f(E)$ and k_0 from three sets of experiments performed at different heating profiles without assuming any functional forms for $f(E)$ and k_0 ⁹. The procedure to estimate $f(E)$ and k_0 is summarized below:

1. Measure V/V^* vs. T relationships at three different heating rates at least.
2. Calculate nominal rates $\bar{k} = dV/dt/(V^*-V)$ at several but same V/V^* values at the different heating rates, then make Arrhenius plots of \bar{k} at the same V/V^* values.
3. Determine activation energies from the Arrhenius plots at different levels of V/V^* , then plot V/V^* against the activation energy E .
4. Differentiating V/V^* by E gives $f(E)$, because the following relation holds approximately:

$$V/V^* = 1 - \int_{E_a}^{\infty} f(E) dE = \int_0^{E_a} f(E) dE \quad (3)$$

5. Calculate k_0 corresponding to each E_s value at all the heating rates using

$$0.545aE_s/k_0RT^2 = e^{-E_s/RT} \quad (4)$$

then employ the averaged k_0 value as a true k_0 value.

No *a priori* assumption is required for the functional forms of $f(E)$ and $k_0(E)$. In other

words we can determine k_0 and E at any levels of V/V^* .

In this paper the method was applied to estimate $f(E)$ and k_0 for the pyrolysis of 19 coals including the Argonne premium coals. It was found that $f(E)$ was significantly dependent on coal rank. However, the k_0 vs. E relationships were found to be classified into three groups depending on coal rank. Using the three k_0 vs. E relationships, we presented to estimate $f(E)$ from a single experimental run performed under a constant heating rate.

EXPERIMENTAL

Table 1 lists the ultimate analyses for the 19 coals used in this work. The weight change accompanying the pyrolysis of coal was measured by use of a sensitive thermobalance (Shimadzu TG-50) under three different heating rates (α) of 5, 10, and 20 K/min in a nitrogen atmosphere. The measured weight-time relationships were converted to the relationships of V/V^* vs. T . Pyrolysis using a Curie point pyrolyzer (Japan Anal. Ind. JHP-2S) was also performed for several coals. The coal particles were heated at 3000 K/s to 280, 386, 485, or 578 °C and kept for 10 s at the temperature. The change in V/V^* was calculated from the total weight change of the coal particles.

RESULTS AND DISCUSSION

$f(E)$ curves and k_0 vs. E relationships estimated by the proposed method for 19 coals

Figure 1 shows the relationships of V/V^* vs. T measured at $\alpha = 20$ K/min. The temperature at which the reaction starts and the shape of the curves are significantly different among the coals.

The relationships between V/V^* vs. E can be obtained through the procedures 1 to 3 mentioned above and are shown for the Argonne premium coals in the figure above and for the other coals in the figure below in Figure 2. Differentiating the curves graphically by E , $f(E)$ curves for the coals could be obtained as shown in Figure 3. The shape of the curves are significantly different among the coals: the peaks appear at $E=220-280$ kJ/mol, and the activation energy E spreads from 150 to 400 kJ/mol. These results clearly show that $f(E)$ can not be represented by a single Gaussian distribution. For the Argonne premium coals, the peak position shifted to higher E values with the increase of coal rank. This is well expected because the higher rank coals are decomposed at higher temperatures as shown in Fig. 1. For the other coals, the order of peak position does not always follow the order of coal rank as shown in Fig. 3b. This is probably because the coals were collected from various countries.

Figure 4 shows the k_0 vs. E relationships estimated for all the coals. Interestingly, the relationships were little dependent on coal types except three low rank coals, SY, MW, and BD. The difference in k_0 was only the order of 10^2 at maximum at a same E without the lower rank coals. This means that the coal pyrolysis consists of similar reactions having almost same rates for these coals. Only the proportions of the reactions are judged to be different among the coals, which is represented by the difference of $f(E)$ curves. The k_0 value increased from the order of 10^{10} to the order of 10^{25} s⁻¹ while E increases from 150 to 400 kJ/mol. The following compensation effect approximately held between the k_0 values and E for all the coals.

$$k_0 = \alpha e^{\beta E} \quad (\alpha, \beta; \text{constants}) \quad (5)$$

It is obvious that k_0 can not be assumed as constants for the pyrolysis of these coals.

Figure 5 compares the experimental TG curves and the curves calculated using $f(E)$ and k_0 estimated for MW coal. Not only the curves ($\alpha = 5, 10, \text{ and } 20$ K/min) utilized for obtaining $f(E)$ and k_0 but the data obtained at $\alpha=3000$ K/s showed good agreement with the calculated curves. This clearly indicates the validity of the presented method.

Figure 6 shows the $f(E)$ curves obtained by Burnham et al.¹⁰ for the Argonne premium coals by the conventional method. The peak position of $f(E)$ is not in the order of the coal rank: the peak position of the lowest rank coal, ND coal, is at $E=260$ kJ/mol, whereas the peak position of the highest rank coal, POC coal, is at $E=220$ kJ/mol. This would be because the k_0 value assigned to ND coal is larger than that assigned to POC coal. In the conventional method the $f(E)$ curve is dependent on the value of k_0 assigned as stated above. Therefore, we must be careful in interpreting the meaning of the activation energy when we resort to the conventional method.

A method to determine $f(E)$ from a single experiment

Figure 4 shows that the k_0 vs. E relationships are little affected by the coal type. This means

that the k_0 vs. E relationships may be represented by several relationships. Then the k_0 vs. E relationships in Fig. 4 were examined in more detail, and they were found to be grouped into three relationships depending on the coal rank as shown in Figs. 7a to 7c, where the relationships were approximated by eq 5.

Once we can know the k_0 vs. E relationship, we can obtain the relationship between E vs. T by using eq 4 for a selected heating rate α . Then $f(E)$ can be estimated from a single TG curve obtained at the heating rate. The procedure is given as follows:

- (1) Measure V/V^* vs. T relationship at a heating rate α .
- (2) Calculate the E vs. T relationship using eq 4 by choosing the k_0 vs. E relationship corresponding to the coal rank from three correlating equations.
- (3) Convert the V/V^* vs. T relationship into V/V^* vs. E relationship using the k_0 vs. E relationship obtained in (2).
- (4) Differentiate the V/V^* vs. E relationship by E gives $f(E)$.

Although the procedure is rather simple, the procedure (2) requires trial and error calculation. Then, the E vs. T relationships for $\alpha = 20\text{K/min}$ were calculated, and shown in Figure 8. Measuring the V/V^* vs. T relationship at $\alpha = 20\text{K/min}$ and using Fig. 8, one can obtain $f(E)$ curve straightforwardly.

Figure 9 compares the $f(E)$ curves estimated by the simple method using the V/V^* vs. T relationship measured at $\alpha = 20\text{K/min}$ and those estimated by the original method for several coals. The $f(E)$ curves estimated using the simple method are rather smooth and the peak intensities are smaller than those estimated using the original method. However, the E values at the peak positions obtained by the two methods are almost same. The V/V^* vs. T relationships were well reproduced using the $f(E)$ curves estimated by the simple method. One of the difficulties in applying the original method was to obtain E at smaller V/V^* region ($V/V^* < 0.1$) and at higher V/V^* region ($V/V^* > 0.1$). This was because the V/V^* vs. T curves obtained under three different heating rates become so close. Using the simple method, we can the procedure to obtain E . This largely facilitates the estimation of $f(E)$. Since the $f(E)$ curves estimated by the simple method are rather close to those obtained by the original method, the simple method is well utilized to estimate $f(E)$ curve.

CONCLUSION

The new method presented by the authors for estimating both the distribution curve $f(E)$ and the frequency factor $k_0(E)$ in the distributed activation energy model (DAEM) was applied to the analysis of pyrolysis reaction of 19 coals. It was found that the $f(E)$ curve spreads over 150 to 400 kJ/mol and that the frequency factor k_0 increases from 10^{12} to 10^{26} s^{-1} with the increase of E . The assumption of a constant k_0 value could not be employed for these coal. The validity of the proposed method was clarified through these works. Furthermore, a simple method was presented for estimating $f(E)$ from a single experiment. The $f(E)$ curves estimated by the simple method are rather close to those obtained by the original method, indicating the validity of the simple method. Using the simple method, we can estimate $f(E)$ easily and straightforwardly.

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Table 1. Ultimate analyses of the coals used

Coal	Ultimate analysis (wt% d.a.f.)			
	C	H	N	O(diff.)
Beulah-Zap (ND)	72.9	4.8	1.2	20.1
Wyodak (WY)	75.0	5.4	1.1	18.5
Illinois#6 (IL)	77.6	5.0	1.4	16.0
BlindCanyon (UT)	80.6	5.8	1.6	12.0
Lewinston-Stockton (ST)	82.5	5.3	1.6	10.6
Pittsburg#8 (PITT)	83.2	5.3	1.6	9.9
UpperFreeport (UF)	85.5	4.7	1.6	8.2
Pocahontas (POC)	91.0	4.4	1.3	3.5
Soya (SY)	66.1	5.2	1.5	27.2
Morwell (MW)	67.1	4.9	0.6	27.4
Baiduri (BD)	72.3	4.7	1.4	21.6
Onbilitin(OB)	78.3	5.6	1.7	14.4
Taiheiyu(TC)	78.7	6.2	1.2	13.9
Ebeneza(EN)	81.2	6.1	1.6	11.1
Tiger Head(TH)	82.3	5.6	1.8	10.3
Taung(TT)	82.7	4.7	1.1	11.5
Ensyutohon(ET)	82.8	5.6	1.5	10.1
Blair Athol (BA)	82.9	4.7	1.8	10.6
Newlands(NL)	85.9	4.9	1.7	7.5

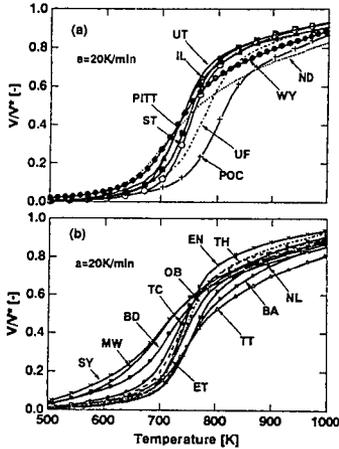


Figure 1. V/V^* vs. T relationships measured at $a=20K/min$ for 19 coals.

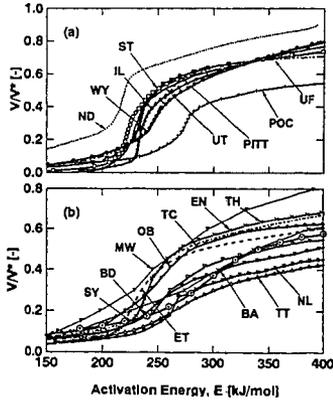


Figure 2. V/V^* vs. E relationships estimated by the proposed method.

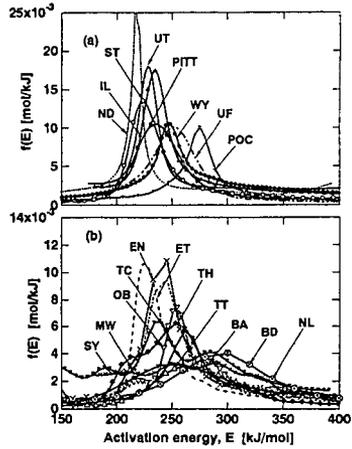


Figure 3. $f(E)$ curves estimated by the proposed method.

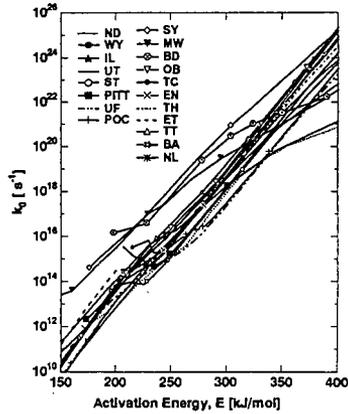


Figure 4. k_0 vs. E relationships estimated by the proposed method.

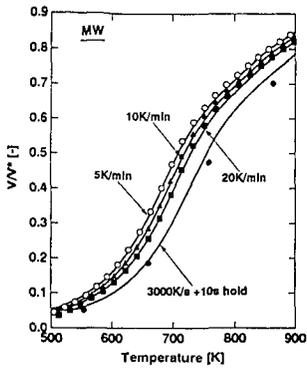


Figure 5. Comparison between the experimental V/V^* vs. T curves and calculated ones using $f(E)$ and k_0 estimated.

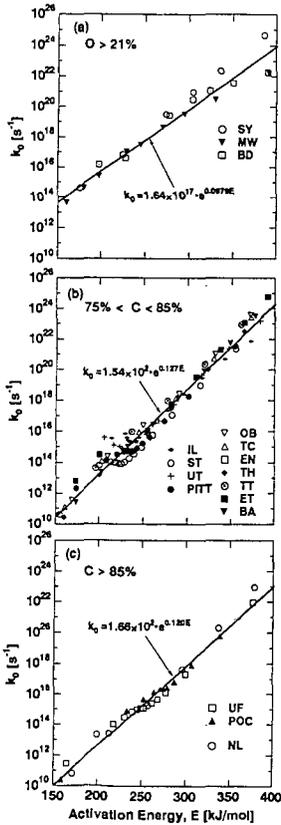


Figure 7. k_0 vs. E relationships approximated for three groups of coal rank.

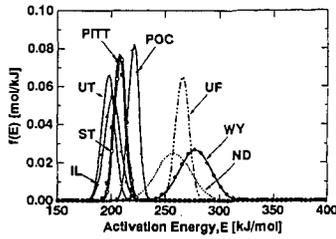


Figure 6. $f(E)$ curves for the Argonne coals estimated by Burnham et al. using the conventional method.

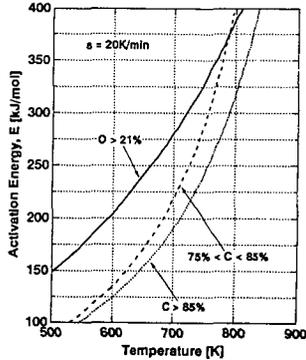


Figure 8. E vs. T relationships for $a = 20$ K/min for three groups of coal rank.

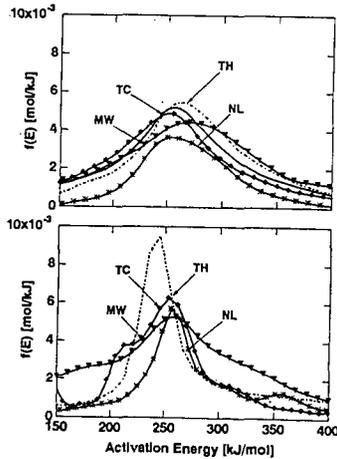


Figure 9. Comparison of the $f(E)$ curves estimated by the simple method (above) and those estimated by the original method (below).