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Mechanism of Coal Pyrolysis (Part 1)

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We have investigated the kinetics of coal pyrolysis at various temperatures below 500°C by means of thermobalance in the nitrogen atmosphere under reduced pressure, and discussed on the accuracy of this method.

We have discussed the mechanism of pyrolysis of coking coal from the calculated activation energies at various temperatures by means of thermogravimetry.

It is concluded that the some relatively lower organic molecules contained in the coal evaporate below about 350°C, and then the pyrolysis of coal commences above this critical temperature, and only depolymerization is recognized above about 420°C.

1. Introduction

There are many investigations of coal pyrolysis by means of thermobalance. Boyer¹⁾ showed that when the coal is heated at a heating rate of 2°C/min, there are two maximum rates of weight loss; one in the temperature range 350°C~550°C and one near 700°C. The former loss is the primary degradation in which compounds containing carbon, hydrogen and oxygen are released, the latter is secondary degradation in which mainly hydrogen is removed. H. A. G. Chermin and D. W. van Krevelen²⁾ calculated activation energy of pyrolysis from differential thermal analysis under some assumption. M. Weltner³⁾ investigated on peat pyrolysis and described that the the maximum loss at 295°C will be the degradation of cellulose and plant residue. N. Berkowitz⁴⁾ reported that diffusion velocity of volatile matter influences the rate of loss. D. W. van Krevelen⁵⁾ also recognized that adsorption of volatile matter on solid affects the rate of vaporization. N. Berlowitz⁶⁾ showed that pyrolysis of coal concerns to free radical mechanism from pyrolysis of coal in nitrogen mono-oxide atmosphere. H. Luther⁷⁾ showed that organic matter in coal has individual pyrolytic temperature. P. L. Walter⁸⁾ used the modified thermobalance in which volatile matter is adsorped with suitable adsorbance and estimated the rate of constituents of volatile matters.

We have discussed the method of kinetics of coal pyrolysis by means of thermobalance, especially at various temperatures below 500°C, and intended to clarify the process of the primary degradation of coal.

This report describes accuracy of experimental method and pyrolytic mechanism of coking coal by our method.

2. Experimental Equipment

Thermobalance is made applying twist of tungsten wire whose sensitivity is 1mg. The crucible of sample holder is platinum cylinder (20 mm. diameter, 20 mm. high) which

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hangs on the balance by platinum wire in the quartz tube whose diameter is 45 mm. and quartz tube is heated externally with electric furnace. Heating temperature is estimated with thermocouple inserted fine quartz tube which is sealed through bottom of quartz tube and the top of fine tube is placed at 5 mm. under crucible.

The apparatus can be evacuated and the coal is heated after the air in the apparatus is replaced with nitrogen avoiding the oxidation of coal.

Heating temperature is automatically controlled by voltmetric controller. When the sample is heated with constant rate, the heating rate is 5°C/min. In the case of constant temperature pyrolysis, we heat to expected temperature as soon as possible and the time of elevation to expected temperature is about 15 mins., but the time that reaches the constant temperature is not reproducible, hence weight loss slightly differs in some case.

As the sample of pulverized coal in the platinum crucible is 0.2 g., the depth of sample in crucible is below 2 mm so that the diffusion of volatile matter for sample layer will be negligible.

3. Sample

The used sample is Japanese Eri-coal, a kind of coking coal.

Chemical analyses of sample are listed in Table 1.

Table 1 Chemical Analyses of Eri-coal

| Substance | Proximate Analysis % | | | Elementary Analysis % (d.a.f.) | | | |
|--------------|----------------------|-------|-------|--------------------------------|------|------|------|
| | H ₂ O | V.M. | Ash | C | H | N | S |
| Raw coal | 0.82 | 29.56 | 15.88 | 86.07 | 5.79 | 1.39 | 0.63 |
| Deashed coal | 1.94 | 34.69 | 0.97 | 86.79 | 5.78 | 1.39 | 0.56 |

The sample was deashed by following procedure in order to remove effect of ash on coal pyrolysis. Deashing method was according to Radmacher's,⁹⁾ i.e. 10 g. of pulverized coal below 200 mesh was taken in polyethylene beaker, adding 500 ml. of ca. 30% HF. then the mixture was placed for an hour at the room temperature, and after decantation of HF solution, residue was treated twice with 50 ml. of 12-N HCl for half an hour. After the concentrated HCl was removed with decantation, diluted with water, then the coal was filtered, and the contaminated HCl was washed further repeatedly with 500 ml. of distilled water. Because long time was needed to remove HCl with distilled water, at first, decanted residue was washed with a little NaOH solution below 0.1-N. then repeatedly with 500 ml. of warm distilled water until washed filtrate became neutral, and Cl ion was free.

Washed coal was dried at about 60°C under reduced pressure, and kept in closed sample bottle. Chemical analyses of deashed coal are listed in Table 1.

4. The effect of pressure to pyrolysis of coal

As the volatilizing rate in the pyrolysis of coal is affected by adsorption and diffusion, it will be desirable to estimate the rate of pyrolysis under reduced pressure to avoid these

effects as much as possible, moreover secondary decomposition of primary volatile matter will be avoided by reduced pressure. We have experienced under pressure of 5, 10, 20, 40, 80, and 760 mm/Hg to observe the effect of pressure on pyrolysis. These results are listed Fig. 1a, of integral curves and Fig. 1b of differential curves. (In these experiments, non-deashing coal was used.) In the differential curves of Fig. 1b, as the sensitivity of thermobalance is 1 mg. and weight of sample is 0.2 g., experimental accuracy is 0.5%, the fine

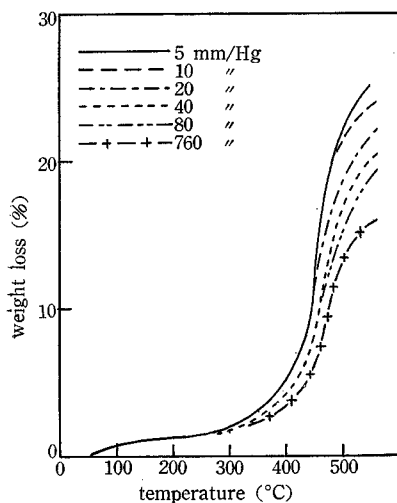


Fig. 1a The relation of weight loss and temperature.

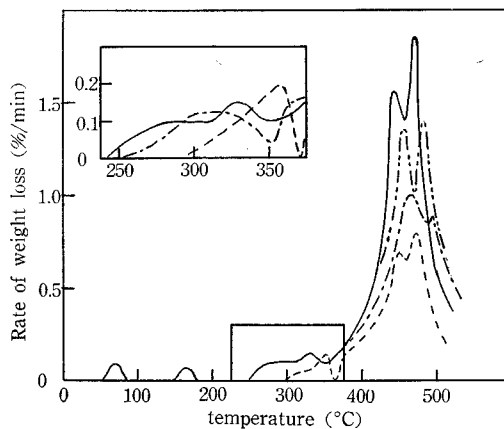


Fig. 1b The relation of weight loss and temperature

structure of differential curves is doubtful, but since there are reproducibility of experimental curves, the curves are represented in the fine structure. In Fig. 1a, the difference of weight loss is little between 5 and 10 mm/Hg below 490°C, but at the pressure above 20 mm/Hg the weight loss becomes smaller than 5 mm/Hg or 10 mm/Hg, therefore the higher the pressure is the less weight loss becomes, while below 390°C the weight losses under each pressure are almost same in each other. In Fig. 1b, when pressure is higher, the temperature of maximum rate of weight loss tends to shift to higher, and maximum rate of weight loss becomes less, though the temperatures of maximum rate are almost same at 5, 10 and 20 mm/Hg.

The maximum peak below 100°C will be due to dehydration in each cases. At higher pressure, for example, at atmospheric pressure, there is no weight loss between 100°C and 280°C but a little peak appears at about 160°C under reduced pressure. Two maximum peaks appear under every pressure between 440°C and 480°C, though these peaks are not certain and these tend to shift to lower temperature according as the pressure decreases but under the pressure of 80 and 760 mm/Hg, the temperature of peaks shift slightly to lower temperature than 40 mm/Hg. The residual coal after experiment do not cake or dilatate at low pressure.

From these results, it will be essential that the experiment should be done under below 10 mm/Hg at least to study kinetics of coal pyrolysis. The following experiments are carried out accordingly under below 3 mm/Hg.

5.1. The rate of pyrolysis

We have investigated the kinetics of coal pyrolysis at various temperatures and calculated the activation energy of pyrolysis to clarify the pyrolytic process of coal. Fig. 2a shows the results that the deashed coal is heated at various constant temperatures under 3 mm/Hg in nitrogen atmosphere. From Fig. 2a, weight loss by pyrolysis almost completes in short time for constant heating below 350°C or upper 420°C. The weight loss becomes predominantly upper about 370°C and the pyrolytic rate becomes very rapid upper 420°C.

From these results, it is assumed that coal component will be pyrolysed selectively by temperature and that coal pyrolysis is regarded to first order reaction (A)

$$\ln(a-x)/a = -kt \quad (\text{A})$$

Where a is weight of sample, and $(a-x)$ is weight loss and t is time. Fig. 2b shows the relation of time to logarithm of weight loss %. In Fig. 2b, linear relation is obtained for short time but this relation is not held for long period. The difference of rate of weight loss by temperature is large in the initial step, but it becomes small with progress of time, for example, the difference of rate after an hour is not observed at 300°C, 320°C, 420°C and 450°C, so it is considered that weight loss after an hour is not due to chemical reaction but physical phenomenon. Since it is considered that the initial rate of weight loss is due to chemical reaction, we calculate the rate constant k according to equation (A) from initial loss between 4 and 10 mins. after temperature becomes constant.

From Fig. 2c of initial rate, it appears that the reaction mechanism in each temperature is different, and the higher the heating temperature is, the greater activation energy becomes, so that its temperature coefficient can not be calculated from the rate constant. To avoid this difficulty, we have considered the pyrolysis below 420°C and above 420°C,

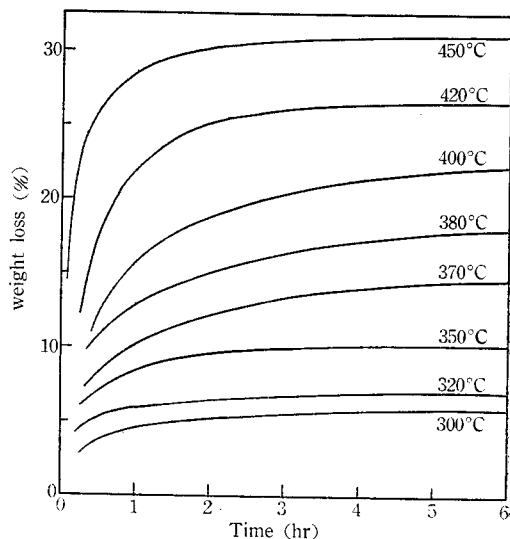


Fig. 2a The relation of weight loss and time.

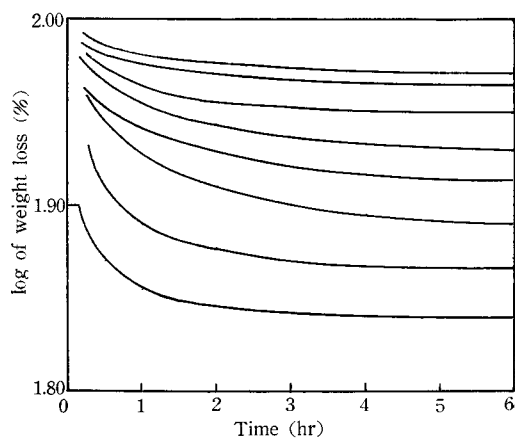


Fig. 2b The relation of logarithm of weight loss and time.

under our assumption of which coal constituents will decompose at the specific temperature.

5.2. The pyrolysis below 420°C

Since Fig. 2a shows apparently that total weight losses for temperatures do not converge, the activation energy can not be estimated strictly from the rate of weight loss. If it is postulated that in narrow range of temperature, the initial rate of pyrolysis is governed by the same component in the coal, approximate activation energy will be obtained. But actually the initial rate is so rapid that it can not be estimated directly. To avoid this difficulty, we calculate the rate of weight loss of each time for heating at constant temperature from the curve of weight loss, and the plot

the rates to residual coal, then extrapolate linear part to 100% of residual coal to obtain the initial rate.

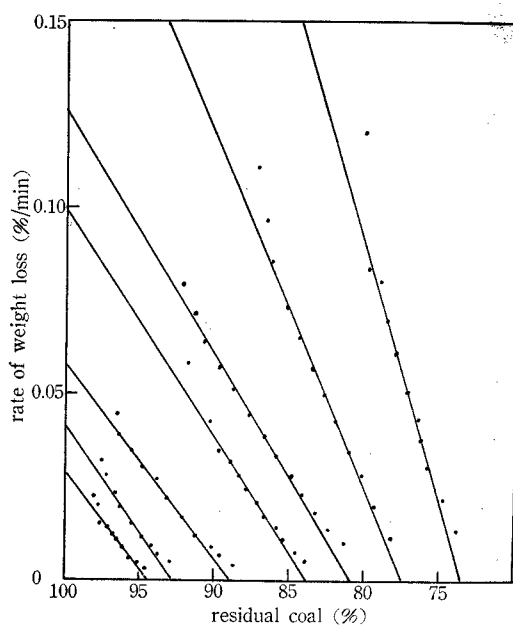


Fig. 3a The relation of rate of weight loss and residual coal.

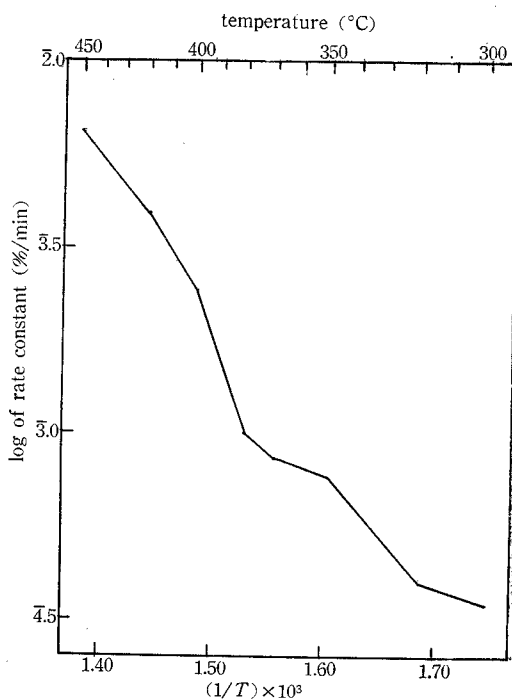


Fig. 2c The relation of rate constant and temperature.

The values by this method correspond to the value of removing of weight loss of very volatilizable component such as moisture. Therefore, it is considered that this value is initial rate of pyrolysis of some simplified component removing of very volatilizable components.

Fig. 3a shows the results by this method below 420°C. In this method, since extrapolating part becomes long in case of pyrolysis of higher temperature, the rate of weight loss is considerably changed by method taking of linear part. Moreover since the rate of weight loss increases rapidly, more volatilizable component is neglected above 420°C by this consideration,

so that it is meaning-less to compare with each rate.

Fig. 3b shows the relation of logarithm of initial rate to temperature. In Fig. 3b, there is a inflection at about 350°C. The activation energies are $E_1=11$ kcal/mole between 300°C and 350°C and $E_2=22$ kcal/mole between 350°C and 420°C.

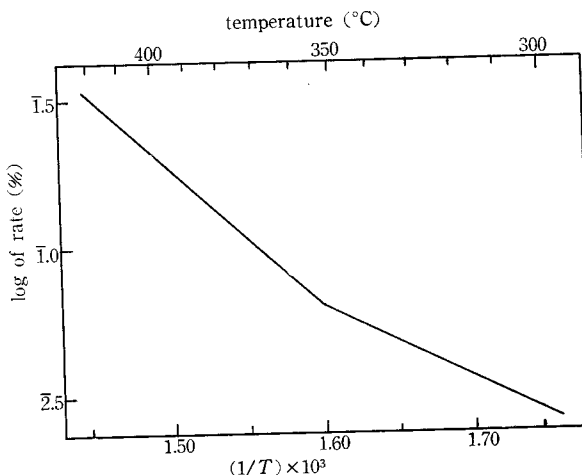


Fig. 3b The relation of logarithm of rate and temperature

If E_1 is activation energy of fission of C-C bond, its value is too small. Since E_1 is approximately molar heat of vaporization of alkyl aromatic compound having 2~3 rings, it is deduced that this value is due to vaporization of lower molecular organic compounds contained in the coal. This deduction is held from difference of the rate of weight loss depending on pressure at about 350°C in the inset diagram of Fig. 1b. If we postulate that vaporizing rate k of volatile matter depends on the monomolecular adsorption, we can show the following equation (B).

$$K = aSe^{-E/RT} \quad (B)$$

Where a is constant, S is area of monomolecular adsorption, E is molar heat of vaporization, R is gas constant and T is temperature.

The amount of vaporization of lower molecular substance will be about 10% from Fig. 2a.

Fig. 1b shows that coal pyrolysis is initiated at about 350°C, but E_2 is too small to consider depolymerization of coal, consequently, pyrolysis above 350°C is considered to be pyrolysis of easily decomposable component.

The weight loss between 350°C and 420°C is about 16%.

5.3. The pyrolysis above 420°C

It is described in previous section that initial rate of pyrolysis can not be estimated by the extrapolating method above 420°C, however, in the consideration of kinetics of coal pyrolysis above 420°C, volatilizable components must be removed to estimate initial rate of decomposition. For this purpose we preheat coal at 380°C, 400°C or 420°C for 6 hours,

until weight loss almost disappears. Then we elevate to expected temperature as rapid as possible, and estimate initial rate from weight loss of this temperature.

In this procedure, the effect of preheating for volatile matter is investigated previously, i.e. after the sample is heated at 380°C, 400°C or 420°C for 6 hours, sample is cooled to 300°C and then heated at the rate of 5°C/min.

Fig. 4 shows these results. The differential curves in Fig. 4 is not so accurate as Fig. 1b for the change below 0.5%/min. Fig. 4 is simplified compared with Fig. 1b and it shows that pyrolysable component is simplified with preheating. This is the same as experiment by Luther.⁷⁾ Therefore, if the rate of weight loss of preheated coal is measured at various temperature, activation energy of simplified component will be obtained. But in this case we must postulate that component of coal which pyrolyse at expected temperature is not changed by preheating.

Fig. 5 shows the relation of logarithm of weight loss to time in which after the coal preheated at 380°C for 6 hours, it is heated to 420°C as rapid as possible and then weight loss to the time is measured. The rate of decomposition is calculated by equation (A), where initial concentration is assumed the residual coal after preheating at 380°C for 6 hours. By the same procedure, logarithm of weight loss percent to time for preheated coal at 440°C, 460°C and 480°C is plotted by the equation (A) in Fig. 5. These curves are the same type as Fig. 2b and the difference of rate at each temperature becomes

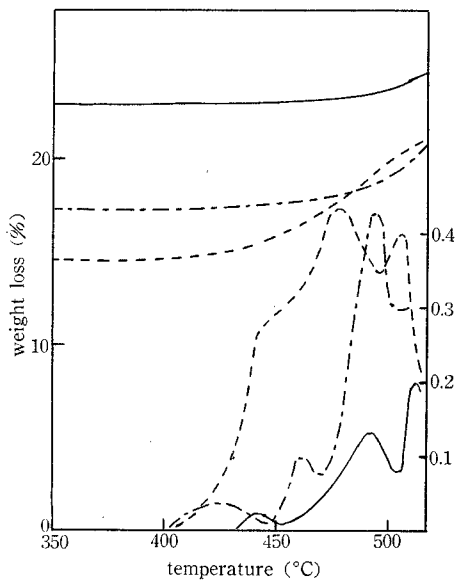


Fig. 4 The relation of weight loss after preheating and temperature.
Preheating temperature
— 420°C
- - - 400°C
- · - 380°C

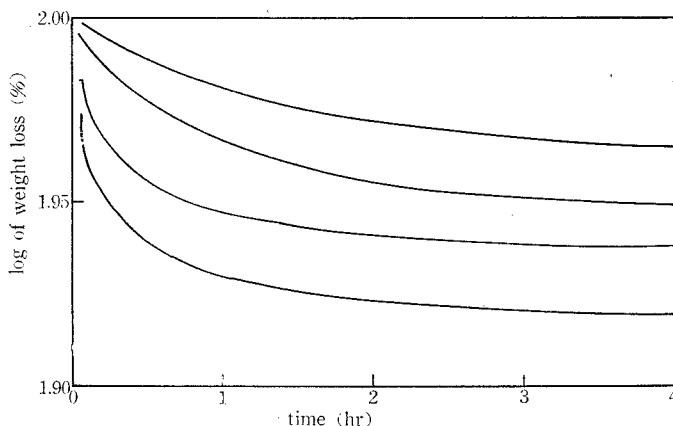


Fig. 5 The relation of logarithm of weight loss (%) and time

smaller as the time elapses, consequently chemical reaction will finish in relatively short time. Therefore, the decomposition rate must be measured from initial weight loss. The value of weight loss at the expected temperature is adopted for 30 mins. after preheating. (expected temperature which elevate during 5 mins. or less.) Sometimes the curve of weight loss has inflection point and it will be caused by the effect of diffusion, but the rate is calculated by equation (A) with neglect of this effect.

Fig. 6a shows the initial rate of weight loss of coal preheated at 380°C for 6 hours and the rate is calculated from inclination of straight line. Fig. 6b is the relation of logarithm of initial rate to temperature under various preheating. From the straight line in Fig. 6b, it is considered that mechanism of initial reaction is almost same, and initial rate is mainly governed by specific component.

The results obtained from preheated coal at 380°C, 400°C, 420°C and 440°C are represented in Table 2.

The activation energy must be large with elevation of preheating temperature, but it becomes small in preheating at 440°C. For this reason, it is considered that in addition to primary decomposition secondary decomposition will take place above 440°C or adsorption and diffusion of heavy volatile matter which is remarkable recognized by the inflection of curve of weight loss might retard the rate of vaporization.

Since the activation energies of pyrolysis of preheated coal at 400°C

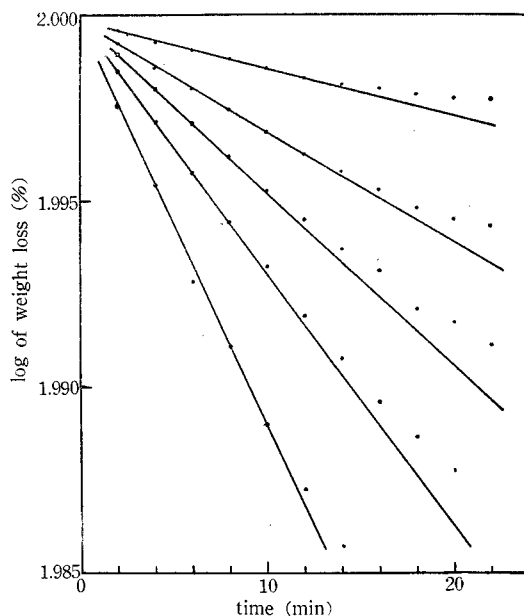


Fig. 6a The relation of logarithm of weight loss (%) and time (after preheated at 380°C for 6 hrs.)

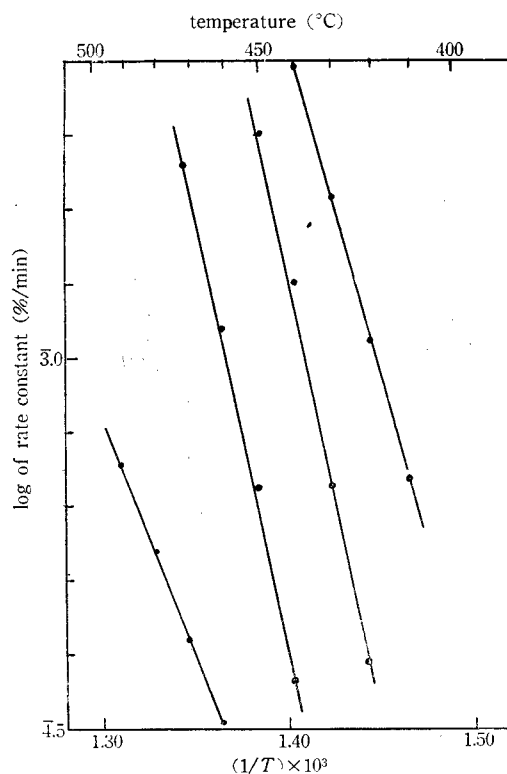


Fig. 6b The relation of logarithm of rate constant and temperature

and 420°C correspond to activation energy of fission of C-C bond of organic compound, it is considered that depolymerization reaction take place above 420°C for the coal pyrolysis.

Table 2 The activation energies above 400°C

| Preheating temperature (°C) | Reaction temperature (°C) | Velocity constant (%/min.) | Activation energy (kcal/mole) |
|-----------------------------|---------------------------|----------------------------|-------------------------------|
| 380 | 410 | 6.00×10^{-4} | 41 |
| | 420 | 1.09×10^{-3} | |
| | 430 | 1.58×10^{-3} | |
| | 440 | 2.47×10^{-3} | |
| 400 | 420 | 4.00×10^{-4} | 56 |
| | 430 | 6.73×10^{-4} | |
| | 440 | 1.26×10^{-3} | |
| | 450 | 2.08×10^{-3} | |
| 420 | 440 | 3.68×10^{-4} | 54 |
| | 450 | 6.79×10^{-4} | |
| | 460 | 1.10×10^{-3} | |
| | 470 | 1.69×10^{-3} | |
| 440 | 460 | 3.19×10^{-4} | 30 |
| | 470 | 4.19×10^{-4} | |
| | 480 | 5.52×10^{-4} | |
| | 490 | 7.18×10^{-4} | |

The weight loss by pyrolysis of coal becomes small at higher temperature, for example, the difference of weight loss between 400°C and 420°C is about 4% and between 420°C and 450°C is about 4.5% from Fig. 2b.

6. Conclusion

We have pointed out the fact that in the study of coal pyrolysis the experiment should be carried out under reduced pressure to avoid as adsorption, diffusion and secondary pyrolysis of volatile matter as possible. Moreover since the pyrolysis of various components in coal takes place parallelly, it is reasonable to preheat at various temperatures in order to study of fractional pyrolysis. It is also pointed out that rate of pyrolysis must be estimated by the initial rate at the certain temperature. Under these consideration, the pyrolytic mechanism of coal is deduced from the activation energies at various temperatures.

It seems that lower molecular organic matter contained in the coal vaporize below 350°C on the basis of activation energy. This concept corresponds to the classical idea of coal bitumen, however, Holden¹⁰⁾ has recently reported that aliphatic and alkylaromatic compounds vaporized between 170°C and 300°C before pyrolysis of coal by the study of mass spectrum and Vahrman¹¹⁾ also has reported that the simple neutral matter is contained in coal.

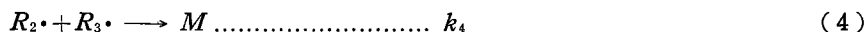
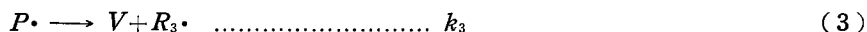
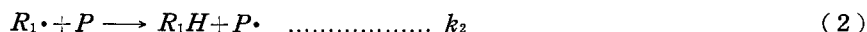
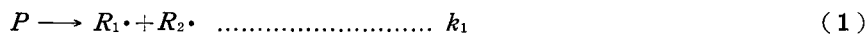
The pyrolysis of coal will take place above 350°C from the ascending curve of weight loss in Fig. 1b. Fitzgerald¹²⁾ and van Krevelen²⁾ show that "meta plast" appears in

temperature range between 350°C and 420°C according to depolymerization of coal, so that at temperature of this range easily pyrolysable component in coal will be decomposed. But if the depolymerization of coal occur at this temperature range, activation energy obtained from our study is smaller than the depolymerization energy of polymer. If the pyrolysis of coal in this temperature range is depolymerization reaction, we can not understand why activation energy becomes small, but the reason perhaps will be due to overlap of vaporization of lower molecular organic compound and some pyrolysis of coal.

In the pyrolysis above 420°C, the activation energy corresponds to the depolymerization of C-C bond fission, so that depolymerization will occur above 420°C in this coal.

It has been considered that the depolymerization reaction of pyrolysis follows by free radical mechanism. Berkowitz⁶⁾ showed that when the low rank coal is heated in nitrogen mono-oxide atmosphere which is inhibitor of propagation reaction, the pyrolysis contains free radical mechanism from the curve of weight loss above 340°C. D. W. van Krevelen and coworkers¹³⁾ investigated pyrolytic mechanism of coal model which is polymer of aromatic compound with formaldehyde, and concluded that primary pyrolysis is depolymerization reaction accompanying disproportionation of aliphatic hydrogen. From these reports we deduced that the pyrolysis of coal above 420°C would be taken place the following mechanism.

If it is postulated that the coal is a kind of high molecular hydrocarbon, and the pyrolysis will take place by following equation



Where P is coal, $R_1\cdot$ and $R_2\cdot$ are fragments of depolymerized free radicals. If the fragment $R_1\cdot$ is enough smaller to volatilize than $R_2\cdot$, $R_1\cdot$ volatilizes abstracting aliphatic hydrogen. $P\cdot$ decomposes in volatilizable smaller fragments V and $R_3\cdot$. Non-volatilizable fragments $R_2\cdot$ and $R_3\cdot$ will combine to semi-cokes M .

k_1 , k_2 , k_3 and k_4 are respectively rate constant.

$$d[R_1\cdot]/dt = k_1[P] - k_2[R_1\cdot][P] \quad (5)$$

$$d[P\cdot]/dt = k_2[R_1\cdot][P] - k_3[P\cdot] \quad (6)$$

At the steady state $d[R_1\cdot]/dt = 0$, $d[P\cdot]/dt = 0$.

$$\text{Therefore, } [R_1\cdot] = k_1/k_2 \quad (7)$$

The equation (5) and (6) introduce the equation (8)

$$[P\cdot] = k_1[P]/k_3 \quad (8)$$

The equation (7) and (8) are substituted to the equation (9) of rate of weight loss

$$d[R_1H]/dt + d[V]/dt = k_2[R_1\cdot][P] + k_3[P\cdot] \quad (9)$$

$$d[R_1H]/dt + d[V]/dt = 2k_1[P] \quad (10)$$

Thus, if pyrolysis is considered as long as short time, the reaction is first order from the equation (10), and the equation (1) will become determining rate of coal pyrolysis. Therefore activation energy calculated from the initial rate of weight loss correspond to the equation (1) and it is depolymerization energy.

In the above equations, the coal has been assumed to be high molecular compound of hydrocarbon, but the coal is more complex compound containing oxygen and others. Therefore the above mechanism will not be strictly applied for coal, but it holds approximate.

The present investigation is summarized that in the primary decomposition of coal below 500°C, at first, relatively low molecular organic substance in the coal evaporizes below about 350°C, then the pyrolysis commences at about 350°C, and the depolymerization predominantly occurs above about 420°C.

This conclusion is due to coking coal, but it is somewhat different in the case of low rank coal. We shall report details in the next paper.

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