

Coal Liquefaction under Atmospheric Pressure

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INTRODUCTION

Liquefaction of coals has been investigated extensively in the recent time to synthesize liquid fuels of petroleum substituent(1). The processes for liquefaction proposed are classified into three major groups. They are direct hydrogenation of coal under high hydrogen pressure, the solvent refining of coal under medium hydrogen pressure, and the hydrogenation of liquid produced by dry distillation of coal. Among them, the solvent refining may be the most skillful method for the largest yield of coal liquefaction under the moderate conditions(2).

The present authors studied the solvolytic liquefaction process (3,4) from chemical viewpoints as for the solvents and the coals in a previous paper(5). The liquefaction activity of a solvent was revealed to depend not only on its dissolving ability but also on its reactivity for the liquefying reaction according to the nature of the coal. The coal which is non-fusible at liquefaction temperature is scarcely liquefied with the non-reactive aromatic compound. This fact indicates the importance of solvolytic reactivity in the coal liquefaction. This conclusion corresponds to the fact that tetraline or hydrogenated anthracene oil assured the high liquefaction yield(6).

In the present study, the liquefaction activities of pyrene derivatives and decacyclene with coals of several ranks are studied to ascertain the previous ideas of liquefaction mechanism. The coals used in the present study are non-fusible or fusible at relatively high temperature and then gave small liquefaction yield with pyrene of non-solvolytic solvent at 370°C.

EXPERIMENTAL

Coals: The coals used in the present study are listed in Table 1, where some of their properties are also summarized. They were gratefully supplied from Shin Nippon Steel Co., Nippon Kokan Co., and National Industrial Research Laboratory of Kyushu.

Liquefaction Solvents: The solvents used in the present study are listed in Tables 2 and 3. Alkylated and hydrogenated pyrenes were synthesized by Friedel-Crafts and Birch reaction, respectively. Details have been described in else places(7).

Procedure and Analysis: Apparatus used in this experiment consisted of a reactor of pyrex glass(diameter 30 mm, length 250 mm, volume 175 ml) with a stirring bar and a cold-trap. After 1~3 g of coal and described amount of the solvent were added in the reactor, of which weight was previously measured, the reactor was heated in a vertical electric furnace under N₂ gas flow. The temperature was increased at the rate of 4°C/min, and was kept at the prescribed temperature for 1 hr. The weight calculated by subtracting the weight of the reactor cooled from the total weight defined 'residual yield'. The weight of oil and sublimed matter captured in the trap

defined 'oil yield'. The difference between the weight of charged substances and the residue plus oil yields defined 'gas yield', which contained the loss during the experiment. The gas and oil yields were usually less than 20 % under the present conditions.

The residual product in the reaction was ground and stirred in 100 ml of quinoline for 1 hr at room temperature, and filtered after centrifugation. This extraction procedure was repeated until the filtrate became colorless (usually 2~4 times). The quinoline insoluble (QI), thus obtained, was washed with benzene and acetone and then dried for weighing. The collected filtrate was evaporated to dryness in vacuo and washed with acetone for weighing. The degree of the solvolytic liquefaction was described with two ways of expression, liquefaction yield (LY) and liquefying efficiency (LE), which are defined by equations (1) and (2), respectively. QI and the coal fed in these equations were moisture and ash free (maf) weights.

$$\text{Liquefaction Yield (\%)} = \left(1 - \frac{\text{QI}^{\text{P}} - \text{QI}^{\text{S}}}{\text{coal fed}}\right) \times 100 \quad (1)$$

$$\text{Liquefying Efficiency (\%)} = \left(1 - \frac{\text{QI}^{\text{P}} - \text{QI}^{\text{S}}}{\text{QI}^{\text{C}}}\right) \times 100 \quad (2)$$

where QI^{P} , QI^{S} , and QI^{C} are weights of quinoline insoluble in the residual product, in the original solvent, and in the heat-treated coal at the liquefaction temperature without any solvent, respectively. LE describes the increased yield of liquefaction by using the solvent, indicating its efficiency for the liquefaction.

RESULTS

Liquefaction of fusible coal at high temperature

The liquefaction of Itmann coal, of which softening point and maximum fluidity temperature are 417° and 465°C, respectively, was carried out at several temperatures using decacyclene as a liquefaction solvent. The results are shown in Fig. 1, where the QI yield was adopted as a measure of liquefaction extent. Because the solubility of decacyclene in quinoline was rather small, the QI contained a considerable amount of decacyclene. Liquefaction of this coal proceeded scarcely below 420°C of the softening temperature. Above this temperature, the QI yield decreased sharply with the increasing liquefaction temperature until the resolidification temperature of the coal. The maximum LY observed at this temperature was estimated 67 %, decacyclene being assumed uncharged under the conditions. Above the resolidification temperature, the QI yield increased sharply. The carbonization may start. Decacyclene was known unreacted at 470°C in its single heat-treatment(8).

Liquefaction of coals in alkylated and hydrogenated pyrenes

Table 2 shows liquefaction activity of alkylated and hydrogenated pyrenes, respectively. Although hexylpyrene was just same to pyrene, propylation and ethylation certainly improved the liquefaction activity of pyrene with these coals of three different ranks. It is of value to note that ethylpyrene showed LY of 80 % with West-Kentucky coal.

Hydrogenation improved quite significantly the liquefaction activity of pyrene with these coals. The LY values with Taiheiyo

and West-Kentucky coals reached to 80 %.

The effect of hydrogenation extent on the liquefaction activity was summarized in Table 3. As the number of hydrogen atoms introduced per one pyrene molecule varied from 2.2 to 4.7 by using a variable amount of lithium in Birch reduction. The liquefaction activity of hydrogenated pyrene was affected slightly, reaching the maximum at around three of hydrogen atoms. It is obviously observed that LY was always larger with Taiheiyo than Itmann.

Structural change of solvent and coals after the liquefaction reaction

To analyse the structural change of solvents and coals after the liquefaction reaction, the solvent and coal should be separated. Because the separation was rather difficult, it was assumed that the benzene soluble and insoluble fractions after the liquefaction were derived from the solvent and coal, respectively. This assumption was verified by the following fact. The amount of BS recovered in the liquefaction of Taiheiyo coal with pyrene was 73.3 % as shown in Table 4. This value correspond to 97.7 % of the starting amount of pyrene and the BS fraction at the same time showed the same NMR pattern to that of pyrene. The recovery percentages of coal and solvent (BI/coal fed, BS/solvent fed, respectively) calculated based on the above assumption are summarized in Table 4. They were more than 85 % except for the significantly low value for the coal recovery when hydropyrene was used as the solvent. In the latter case, some extent of the coal may be converted into the benzene soluble. Nevertheless, analyses of BS and BI fractions may inform the structural change of coal and solvent after the liquefaction.

Figures 2 and 3 show the NMR spectra of benzene solubles after the liquefaction reaction using hydropyrene and ethylpyrene, respectively, together with those of the solvents before liquefaction for comparison. The BS derived from hydropyrene after the liquefaction lost the resonance peaks at 2.5, 3.2 and 4.0 ppm, extensively, although peaks at 2.0 and 2.8 ppm remained uncharged as shown in Figure 2. In contrast, there was essentially no change in the NMR spectra of ethylpyrene and its BS derivative as shown in Figure 3, indicating that the BS derivative contained unchanged ethylpyrene. However, the relatively low BS recovery of this case suggests that the conversion of this compound into BI may increase the BI yield in comparison with other cases as shown in Table 4.

Table 5 shows the ultimate analysis of benzene insoluble fractions after the liquefaction. H/C ratios of these fractions were similar when no solvent or pyrene was used, however when ethylpyrene and hydropyrene were used, the values were significantly low and high, respectively. The hydrogenation of coal by the hydrogen transfer from the hydrogen donating solvent is strongly suggested in the latter case. The low H/C value in the case of ethylpyrene may be explained in terms of certain extent of carbonization, as suggested by the low recovery of the solvent.

Discussion

In a previous paper(5), the authors described the liquefaction mechanism according to the properties of the coal and the solvent. The coal was classified into two categories,

- (1) fusible at the liquefaction temperature,
- (2) non-fusible at the liquefaction temperature.

The fusible coals can give a high liquefaction yield if the high fluidity during the liquefaction is maintained by the liquefaction solvent to prevent the carbonization. The properties of the solvent required for the high yield with this kind of coal are miscibility, viscosity, radical quenching reactivity and thermal stability not to be carbonized at the liquefaction temperature as reported in literatures (9).

In contrast, the non-fusible coal requires the solvation or solvolytic reaction to give the high liquefaction yield. The solvation of non-polar organic compounds including the pitch is expected low, so that the solvolytic reaction is necessary between the coal and the solvent.

The present results are well understood by the above mechanism. Itmann which is fusible at relatively high temperature was not liquefied below 420°C with a non-solvolytic solvent such as pyrene, however it was significantly liquefied at 480°C in decacyclene of a stable aromatic compound. Decacyclene is reported to be fused but stable for 1 hr heat-treatment at 500°C (8).

With solvolytic solvents, the fluidity of the coal may not be a principal factor any more. Taiheiyō, West-kentucky and Itmann coals of three different ranks were sufficiently liquefied with hydropyrene under atmospheric pressure at 370°C regardless of their fusibility. Lower rank coals show higher reactivity in such liquefaction.

The analyses of hydropyrene and the coal before and after the liquefaction clearly indicate the hydrogen transfer from the solvent to the coal substance. Transalkylation might be expected another kind of the solvolytic reaction. However, the present results suggest low probability with alkylated pyrenes as suggested by the NMR analysis. Instead, the increased polarity by alkyl group and the reactivity of the carbonization precursor from alkylpyrene, especially ethylpyrene, may be responsible for a considerable liquefaction yield. The recovery of the solvent becomes difficult by its latter conversion as observed in the present study

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Table 1 Coals and their properties

Properties	coal	Itmann	West Kent.14	Taiheiyo
Proximate analysis (wt%)	ash	7.3	12.8	10.1
	volatile matter	19.9	53.0	45.9
	fixed carbon	72.8	34.2	37.9
ultimate analysis (wt%)	C	90.1	79.0	77.8
	H	4.6	5.1	6.0
	N	1.3	1.7	1.1
	S	0.5	4.6	0.2
	O(diff)	3.5	9.6	14.9
plasticity analysis	soften.temp.(°C)	417	387	
	max.fluid.temp.(°C)	465	425	non-fusible
	max.fluid.(ddpm)	64	45	
	final temp.(°C)	487	445	

Table 2 Coal liquefaction by pyrene derivatives (reaction temp.=370°C, solvent/coal=3/1)

solvent	n*	coal	residue(%),distillate(%)				L.Y.**	L.E.**
			QI	QS	oil	gas		
none	—	West Kent.	85.1	9.2	0.8	4.9	17	0
		Itmann	97.5	0.0	0.8	1.7	3	0
		Taiheiyo	85.4	0.0	2.2	12.4	16	0
pyrene	0	West Kent***	19.9	69.9	6.0	4.2	24	8
		Itmann	20.4	75.2	3.1	1.3	23	18
		Taiheiyo	19.3	75.0	2.5	3.2	25	11
hydro-pyrene (No.1)	—	West Kent.	7.6	73.4	9.6	9.4	80	76
		Itmann	9.1	79.6	5.8	5.5	69	68
		Taiheiyo	6.3	85.0	4.5	4.2	83	80
hexyl-pyrene	0.83	West Kent.	19.3	51.3	12.8	16.5	26	11
		Itmann	20.9	63.1	8.5	7.5	17	15
		Taiheiyo	19.7	56.2	11.8	12.8	25	9
propyl-pyrene	0.85	West Kent.	14.4	66.3	3.5	16.1	49	38
		Itmann	14.9	66.3	7.2	11.6	43	42
		Taiheiyo	15.7	65.7	6.7	11.9	42	30
ethyl-pyrene	0.33	West Kent.	7.6	79.3	12.4	0.7	80	76
		Itmann	11.4	77.8	5.5	5.7	59	58
		Taiheiyo	13.4	76.8	2.9	6.9	52	42

* number of alkyl groups introduced/one pyrene molecule

** L.Y.=Liquefaction Yield(%); L.E.=Liquefying Efficiency(%)

*** reaction temp.=390°C

Table 3
Effect of hydrogenation extent on the liquefaction activity
(reaction temp. 370°C, solvent/coal=3/1)

solvent	n*	Itmann Taiheiyo				
		L.Y.	L.E.	L.Y.	L.E.	
		(%)	(%)	(%)	(%)	
hydro- pyrene	No.1	2.2	69	68	83	80
	No.2	2.8	78	78	90	88
	No.3	4.3	72	71	85	82
	No.4	4.7	72	71	83	79

L.Y.=Liquefaction Yield

L.E.=Liquefaying Efficiency

* n = number of hydrogen atoms
introduced one pyrene molecule

Table 4 Benzene extraction of solvolysis pitches
(coal=Taiheiyo, reaction temp. 370°C, solvent/coal=3/1)

solvent	residue		distillate		recovery	
	BI (%)	BS (%)	oil (%)	gas (%)	coal (%)	solvent (%)
none	86.4	10.0	0.5	3.2	86.4	-
hydro- pyrene (No.2)	18.4	70.6	3.6	7.4	74.6	94.1
ethyl- pyrene	23.9	64.0	7.9	4.2	96.0	85.3
pyrene	22.4	73.3	0.9	3.4	89.6	97.7

$$* \text{ recovery coal}(\%) = \frac{\text{BI}}{\text{coal fed}}$$

$$\text{solvent} = \frac{\text{BS in residue}}{\text{solvent fed}}$$

Table 5 Ultimate analysis of benzene
insoluble part of solvolysis pitch
(Coal=Taiheiyo, reaction temp. 370°C, solvent/coal=3/1)

solvent	C (%)	H (%)	N (%)	others (%)	H/C
none	75.05	5.29	1.40	18.26	0.840
pyrene	76.25	5.43	1.53	16.75	0.849
ethyl- pyrene	82.24	4.93	1.80	11.03	0.714
hydro- pyrene	72.47	5.48	1.38	20.67	0.901

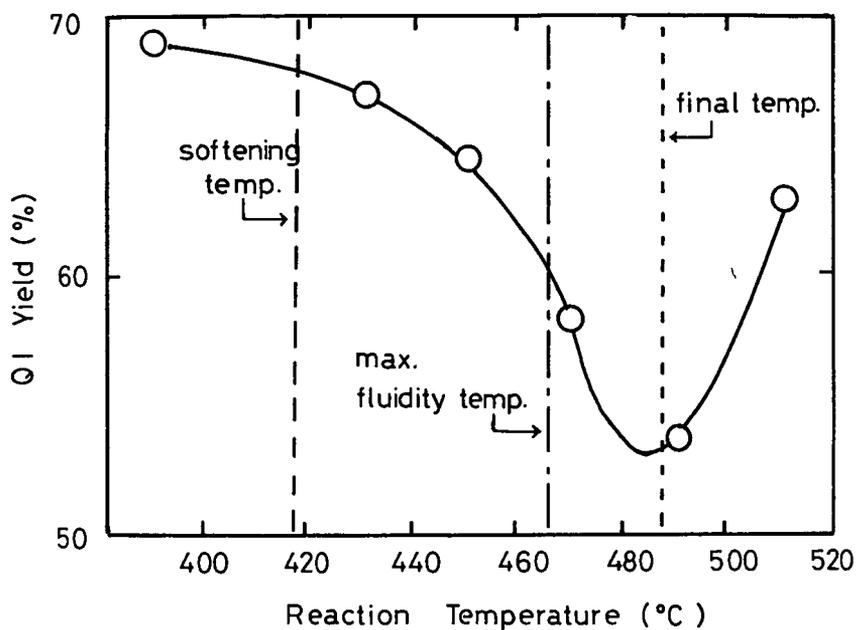


Fig.1 Effect of Reaction Temperature on Coal Liquefaction

(coal : Itmann, solvent : decacyclene
 solvent / coal = 3/1)

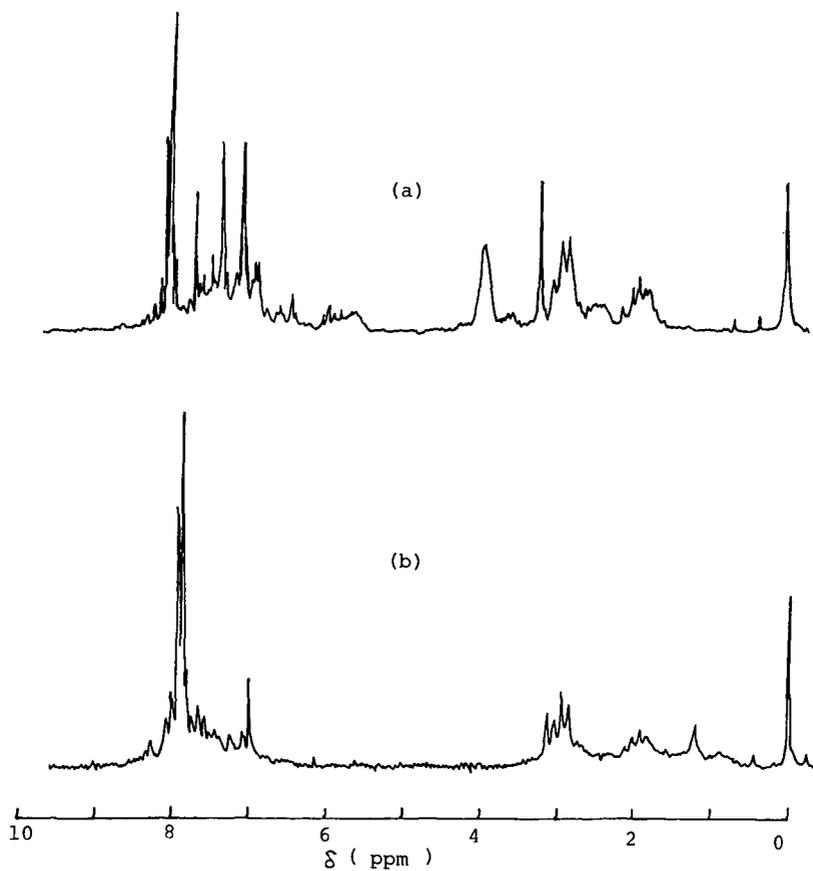


Fig. 2 NMR spectra of hydropyrene (a) and its BS derivative after the liquefaction (b). liquefaction conditions: see Table 4

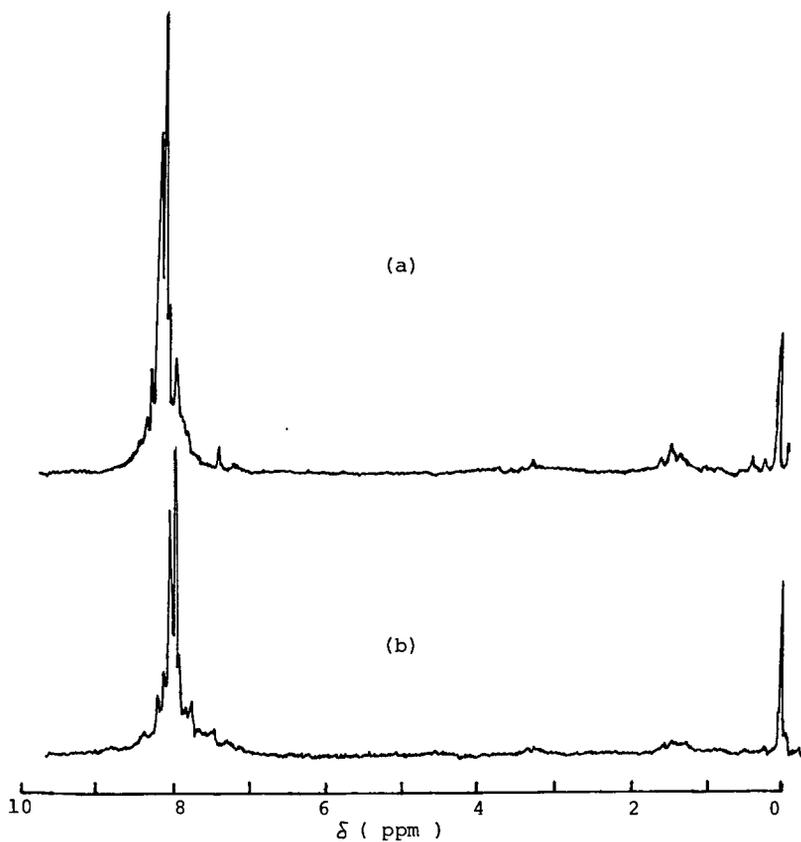


Fig. 3 NMR spectra of ethylpyrene (a) and its BS derivative after the liquefaction (b). liquefaction conditions: see Table 4.