

Kinetics of Direct Liquefaction of Coal  
in the Presence of Mo-Fe Catalyst

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INTRODUCTION

Many studies on direct coal liquefaction have been carried out since the 1910's, and the effects of kinds of coal, pasting oil and catalyst, moisture, ash, temperature, hydrogen pressure, stirring and heating-up rate of paste on coal conversion, asphaltene and oil yields have been also investigated by many workers. However, few kinetic studies on their effects to reaction rate have been reported.

In this present study, the effects of kinds of coal, pasting oil, catalyst and reaction temperature on coal liquefaction are illustrated, and a few kinetic models for catalytic liquefaction of five coals carried out in a autoclave reactor are proposed.

RESULTS and DISCUSSION

(I) Experimentals in catalyst and reaction rate

(I-1) Experimental procedure

Five coal materials were used in this study. These were Miike, Taiheiyo, Hikishima (Japanese coals), Morwell (Australian) and Bukit Asam (Indonesian) coals. The proximate and ultimate analyses of these coals, on a moisture-free basis, are shown in Table 1. All of catalysts were powdered before use. In all of the experiments powdered coal (passed through 80-mesh sieve), 3.3 % of catalyst (calculated on the coal charge), a steel ball (10 mm $\phi$ ) and vehicle were charged to the 0.3 or 0.5-liter autoclave reactor in the required ratio. The reactor was flushed and filled with cold hydrogen to an initial pressure of 100 kg/cm $^2$ -gauge at room temperature, heated to reaction temperature at a heat-up rate of about 4°C per minute, held at constant temperature for the desired length of time, and cooled to room temperature at a heat-down rate of about 3°C per minute. Then the autoclave residue was extracted with benzene and n-hexane in Soxhlet apparatus, and the proportion of "asphaltene" (defined as the benzene-soluble, n-hexane insoluble material), and "oil" (the benzene, n-hexane soluble material) in the liquefied product was determined.

(I-2) Results of experiments

(A) Effect of pasting oil on liquefaction

(1) Charged ratio of coal to pasting oil

Coal conversion per cent on a moisture- and ash-free was independent of the charged ratio and had constant value about 80-90 %, while liquefaction percentage was decreased with increasing the charged ratio. This result was considered to be responsible for gasification with thermal decomposition and resinifying of coals on inner wall of the reactor; temperature at the wall would be higher due to worse stirring as coal pastes were more viscous when coal concentration was higher. Therefore, well mixing was necessary to obtain a good liquefaction percentage under higher coal concentration.

(2) Kind of pasting oil

Using four pasting oils with boiling temperature of 330°C to 380°C, liquefaction was carried out under the same reaction condition.

When hydrogenated pasting oil were used, reaction rate was greater than that with non-hydrogenated pasting oils. This higher liquefaction rate for the hydrogenated pasting oil was interpreted by the action of greater proton-donner ability with them.

(B) Effect of catalyst on liquefaction

Figs. 1 to 5 were experimental results of Miike coal liquefaction for  $\text{MoO}_3$ ,  $\text{Fe}(\text{OH})_3$ -S,  $\text{MoO}_3$ - $\text{Fe}(\text{OH})_3$ -S,  $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$  and  $\text{Fe}(\text{OH})_3$ - $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ -S catalysts. Figs. 6 to 9 were those of Taiheiyo, Hikishima, Morwell and Bikit Asam coals for  $\text{MoO}_3$ - $\text{Fe}(\text{OH})_3$ -S. In Figs. 10, 11 and 12, fraction of unreacted coal was plotted as a function of nominal reaction time on semilogarithmic graph paper. Reaction rate was first order with coal concentration in the same way as Takeya et al. (3) showed in Taiheiyo coal liquefaction, since at lower temperature plots gave straight lines. At higher temperatures semilogarithmic plots didn't give only one decreasing straight line. This characteristic was explained from greater gasification and resinification of coal under these temperatures. Specific reaction rates calculated from slope of lines were shown in Table 2. From these results activities of the catalysts were compared. Conclusions were shown as follows;

(a)  $\text{MoO}_3$  was more active under lower temperatures, while  $\text{Fe}(\text{OH})_3$ -S was more active under higher temperatures.

(b)  $\text{MoO}_3$  and  $\text{Fe}(\text{OH})_3$  were complements each of the other,  $\text{MoO}_3$ - $\text{Fe}(\text{OH})_3$ -S being more active than both under the lower and higher temperatures.

(c)  $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$  of the catalyst containing  $\text{H}_2\text{O}$ , but having a tendency of resinifying and gasification.  $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ - $\text{Fe}(\text{OH})_3$ -S was not so active as expected.

(d) The action of the catalyst to Taiheiyo coal was the same that to Miike coal.

Fig. 3 showed reaction course for Miike coal under several reaction temperatures with nominal reaction time for  $\text{MoO}_3$ - $\text{Fe}(\text{OH})_3$ -S which is the most active among the catalysts. This result showed that under temperature range 350°C to 410°C reaction rate increased with increasing temperature and oil yield became greater with increasing nominal reaction time, whereas at the highest temperature 450°C oil yield decreased, and both organic benzene insoluble and asphaltene increased with increasing nominal reaction time. Reaction courses of Hikishima, Morwell and Bukit Asam coals for  $\text{MoO}_3$ - $\text{Fe}(\text{OH})_3$ -S catalyst were shown in Figs. 7 to 9, respectively. In Figs. 8 and 9, it was shown that reaction rates and oil yield in the product Morwell and Bukit Asam were larger than <sup>any</sup> other tested coal at lower temperatures. Reaction courses for Taiheiyo and Hikishima coals, when the same catalyst was used, were shown in Figs. 6 and 7. They showed that at the highest temperature formed oil degraded to organic benzene insolubles in a similar way to that for Miike coal at the highest temperature. This characteristic was explained from forming of organic benzene insolubles by resinification of produced asphaltene and oil. Degree of resinification were dependent on both reaction temperature and kinds of catalyst, being considerable at the highest temperature. No resinification was observed for  $\text{Fe}(\text{OH})_3$ -S.

(II) Mechanism and kinetics of coal liquefaction

Various mechanisms and kinetics of coal liquefaction have been proposed and examined by many investigators (1 to 10).

We assumed the reaction mechanism shown in scheme 1 as a general kinetic model of coal liquefaction. The mechanism in scheme 1 with all reaction rates assumed to be pseudo first order with respect to reacting species and dissolved hydrogen to be in excess, seems to be somewhat similar to those reported in above many literatures. A few typical cases of a general kinetic model are shown in Table 3, and only

the general characteristics for their cases are illustrated on Table 3. When compared these typical figures, the curves are apparently different in shape, but if proper rate constants were selected, the curves would be similar in shape, making it difficult to determine the correct mechanism. Therefore, it is necessary to get initial rate data at lower temperatures (i.e. 350~400°C) in distinguishing between series reactions (case 1, 2, 3) and parallel reactions (case 4, 5), since for series reaction the reaction time-concentration curve for oil (C) has a zero slope and for parallel reaction the time-log(unreacted coal, %) curve does not give a straight line but two ones. A typical curve in Table 3 shows that when the apparent coal and asphaltene concentration begin to increase gradually, a further series reaction, oil→resin→coke, should be assumed. The magnitude of the rate constant of each step is different from kinds of catalyst, and it is possible that the catalyst which is very effective for promoting the reaction rate of any step in a kinetic model is to be found, resulting in the change of mechanism.

In this study oil yield decreased with reaction time, as oil was polymerized at higher temperature for Miike, Taiheiyo and Hikishima coals. Thus a kinetic model (case 2 or 3) in which involves two steps of polymerization and coking, correlated data reasonably well for above coals, whereas for Morwell and Bukit Asam coals, case 5 was more favorable.

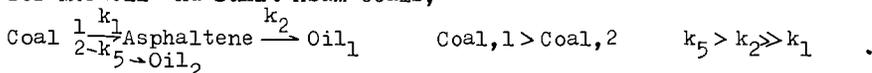
Though kinetic experiments are generally carried out with the autoclave at high temperature and pressure, reaction temperature is not sufficient isothermal but nonisothermal from start of experiment to end. As long as nominal reaction time which consists of heat-up, constant temperature and heat-down periods, is used, it will be difficult for true rate constants to be estimated under isothermal condition. Therefore, the rate constants, k-values were estimated by a non-linear least square which involves minimization of the sum of squares of deviations (between measured and calculated values). The temperature dependence of the rate constants on Miike coal was determined for temperature between 350°C and 450°C. The result was shown in Table 4.

## CONCLUSIONS

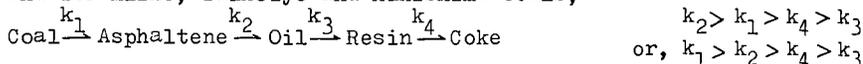
Effects of various reaction conditions on reaction rate and mechanism of coal liquefaction were investigated. Conclusions were summarized as follows;

(1) The order of the reaction, reaction rate, oil yield and composition were affected by kinds of pasting oil and ratio of coal to pasting oil.

(2) Under same reaction conditions, reaction rate and mechanism of coal liquefaction differs from kinds of coal and catalyst. The reaction rate was in the order; Morwell > Bukit Asam > Miike > Taiheiyo = Hikishima coal. Kinetic scheme of coal liquefaction was expressed as follows; for Morwell and Bukit Asam coals,



and for Miike, Taiheiyo and Hikishima coals,



The magnitude of the rate constants is different from kinds of catalyst.

(3) Activities of catalysts were as follows;  $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O} > \text{Fe}(\text{OH})_3 - \text{MoO}_3 - \text{S} > \text{MoO}_3 > \text{Fe}(\text{OH})_3 - \text{S}$ . The activity of  $\text{Fe}(\text{OH})_3 - \text{MoO}_3 - \text{S}$  catalyst may be due to the concerted action with  $\text{MoO}_3$  and  $\text{Fe}(\text{OH})_3 - \text{S}$ , and degrees of resin-

fication and coking were dependent on kinds of catalyst.

(4) In making a kinetic analysis of the experimental data with auto-clave, a non-linear least square method was used to estimate the parameters in the Arrhenius equation under nonisothermal conditions. The theoretical values of component, calculated by substituting the estimated values into the rate equations, were in good agreement with experimental values.

#### LITERATURE CITED

- 1) Weller et al., Ind. Eng. Chem., 43, 1575 (1951)
- 2) Falkum E. and R. A. Glenn, Fuel, 31, 133 (1952)
- 3) Takeya and Ishii et al., Kagakukogaku, 29, 988 (1965)
- 4) Struck et al., Ind. Eng. Chem. Proc. Des. Develop., 8, 546 (1969)
- 5) Liebenberg B. J. et al., Fuel, 52, 130 (1973)
- 6) Plett et al., paper presented University-ERDA Contractor Conference, Salt Lake City, Utah, Oct 22-23, 1975
- 7) Guin et al., Am. Chem. Soc. Div. Fuel Chem., Prepr., 20(1), 66 (1975), 21(5), 170 (1976)
- 8) Whitehurst et al., EPRI Annual Report No. AF-252, Rp 410-1, (Feb 1976)
- 9) Reuther et al., Ind. Eng. Chem. Process Des. Dev., 16, 249 (1977)
- 10) Shah et al., Ind. Eng. Chem. Process Des. Dev., 17(3), 281, 288 (1978)

Table 1 Analysis of sample coals

Coal	%			% (d.a.f.)	
	Moisture	F.C.	V.M.	C	H
Miike	0.9	45.9	39.8	82.9	6.2
Taiheiyo	4.9	27.7	47.0	79.8	5.7
Hikishima	1.2	50.7	26.0	86.2	6.2
Morwell	12.6	52.4	34.2	65.3	5.2
Bukit Asam	9.5	44.8	45.0	68.6	5.2

Table 2 Rate constants on various catalysts ( $\text{min}^{-1}$ )

Catalyst \ R.T.(°C)	350	380	410	450
MoO <sub>3</sub>	0.0145	0.0212	0.0253	-
Fe(OH) <sub>3</sub> -S	0.0039	0.0113	0.0207	0.0338
MoO <sub>3</sub> -Fe(OH) <sub>3</sub> -S	0.0192	0.0253	0.0305	-
H <sub>2</sub> MoO <sub>4</sub> ·H <sub>2</sub> O	0.0188	0.0322	-	-
Fe(OH) <sub>3</sub> -S-H <sub>2</sub> MoO <sub>4</sub> ·H <sub>2</sub> O	0.0023	0.0069	0.0230	-

(Coal:Miike)

Table 4 Rate constant calculated by non-linear least square method under non-isothermal condition (coal:Miike)

Catalyst	Rate const. ( $\text{min}^{-1}$ )	Reaction Temperature (°C)			
		350	380	410	450
MoO <sub>3</sub>	K <sub>1</sub>	0.01080	0.02000	0.03500	0.06880
	K <sub>2</sub>	0.05040	0.09170	0.1580	0.3060
	K <sub>3</sub>	—	—	—	—
	K <sub>4</sub>	—	—	—	—
Fe(OH) <sub>3</sub> -S	K <sub>1</sub>	0.00785	0.01460	0.02570	0.05080
	K <sub>2</sub>	0.01880	0.03490	0.06130	0.1210
	K <sub>3</sub>	—	—	—	0.00276
	K <sub>4</sub>	—	—	—	0.02910
MoO <sub>3</sub> -Fe(OH) <sub>3</sub> -S	K <sub>1</sub>	0.01760	0.02930	0.04660	0.08150
	K <sub>2</sub>	0.00636	0.01140	0.01930	0.03640
	K <sub>3</sub>	—	—	0.00129	0.00732
	K <sub>4</sub>	—	—	0.00213	0.01590
H <sub>2</sub> MoO <sub>4</sub> ·H <sub>2</sub> O	K <sub>1</sub>	0.02040	0.03420	0.05480	0.09590
	K <sub>2</sub>	0.05020	0.1100	0.2230	0.5190
	K <sub>3</sub>	—	—	0.00321	0.01710
	K <sub>4</sub>	—	—	0.00977	0.05730
Fe(OH) <sub>3</sub> -S-H <sub>2</sub> MoO <sub>4</sub> ·H <sub>2</sub> O	K <sub>1</sub>	0.01680	0.02020	0.02380	0.02920
	K <sub>2</sub>	0.08120	0.1280	0.1930	0.3180
	K <sub>3</sub>	—	—	—	0.000451
	K <sub>4</sub>	—	—	—	0.00258

Scheme 1 Kinetic Model of Direct Liquefaction of Coal

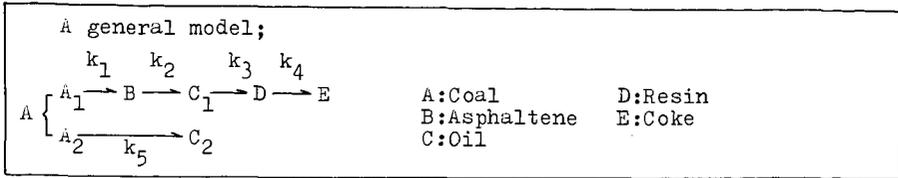
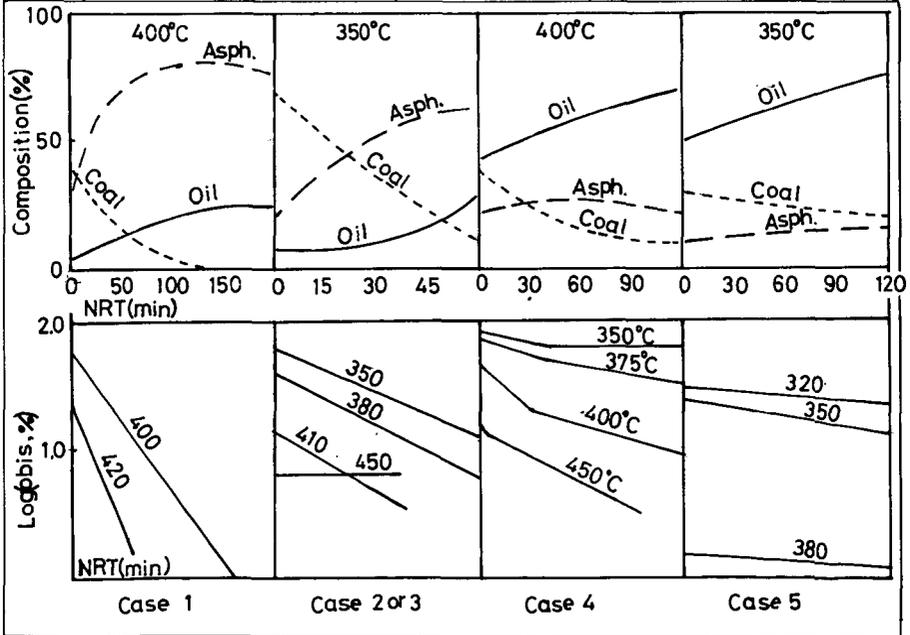


Table 3 Typical Cases of a General Kinetic Model

Case	Condition	Model	Coal	Catalyst	Worker
1	$A_1 \gg A_2 \neq 0$ $k_1 > k_2 \gg k_3, k_4$	$A \rightarrow B \rightarrow C$	Pittsburg Seam	$\text{SnCl}_2\text{-NH}_4\text{Cl}$	S. Weller et al.
2	$A_1 \gg A_2 \neq 0$ $k_2 > k_1 > k_4 > k_3$	$A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$	Taiheiyo Miike	$\text{Fe(OH)}_3\text{-S}$ $\text{H}_2\text{MoO}_4\text{-S}$	M. Morita et al.
3	$A_1 \gg A_2 \neq 0$ $k_1 > k_2 > k_4 > k_3$	$A \rightarrow B \rightarrow C \rightarrow D \rightarrow E$	Miike	$\text{Fe(OH)}_3\text{-}$ $\text{MoO}_3\text{-S}$	M. Morita et al.
4	$A_1 > A_2$ $k_5 > k_1 > k_2$	$A_1 \rightarrow B \rightarrow C_1$ $A_2 \rightarrow C_2$	Yubari, Soya Sumiyoshi	Red Mud	G. Takeya et al.
5	$A_1 > A_2$ $k_5 > k_2 \gg k_1$	$A_1 \rightarrow (B) \rightarrow C_1$ $(A_2 \rightarrow C_2)$	Morwell Bukit Asam	$\text{Fe(OH)}_3\text{-}$ $\text{MoO}_3\text{-S}$	M. Morita et al.



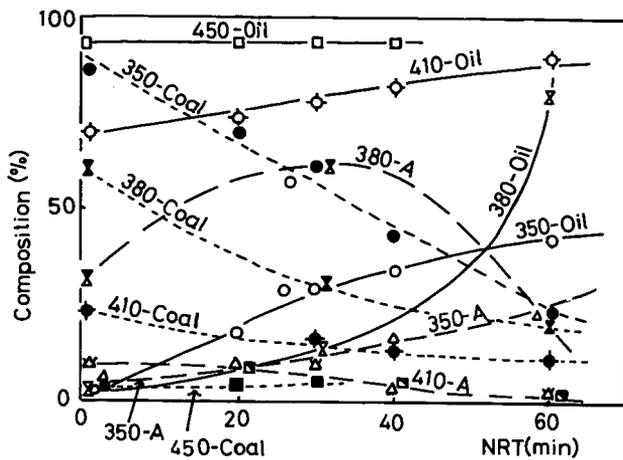


Fig.1 Change of composition on catalyst  $\text{MoO}_3$  at various react. temp.  
 at  $350^\circ\text{C}$  (●△○)  $410^\circ\text{C}$  (◆◇◇)  
 $380^\circ\text{C}$  (×××)  $450^\circ\text{C}$  (■□□)

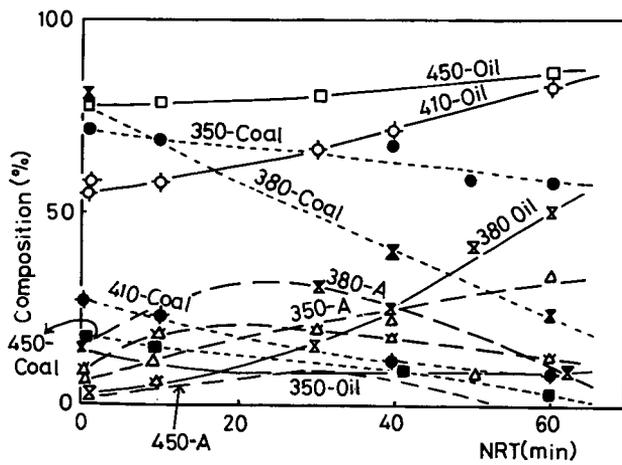


Fig. 2 Change of composition on catalyst  $\text{Fe}(\text{OH})_2\text{S}$  at various react. temp.  
 at  $350^\circ\text{C}$  (●△○)  $410^\circ\text{C}$  (◆◇◇)  
 $380^\circ\text{C}$  (×××)  $450^\circ\text{C}$  (■□□)

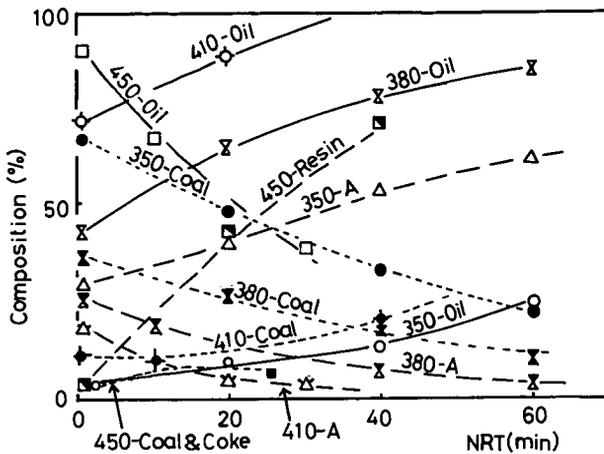


Fig. 3 Change of composition on catalyst  $\text{Fe}(\text{OH})_2\text{MoO}_4\text{-S}$  at various R.T. (Miike-coal)  
 350°C (●△○) 410°C (◆◇◊)  
 380°C (⊠⊞⊡) 450°C (■□◻)

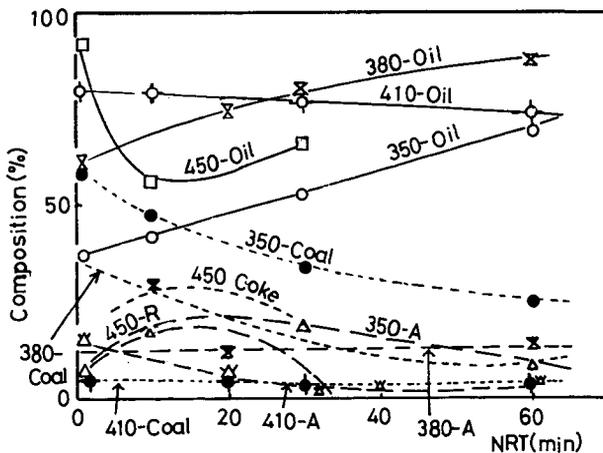


Fig. 4 Change of composition on catalyst  $\text{H}_2\text{MoO}_4$  at various react. temp.  
 at 350°C (●△○) 410°C (◆◇◊)  
 380°C (- ⊠⊞) 450°C (■□◻)

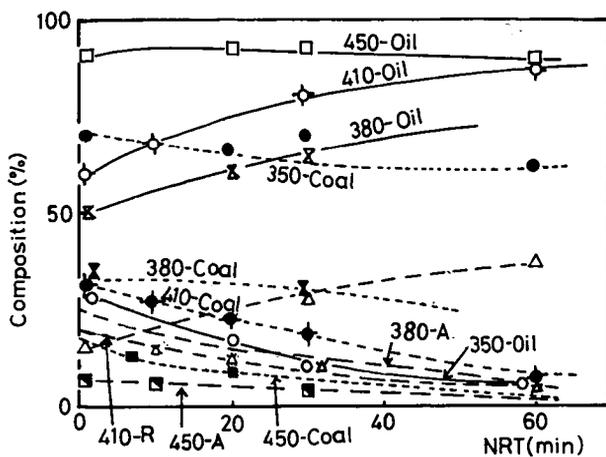


Fig. 5 Change of composition on catalyst  $\text{Fe}(\text{OH})_2 \cdot \text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O} \cdot \text{S}$  at various react. temp  
 at 350°C (● Δ ○) 410°C (◆ Δ ◇)  
 380°C (x-x) 450°C (■ □ □)

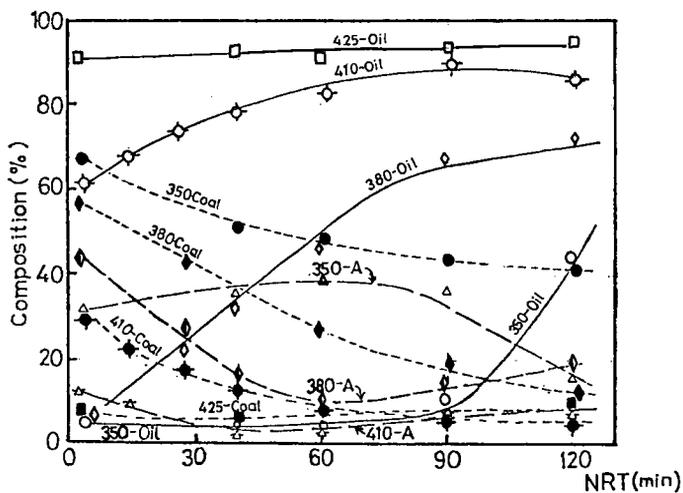


Fig. 6 Change of composition on Taiheiyo coal (Numerals; React. temp, A; Asphaltene)  
 350°C (● Δ ○) 410°C (◆ Δ ◇)  
 380°C (◆ ◆ ◆) 425°C (■ □ □)

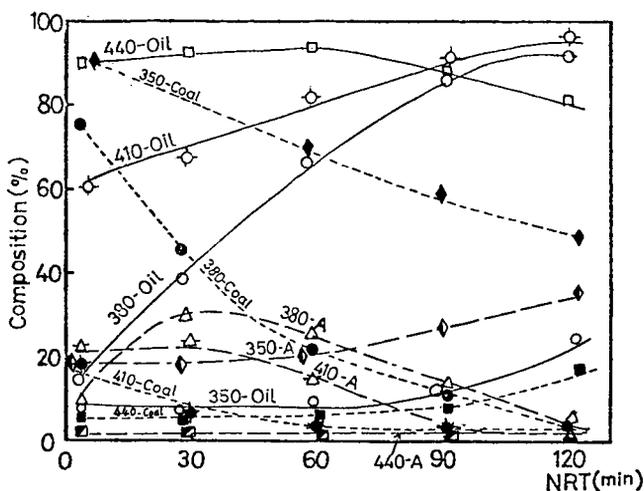


Fig.7 Change of composition on Hikishima coal (Numerals; React. temp., A: Asphaltene) at 350°C (● △ ○) 410°C (◆ ▲ ◇) 380°C (♦ ♦ ♦) or 440°C (■ □ □)

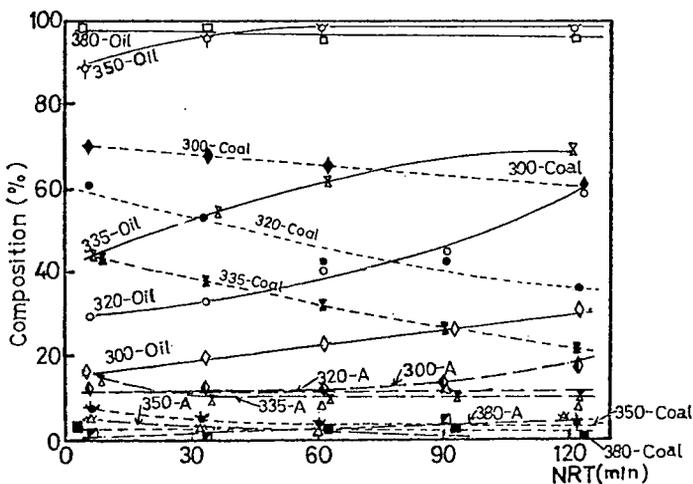


Fig. 8 Change of composition on Morwell coal (Numerals; React. temp., A; Asphaltene) at 300°C (● △ ○) 350°C (▽ ✕ ▽) 320°C (◆ ♦ ♦) or 380°C (■ □ □) 335°C (✕ ✕ ✕)

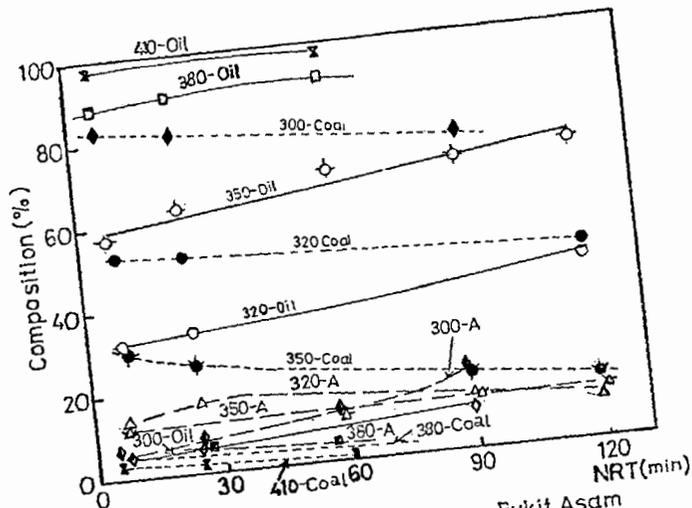


Fig. 9 Change of composition on Bukit Asam coal (Numerals; React. temp, A; Asphaltene) at 300°C (●, △, ○), 350°C (◆, ▲, ◇), 410°C (×, x, x) 320°C (◆, ◇) or 380°C (■, □)

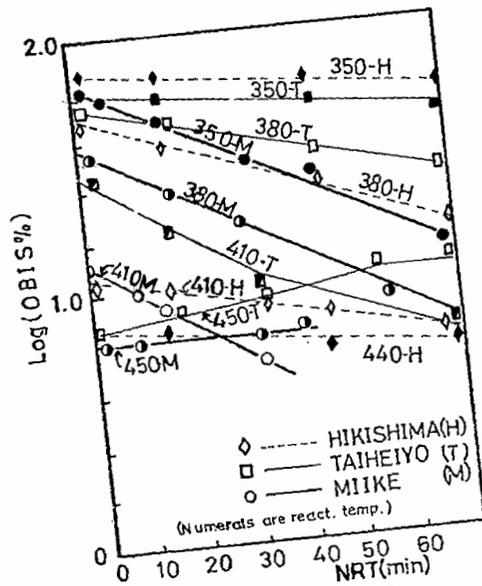


Fig.10 Log(OBIS%) vs. NRT for various coals

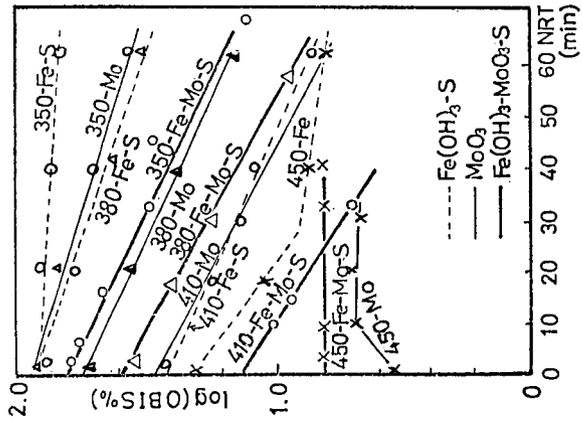


Fig.11 Log(OBIS%) vs. NRT on various temp.(Miike coal)

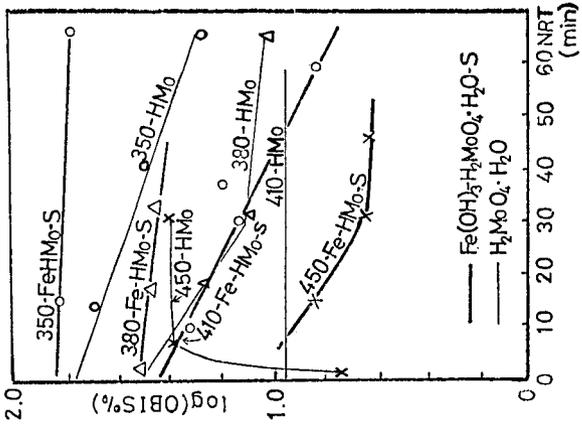


Fig.12 Log(OBIS%) vs. NRT on various temp.(Miike coal)