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Refining of Coal Liquid —Structural Analysis of Hydrogenated SRC-II Distillates with HPLC-GC/MS—

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An SRC-II heavy distillate and twelve hydrogenated coal liquids derived thereof were separated into compound class fractions by an HPLC equipped with an amine column. Compound type analysis of each aromatic compound class was performed by MS to investigate changes in the composition of the coal liquefaction solvent as a function of the severity of hydrogenation reactions. The hydroaromatics yields of the solvent increased with increasing severity of hydrogenation at the expense of aromatic and polar compounds. The reaction conditions of 400°C, 30 min are suitable for hydrogenation of SRC-II heavy distillate from the viewpoint of a coal liquefaction solvent. It appears that production of organic gasses is consistent with the reduction of yields of alkyl side carbon and naphthenic rings, and production of light oil is in agreement with the decrease of a yield of aromatic rings.

1. Introduction

It is generally accepted that the most important role of the coal liquefaction solvent is to donate hydrogen enough to stabilize free radicals derived from coal pyrolysis. The reaction rate depends on the temperature, pressure, catalyst and quality of the solvent. A hydrogenated anthracene oil and/or tetralin, which have high hydrogen-donor properties, increase the reaction rate and also reduce the effect of pressure and catalyst on the reaction rate. The solvent is recovered from liquefied products by distillation in commercial scale processes. There are some commercial scale processes, which increase the hydrogen donor quality of recycle solvents. To improve the hydrogen-donor property of the solvent, a recycle solvent is often hydrogenated with a Co-Mo or a Ni-Mo catalyst. There must be suitable conditions for the hydrogenation of the solvent. For instance, tetralin is a hydrogen-donor, but decalin is not. Hydrogen-donor property of the solvent was deteriorated by isomerization and ring opening under highly severe conditions. It may, therefore, be thought that there is an optimum condition for hydrogenation of each solvent. It is highly important to understand the hydrogenation

reaction of the coal liquefaction solvent, for continuous operation of a commercial plant.

On the other hand, it is necessary to conduct a detailed and rapid analysis of the chemical composition of the hydrogenated solvent, for the purpose to understand the hydrogen-donor property of the solvent. Several methods were reported for the evaluation of average structural parameters of the solvent with NMR and IR^{1)~8)}. In the meanwhile, some studies on the complex organic structures of the solvent by MS analysis were performed by Swansiger *et al.*⁹⁾, Boduszynski *et al.*¹⁰⁾ and Niwa *et al.*¹¹⁾. In the authors' preceding papers^{12)~15)}, detailed 'compound type' analysis for coal hydrogenation liquids according to aromatic rings (*Ra*), naphthenic rings (*Rn*) and alkyl carbon (*Cal*) diagram parameters were reported, with the HPLC-MS procedure. Aromatic/hydroaromatic compound type and alkyl side chain carbon distribution of complex mixture oils were clarified, based on the separating behavior of HPLC and the type analyses according to *Z* value by MS.

Numerous studies have been reported on hydrogenation of model compounds; phenanthrene and pyrene. On the other hand, a few studies on changes in composition of the coal liquefaction solvent as a function of severity of hydrogenation have been performed. Green *et al.*¹⁶⁾ have reported on changes in chemical class-type fractions resulting from hydrotreatment of SRC-II distillates at different levels of severity. Boduszynski *et al.*¹⁷⁾

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have studied changes of fifty homologous series of aromatic and hydroaromatic hydrocarbons at mild and severe hydrogenation of SRC distillates. Rosal *et al.*¹⁸⁾ have studied the changes in composition during hydrogenation of an anthracene oil. Detailed information on how the structure of solvents changes with variations in severity of hydrogenation has been extremely limited.

This work was pursued to obtain detailed information on hydrogenation reactions affecting coal liquefaction solvent. Two kinds of hydrogenation experiments using SRC-II heavy distillate were performed, using a conventional petroleum hydrotreating catalyst. Hydrogenation products were analyzed by the HPLC-MS method to observe aromatic and hydroaromatic structural changes with severity of the reaction.

2. Experimental

2.1. Materials

A heavy fraction of SRC-II distillate, obtained

Table 1 General Properties of Feed

Sample kind		SRC-II heavy distillate	
Density	[g/ml]	1.077	
Viscosity	[cSt, 98.9°C]	3.83	
Flash point	[°C]	163	
Distillation		ASTM D-86	ASTM D-2887
	IBP	286	236
	5%	303	280
	10%	309	291
	20%	317	308
	30%	326	318
	40%	334	330
	50%	342	343
	60%	353	357
	70%	370	373
	80%		395
	90%		434
	95%		469
	EP	371	545
	Recovery, %	73	
Ash	[wt%]	0.08	
Carbon	[wt%]	89.1	
Hydrogen	[wt%]	7.7	
Nitrogen	[wt%]	1.1	
Sulfur	[wt%]	0.5	
Oxygen ^{a)}	[wt%]	1.6	
Pyridine insolubles	[wt%]	trace	
Benzene insolubles	[wt%]	trace	
<i>n</i> -Hexane insolubles	[wt%]	3.90	

a) by difference.

from the pilot plant of The Pittsburgh & Midway Coal Mining Company, was used here as a feed oil, and general properties are shown in Table 1. The boiling temperature range was from 236 to 545°C, at atmospheric and reduced pressures. A commercially available petroleum hydrotreating catalyst, consisting of cobalt, molybdenum and nickel supported on alumina, was used. Prior to use, the catalyst was pulverized by an agate mortar.

2.2. Hydrogenation

A 500 ml capacity conventional autoclave was used in the experimental hydrogenation. The feed oil (30 g) was placed in the autoclave with 3 g of the catalyst. A feed pressure of hydrogen was initially 10.1 MPa at room temperature. Experimental hydrogenation was conducted, subjected to the conditions shown in Table 2. There were two series of experimental hydrogenation in this study. In Experiment 1, the duration was 30 min and the reaction temperature was varied from 360 to 460°C. In Experiment 2, the temperature was fixed at 400°C and the duration was increased to 120 min. The reactor was heated at a rate of 3°C/min to the reaction temperature, and maintained for the duration. After the reaction, the autoclave was rapidly cooled to room temperature by blowing air. The gas in the autoclave was partially collected in a sampling bottle during purging, and the liquid product was recovered with benzene.

2.3. Separations

The scheme of the experiment is shown in Fig. 1. The SRC-II heavy distillate and products of hydrogenation were separated into solvent fractions and 'compound class' fractions. First, the liquid product was separated into oil (*n*-hexane soluble) and asphaltene (*n*-hexane insoluble-benzene soluble) by solvent extraction with a sequence of benzene and *n*-hexane. An oil fraction was distilled at atmospheric pressure, and a solvent fraction (>200°C) was obtained.

The solvent fractions were separated into six hydrocarbon fractions, called 'compound classes,' according to the number of aromatic rings confirmed by HPLC^{12),13)}. The liquid chromatograph used was a Jasco model Tri-Rotor equipped with a Zorbax NH₂ column (7.9 mm×250 mm, Du Pont Ltd.). These compound classes were paraf-

Table 2 Conditions of Hydrogenation

		Experiment-1	Experiment-2
Reaction temperature	[°C]	360, 380, 400, 410, 420, 430, 440, 460	400
Reaction time	[min]	30	15, 30, 60, 120
Oil feed	[g]	30	30
Catalyst	[g]	3	3
Hydrogen feed pressure	[MPa]	10.1	10.1

Fig. 1 Scheme of Experiments

fin (P), monoaromatics (M), naphthalene type diaromatics (D1), biphenyl type diaromatics (D2), tri- and/or tetra-aromatics (T), poly-aromatics and/or polar compounds (PP). A 50 mg sample was passed through the column, and the compound classes were separated according to the retention volume. Fractions were developed by sequential elution with a series of *n*-hexane and chloroform. The samples were injected repeatedly, and a total of 400 mg of the samples were recovered. After recovery of the elute by evaporation, the content of each compound class was determined by gravimetric method.

2. 4. Analyses

The analysis of the sampled gas, which included both hydrocarbon and inorganic gas, was performed with Shimadzu models GC-6A (FID, TCD), respectively. The volume of hydrogen consumed by the hydrogenation reaction was calculated from the pressure drop during the reaction, based on the ideal gas equation.

The distillation curves of the oil fractions were obtained by SD-GC method¹³⁾ with a Shimadzu model GC-D1. The calibration of the boiling point of the simulated distillation was based on *n*-paraffins (*n*-C10, C13, C15, C17, C21, C26, C30, C36, C40) as reagents. Also, elemental analysis was performed on the oil fractions. Determination of the carbon, hydrogen and nitrogen content was performed by the Analytical Center of Hokkaido University.

The low voltage ionization (10 eV) EI-MS technique was used to analyze the aromatic hydrocarbon compound classes (M, D1, D2 and T). The spectra were obtained at scanning intervals of 3 sec with a Hitachi model M-52 GC-MS system and were processed by a Hitachi model 002B computer system. The details of the EI-MS procedure were described previously¹³⁾⁻¹⁵⁾.

3. Results and Discussion

3. 1. Material Balance

The results of the experimental hydrogenation are shown in Table 3. In this table, the percentages of recovery are summarized as a function of severity of hydrogenation. It is clear that a major

Table 3 Overall Material Balances of Hydrogenation

Sample	Feed	Experiment-1								Experiment-2			
		H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9	H-10	H-11	H-12
Temperature [°C]		360	380	400	410	420	430	440	460	400	400	400	400
Time [min]		30	30	30	30	30	30	30	30	15	30	60	120
Feed [wt%]		100	100	100	100	100	100	100	100	100	100	100	100
Hydrogen consumption [wt%]		0.9	1.3	2.2	2.2	2.5	3.3	4.3	5.6	1.6	2.1	3.1	6.2
Organic gas [wt%]		0.8	0.9	2.1	3.6	2.8	7.2	9.8	19.7	1.2	1.9	4.7	5.0
Oil fraction													
Light oil (<200°C) [wt%]		1.0	1.4	2.4	3.6	2.7	3.5	4.6	3.4	2.0	3.2	4.5	3.7
Solvent (200°C<) [wt%]		96.1	93.5	89.4	86.5	80.2	81.3	74.7	62.7	89.2	89.3	79.3	74.4
Hexane insoluble [wt%]		3.9	0.4	0.5	0.1	0.0	0.2	0.3	0.5	0.3	0.1	0.0	0.1
Benzene insoluble [wt%]		trace	2.4	3.2	2.2	0.5	2.5	3.1	1.0	2.7	0.0	1.4	7.1
Recovery [wt%]		98.1	95.4	93.3	87.9	89.5	88.8	78.4	74.1	92.7	95.9	95.6	84.8
Loss [wt%]		1.9	4.6	6.7	12.1	10.5	11.2	21.6	25.9	7.3	4.1	4.4	15.2
H/C of oil fractions		1.03	1.03	1.06	1.06	1.07	1.04	0.98	0.88	1.07	1.08	1.07	1.09
Elementals of oil fractions [wt%]													
C		89.1	89.8	90.5	90.6	91.2	90.7	91.4	91.8	92.6	90.7	90.9	91.4
H		7.7	7.8	8.0	8.0	8.2	8.2	8.0	7.6	6.8	8.1	8.3	8.2
N		1.1	0.8	0.3	0.6	0.4	0.4	0.4	0.0	0.4	0.6	0.3	0.0
O ^{a)}		2.1	1.6	1.2	0.8	0.2	0.7	0.2	0.6	0.2	0.6	0.5	0.4

a) by difference.

Fig. 2 Hydrogen Consumption and Organic Gas

part of SRC-II distillate was oil and that there was a small amount of asphaltene. Obviously, no coking reaction occurred, because there was a small amount of asphaltene and benzene insoluble in the recovered material. The yield of solvent decreased with raise of the reaction temperature, and this tendency became pronounced over 430°C. The solvent obtained by the reaction at 460°C was close to 50% of the product's yield. Further, at this temperature, the amount of light oil having a boiling point below 200°C, organic gasses and loss increased. The loss was a part of the light oil fraction that escaped during distillation and recovery of the extraction solvent. It could be supposed that at over 430°C this gas and light oil were produced by a dealkylation reaction and a hydrocracking reaction.

The results of reactions at 400°C are also shown in Table 3. The yield of solvent fraction shows a slight decline as duration was increased. The yield of the solvent fraction obtained by the reaction after 120 min was about 74%. For recovery of the recycle solvent, it was proposed that a duration of reaction less than 30 min is suitable because it produces a small amount of gas and light oil.

3. 2. Hydrogen Consumption

The amounts of hydrogen and organic gasses (C₁-C₄) produced through the reaction were measured by GC analysis. The volume of gasses was calculated from the pressure and the volume of the autoclave based on the ideal gas equation. The hydrogen consumption and the organic gasses produced are shown in Fig. 2. In these figures, ΔH_2^* is the amount of hydrogen consumed mainly by the hydrogenation of aromatic rings. ΔH_2^* was calculated by subtracting the hydrogen consumed by the production of organic gasses from the total hydrogen consumed in the reaction. For these calculations, it is assumed that one mole of hydrogen gas is consumed to produce one mole of organic gas. Accordingly, ΔH_2^* was only consumed by hydrogenating aromatic rings, breaking naphthenic rings, denitrogenizing and deoxygen-

izing.

As shown in Fig. 2, the plots of ΔH_2^* corresponding to respective reaction temperatures formed a near straight line and it may be assumed that the hydrogenation reaction had occurred. On the other hand, the organic gasses produced increased slightly with rise of the reaction temperature under 420°C. Substantial production of organic gas, however, occurred at over 430°C. The yield of the organic gasses obtained at 460°C amounted to about 20%. It is also assumed that dealkylation and decomposition of naphthenic rings occurred at over 430°C. Shown also in Fig. 2, ΔH_2^* and organic gasses were produced in reactions after 15 to 120 min, at 400°C. ΔH_2^* increased linearly with extended duration of reaction, which is the same as in Experiment 1. On the other hand, the organic gasses varied from 4.7 wt% after 60 min, to 5.0 wt% after 120 min. Accordingly, it is assumed that the temperature limits dealkylation and decomposition. Obviously, olefin and carbon oxide were not produced in these experiments. It was seen that the amounts of propane and butane increased with a rise in the reaction temperature (the data is not included in this paper). But, it is noted that for the duration of reaction, the amount of organic gasses remains constant.

3. 3. Oil Fraction

The results of elemental analysis of the oil fraction (hexane soluble) are also shown in Table 3. It is noted that both nitrogen and oxygen were removed by hydrogenation and, therefore, a deheteroatom reaction occurred. It is thought that under 400°C, nitrogen compounds decomposed more easily than oxygen compounds. H/C atomic ratio of the oil fractions was slightly increased by a raising the reaction temperature to 430°C. On the other hand, it was reduced to below that of SRC-II distillate at over 430°C. The H/C atomic ratio was increased by hydrogenation in the low range of severity of reactions, and at greater range of severity, ring-opening reactions

Fig. 3 Distillation Curves of the Oil Fractions

Fig. 4 HPLC Separations of Solvent Fractions

and dealkylation occurred. A change in the amounts of alkyl side chains will be discussed later.

Distillation curves derived by SD-GC for feed and oil fractions are shown in Fig. 3. 90 wt% of SRC-II distillate is limited to a boiling range from 250 to 450°C. The distillation curves shifted to lower temperatures with increase of severity of reaction. The boiling point of 50% oil fraction distillation was at 420°C, which was 40°C lower than that of SRC-II distillate. It has been found that the shapes of these distillation curves, of the oil fraction derived at higher reaction temperature, vary incrementally. Hence, the removal of alkyl groups occurred at higher temperatures.

3. 4. HPLC Fractions

Solvent fractions (>200°C) of SRC-II distillate and its hydrogenated products are separated into six compound class fractions by an HPLC equipped with an amine column. The compound class contents of solvent fractions determined by gravimetry are shown in Fig. 4. P, M, D1, D2, T

and PP stand for paraffin, monoaromatics, naphthalene type diaromatics, biphenyl type diaromatics, tri/tetra aromatics, and poly/polar compounds, respectively. The compound classes are indicated along with the feed. The yield of PP definitely decreased with raise of temperature and extended duration of reaction. It is obvious that a decrease of T and an increase of M, D1 and D2 are brought about by hydrogenation of aromatic rings of tri/tetra-aromatics. All compound class fractions, however, decreased at over 430°C, owing to reduced solvent fractions. The reason for this decrease has been explained by a naphthenic ring opening reaction and dealkylation. It should be noted, however, that P did not increase, significantly. Judging from this fact, it is apparent that a high degree of hydrogenation of aromatic rings did not occur. In contrast with the Experiment 1, PP decreased slightly from 30 to 120 min in Experiment 2. We believe that a higher temperature will be necessary to reduce

heteroatom compounds completely.

3. 5. Compound Type

Compound type analyses of the aromatic compound classes (M, D1, D2, T) separated by HPLC were carried out by EI-MS. Molecular ions without fragmentation were detected by the LV (10 eV)-EI method¹³⁾. Consequently, the m/z peaks are the molecular weights. The molecular weight distribution measured included odd mass numbers because of the presence of isotopes. In this study, the odd mass numbers were intentionally neglected to simplify the mass spectrum. The identification of compound type was performed to assign the Z value by selecting the molecular ion peaks belonging to the same compound type. In the cited condition of hydrogenation, it was thought that there were no olefins. The structural assignment of components in the solvents was carried out on the basis of a combination of HPLC separation characteristics and compound type analyses by MS¹³⁾. The respective m/z peaks correspond to the mass number of the molecules and the m/z distribution represents the profile of molecular weight distribution. The identification of compound types by mass was performed to assign the Z value by selecting the molecular ion peaks belonging to the same compound type. These peaks appear at 14 mass number intervals, and a homologous series of alkylated aromatic compounds differing by 14 mass units (equivalent to a CH_2 group) show an increase of the carbon number of alkyl side chains (*Cal*).

The Z value of a component, which indicates hydrogen deficiency compared with the n -paraffin with the same carbon number, is related to the aromatic carbon number (Ca) and total ring number (Rt), representing the sum of aromatic (Ra) and naphthenic rings (Rn), in the Eq. (1):

$$Z = 2 - (Ca + 2Rt) \quad (1)$$

Compound class separation by HPLC specifies a limited range of Z values (e.g. Fr-P, $Z \leq +2$; Fr-M, $Z \leq -6$; Fr-D1, $Z \leq -12$; Fr-D2, $Z \leq -14$; Fr-T, $Z \leq -18$), because fractions at a given elution volume contain specific aromatic ring classes (aromatic carbon number Ca). Then the real Z value can easily be chosen from the apparent Z values, differing by intervals of 14. Real Z values are further confirmed by the following evidence. The molecular weights of bare aromatic/hydroaromatic ring systems (MM) are compared with the lightest compound belonging to the homologous series. When the value of MM for a specific ring system agree with the molecular

Fig. 5 *Ra-Rn-Cal* Diagram of SRC-II Distillate

weight at the lowest end of the m/z distribution for the corresponding Z series, the aromatic/hydroaromatic ring system can be assigned this Z value.

The *Ra-Rn-Cal* diagram¹⁴⁾ of the SRC-II distillate is shown in Fig. 5. SRC-II distillate was mainly composed of D1 and T, especially acenaphthenes ($Z = -14$), anthracenes ($Z = -18$) and pyrenes ($Z = -22$). These three components made up over 40 wt% of the SRC-II distillate. It has been found that the average molecular weights of all compound class were almost 200 regardless of the bare aromatic/hydroaromatic ring structure, and whether the naphthenic ring numbers were 1 or 2. For the fraction D1, $Z = -12$ only includes naphthalenes but $Z = -14$ includes acenaphthenes (minimum molecular weight; 154) and/or tetrahydro-anthracenes (minimum molecular weight; 182). As can be seen in this figure, the distribution of $Z = -14$ has a discontinuity at $m/z = 182$, representing the presence of tetrahydro-anthracenes. It is difficult to separate C_2 -acenaphthene from tetrahydro-anthracene in the peak of $m/z = 184$ only by the HPLC-MS method. Ishikawa *et al.*¹⁹⁾ reported that it is possible to distinguish C_2 -phenanthrene from tetrahydro-

pyrene assuming that a distribution of alkyl carbons of one aromatic/hydroaromatic ring system compound is smooth. In this study, acenaphthenes and tetrahydro-anthracenes were distinguished by a distribution of alkyl side chains. It was assumed that the *Cal* distribution of the acenaphthenes decreases from the maximum of C₁-acenaphthene in a constant rate. Contents of acenaphthenes and tetrahydro-anthracenes were calculated as follows;

$$m = 1.1 \quad (2)$$

$$I_{n+1,ac} = I_{n,ac} / m \quad (n = 1, 2, 3, \dots) \quad (3)$$

$$I_{n-1,4H-an} = I_{n+1} - I_{n+1,ac} \quad (4)$$

where: $I_{n,ac}$ = wt% of C_n-acenaphthene; $I_{n-1,4H-an}$ = wt% of C_{n-1} tetrahydro-anthracene; I_{n+1} = wt% of a molecule with $m/z = 154 + 14 \times (n+1)$.

Then a correlation coefficient of a linear regression analysis of the *Cal* distribution of tetrahydro-anthracene was calculated. The same calculations were performed from $m=1.2$ to $m=5.0$ by 0.1 step. The *Cal* distributions of acenaphthene and tetrahydro-anthracene were finally determined so as to give the best correlation coefficient. Shown in Fig. 5 are break lines exhibiting different ring structures which have the same *Z* number.

Detailed compound type distributions could be understood from those compound type analyses, and then changes of compound contents with severity of reaction were recognized from several view points. A discussion was conducted on changes of major chemical components, total ring numbers and hydrogen numbers added to

aromatic/hydroaromatic ring system.

Shown in Fig. 6 are the major components of SRC-II heavy distillate and hydrogenated coal liquids derived thereof in terms of reaction temperatures. SRC-II heavy distillate contained mainly pyrene, anthracene, tetrahydro-anthracene, acenaphthene and naphthalene. For the naphthalenes, naphthalene decreased and tetralin increased significantly up to 420°C, but at 460°C, naphthalene increased and tetralin decreased. The total amount of naphthalenes increased gradually at 420 and 460°C. The anthracenes included dihydro-, tetrahydro-, octahydro- and anthracene, and the pyrenes included dihydro-, tetrahydro-, hexahydro- and pyrene. It was found that raise of reaction temperature caused anthracene and pyrene to decrease, and on the other hand, dihydro-, hexahydro-anthracene and all the hydro-pyrenes increased, and later on decreased. The total amount of anthracenes and pyrenes increased at 380°C, and later on decreased.

Many studies were reported on hydrogenation reactions of poly fused aromatics. Shabtai *et al.*²⁰⁾ have reported that 9,10-dihydro-phenanthrene and 1,2,3,4-tetrahydro-phenanthrene were primary products. Perhydro-phenanthrene was formed, only slowly, presumably because of the sterically hindered central ring of its precursor, sym-octahydro-phenanthrene. Wu *et al.*²¹⁾ have also reported that the saturated outer ring cracked at temperatures exceeding 427°C, forming mostly *n*-butyltetralins. In this study, the same tendency was observed with the complicated aromatic and hydroaromatic mixtures by detailed compound type analyses using HPLC-MS method. A scheme of the hydrotreating reaction is shown in Fig. 7. It was clear, that at 380°C hydroaromatic

Fig. 6 Distributions of Compound Type

Fig. 7 Possible Reaction Paths

compounds greatly increase with hydrogenation of aromatic rings, and that total aromatic and hydroaromatic compounds increase with deheteroatom reaction of polar components. At 420 and 460°C, hydroaromatics almost always decreased and naphthalenes rapidly increased, because of naphthenic ring opening and dealkylation.

By continuing hydrogenation, pyrene becomes dihydro, tetrahydro, hexahydro, decahydro, hexadecahydro-pyrene, but the total ring number (aromatic and naphthenic rings) is constant at 4 rings through the entire reaction. Stephens *et al.*²²⁾ have found that for hydrogenation of pyrene at 348°C and 1250 psig the hydrogenated species with the largest concentration is dihydro-pyrene followed by hexahydro-pyrene and tetrahydro-pyrene. For these experiments, the concentration of decahydro- and perhydro-pyrene was less than 1% of the product mixture. Shown in Fig. 8 are the changes in the hydropyrene contents for more detailed reaction temperatures. Dihydro-pyrene, tetrahydro-pyrene, hexahydro-pyrene were most abundant at 380, 410, 420°C, respectively. It is clear that the preferable hydrogenation temperature of pyrenes as coal liquefaction solvent is thought to be from 410 to 420°C, because of its more abundant hydroaromatic content. At over 430°C, hexahydro-pyrene decreased remarkably and the total amount of pyrenes also decreased. Dehydrogenation of hydroaromatics did not cause changes in the total amount of pyrenes. This is, therefore, one evidence of ring opening and dealkylation. This is consistent in the production of large amounts of organic gasses.

A study of the changes of aromatics, hydroaromatics, poly aromatics and polar compound, paraffin and light oil (>200°C) is shown in Fig. 9. Up to 380°C, the increase of hydroaromatics is greater with consumption of aromatics. On the other hand, at over 440°C, hydroaromatics markedly decrease, while light oil and aromatics

Fig. 8 Contents of Pyrene and Hydro-pyrenes

Fig. 9 Contents of Hydroaromatics, Aromatics, Poly/polar Compound, Paraffin and Light Oil, according to Reaction Temperature

increase. The same changes of chemical components such as pyrenes were observed in the whole solvent. Since the main purpose of hydrogenation of the solvent is to optimize conversion of aromatics to hydroaromatics that are potential hydrogen donor, the optimum reaction temperature is thought to be 420°C. A light oil yield is about 13 wt% at 420°C, however, and then an excess yield of light oil is undesirable for recycle solvents. It is clear, therefore, that the optimum reaction temperature will be at 400°C.

To determine the optimum duration of a reaction, reaction temperature was held constant at 400°C in Experiment-2. Shown in Fig. 10 are the changes in the yield of hydroaromatics, aromatics, PP, P and light oil in terms of reaction duration. Over 60 min hydroaromatics decreases and light oil and gas increase. In other words, extended reaction decreases the solvent yield. It is recognized in this experiment that the optimum hydrogenation conditions for SRC-II heavy distillate are at 400°C for 30 min from the viewpoint of the economy of coal liquefaction solvent.

3. 6. Distribution of Ca, Cn and Cal in the Solvent Fraction

The distribution of compound classes separated by HPLC and the distribution of compound types

Fig. 10 Contents of Hydroaromatics, Aromatics, Poly/polar Compound, Paraffin and Light Oil, according to Reaction Time

assigned by MS were described above. From the analysis of the chemical structures, the distribution of the alkyl carbon number was discussed. Average carbon number of alkyl side chains was calculated by the equation below;

$$Cal(av.) = \frac{\sum_i Cal_i \times Mol_i}{\sum_i Mol_i} \quad (5)$$

where: $Cal(av.)$ =average alkyl carbon number per molecule; i = i molecule, Cal =alkyl carbon number of each molecule; Mol =mol percent of each molecule based on the solvent fraction.

The average alkyl carbon number is plotted as a function of the reaction temperature and duration (Fig. 11). For feed, naphthalenes and acenaphthenes have an alkyl carbon number of 3.5. Biphenyls and fluorenes, anthracenes and pyrenes have an alkyl carbon number close to 1.0. With a rise of reaction temperature the $Cal(av.)$ of the naphthalenes and acenaphthenes decreased by a value of 2.0 while that of the anthracenes and pyrenes decreased by a value of 0.5. The $Cal(av.)$ of biphenyls and fluorenes firstly increased and decreased to become in the same as the SRC-II. This was caused by a mistake in the assignment of mass spectra or by ring opening reactions. The $Cal(av.)$ of most of the compounds decreased with

a rise in temperature. In this figure the relationship between $Cal(av.)$ and the duration of reaction is also shown. At 120 min the $Cal(av.)$ of naphthalenes and acenaphthenes decreased by a value of 2.0 while that of the anthracenes and pyrenes decreased by a value of 0.3.

The greater the reaction severity (temperature or duration), the less the $Cal(av.)$. This represents dealkylation. It can be assumed that organic gasses were thought to be derived from the alkyl side chains. The calculations of the weight ratios of the alkyl chains were, therefore, performed. For this purpose it was necessary to calculate the weight percentage of Ca , Cn and Cal . Bare aromatic/hydroaromatic ring systems (Ra and Rn) can be decided as shown in Fig. 5 by the compound type analyses. The weight percentages of Ca , Cn and Cal of aromatic compound classes based on the solvent fractions were, therefore, calculated using the equation;

$$Wal = \sum_i \frac{Cal_i \times 14}{MW_i} \times wt\%i \quad (6)$$

$$Wn = \sum_i \frac{Cn_i \times 14}{MW_i} \times wt\%i \quad (7)$$

$$Wa = 100 - (P + PP) - (Wal + Wn) \quad (8)$$

where: Wal , Wn , Wa =weight percent of alkyl side chains, naphthenic rings, aromatic rings; i = i molecule; Cal =alkyl carbon number; Cn =naphthenic carbon number; MW =molecular weight of each molecule; P =wt% of paraffin; PP =wt% of poly/polar compound.

It is difficult to determine Wa , Wn and Wal of PP fractions directly, therefore it is assumed that those of the PP fractions are equal to those of the hydroaromatic fractions. Total yields of Cal , Cn and Ca (Wal^* , Wn^* and Wa^*) were calculated as below;

Fig. 11 The Average Alkyl Carbon Number

$$Wal^* = Wal + \frac{Wal}{100 - (P + PP)} \times (PP - Het) \times wt\% \quad (9)$$

$$Wn^* = Wn + \frac{Wn}{100 - (P + PP)} \times (PP - Het) \times wt\% \quad (10)$$

$$Wa^* = Wa + \frac{Wa}{100 - (P + PP)} \times (PP - Het) \times wt\% \quad (11)$$

where: P , PP =wt% of paraffin, poly/polar compound; Het =wt% of oxygen and nitrogen calculated by elemental analysis; $wt\%$ =yield of solvent fraction.

Weight percent of Ca , Cn and Cal of each solvent fraction is shown in **Fig. 12**. The yields of Ca , Cn and Cal in SRC-II heavy distillate are 67.5, 11.0 and 9.0 wt% and those in the solvent fraction derived from it at 460°C are 39.6, 4.6, 3.7 wt%, respectively. It is clear that each yield of Ca , Cn and Cal decrease significantly. As shown in **Fig. 7**, the decreases of

Ca , Cn and Cal should be converted to the organic gasses and the light oil. When naphthenic ring openings only occur, it has been observed that Cal increases in proportion to the decrease of Cn . Cal of all hydrogenated solvent fractions, however, are less than that of SRC-II distillate in this study. It is thought, therefore, that naphthenic ring openings are always followed by dealkylation. It is reasonable to believe that most parts of the decreases of Cn and Cal is converted into organic gasses. The decrease of Ca , Cn and Cal was supposed to have shifted to the organic gasses and the light oil fraction.

Shown in **Fig. 13** are the decrease of Ca , Cn and Cal (ΔCa , ΔCn and ΔCal) vs. the production of light oil and organic gasses. In Experiment-1, at temperature below 420°C, Ca and Cal only decrease, and at over 440°C, Cn also decreases. On the other hand, in Experiment-2, when duration is over 60 min, Cn decreases. It is generally accepted that there are several pathways of Ca , Cn and Cal , shifted to the light oil and organic gasses, as shown in **Fig. 7**. It is also considered that Ca , Cn and Cal decrease by

Fig. 12 The Yields of Ra , Rn and Cal for Solvent Fractions

Fig. 13 Organic Gas and Light Oil vs. ΔCal , ΔCn and ΔCa

hydrogenation, naphthenic ring opening reaction and dealkylation, respectively. As shown in Fig. 13, the decrease of *Cn* and *Cal* are in good agreement with the production of organic gasses. On the other hand, the decrease of *Ca* is in agreement with the production of light oil. We have come to the conclusion, therefore, that the organic gasses are produced from alkyl carbons and naphthenic rings, and the light oil is shifted from aromatics that have lower boiling points by dealkylation and breaking of naphthenic rings.

4. Conclusions

This study of hydrogenation of SRC-II heavy distillate over conventional Co-Mo-Ni/Al₂O₃ catalyst at varying severity of reactions led us to the following conclusions:

- (1) The detailed chemical structures of hydrogenated products were revealed by the HPLC-MS analytical method. Using this method, distributions of aromatics, hydroaromatics and alkyl carbon in complicated aromatic and hydroaromatic compounds mixtures could be evaluated.
- (2) The reaction condition of 400°C, 30 min is suitable for the hydrogenation of SRC-II heavy distillate, from the viewpoint of the coal liquefaction solvent. At these conditions, the content of hydroaromatics as hydrogen donor components and recovery of the solvent fraction were maximized.
- (3) It appears, that production of organic gasses is consistent with the reduction of alkyl side carbon and naphthenic rings, and production of light oil is in agreement with the decrease of aromatic rings.

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要 旨

石炭液化油の改質
—HPLC-GC/MS による水素化 SRC-II 重質留分の構造解析—

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SRC-II 重質留分および水素化反応の過酷度の異なる 12 種の水素化生成油を, アミン系カラムを装着した高速液体クロマトグラフィーにより芳香環数毎の化合物クラスに分離した。ついで, 水素化反応の過酷度と生成油の石炭液化用溶剤留分の化学組成変化の関係を調べるため, 各々の芳香族化合物クラスについて質量分析計による Z 数別化合物タイプ分析を実施した。水素化反応の過酷度が増すに従い溶剤留分中の部分水素化芳

香族収率が増加し, 芳香族収率および極性化合物収率は減少した。SRC-II の水素化は部分水素化芳香族を最大にすること, および溶剤留分の確保という観点から, 400°C, 30 分が最適であった。

また見かけ上, 生成有機ガス量はナフテン環およびアルキル側鎖減少量と, 軽質油生成量は芳香環減少量とよく一致した。

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Keywords

Coal liquid, Hydrogenation, Composition, HPLC-GC/MS method