The Hydrocracking of Solvent Refined Coals over Molten Salt Catalysts[1)]

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The hydrocracking of Yūbari SRC and Tempoku SRC over $ZnCl_2/CuCl$ or $ZnCl_2$ molten salt was examined at 350 or 400 °C for 3 h in a batch autoclave system. The reactivity of SRC under the hydrocracking conditions with the molten salts was estimated mainly by comparison with the results obtained in the study using a variety of polynuclear aromatic hydrocarbons. The presence of hetero atoms (especially, the hydroxyl group) in SRC may be supposed to play an important role in this hydrocracking using molten salts. In addition, the average structures of SRC, according to the CAMSC method, are offered, and the usefulness is examined from the point of view of the reactivity of SRC in the presence of molten salts.

Although the structure of coal has not been appreciably clarified in detail, some structural analyses suggest that coal is a natural polymer consisting mainly of condensed rings. Consequently, in order to obtain liquid fuels from coal, it is necessary to decompose the condensed rings in addition to effecting the scission of the bonds between structural units. From this standpoint, the hydrocracking of model substances of coal (that is, a heavy anthracene oil[2)] and polynuclear aromatic hydrocarbons[3)]) over molten salts was investigated. On the basis of detailed product analyses, $ZnCl_2/CuCl$ molten salt was found to be a superior hydrocracking catalyst for coal-related substances. In this paper, we will apply this catalyst system to the hydrocracking of solvent refined coals (SRC), which are considered to be representative of some of structural units of coal, and will clarify the catalytic action for SRC in comparison with that of $ZnCl_2$.

Experimental

The NMR spectra were recorded on a JEOL JNM-PS-100 spectrometer, using tetramethylsilane as the internal standard. $CDCl_3$ was used as the solvent for all the substances. The GLC analyses were performed on a Shimadzu GC-3AH apparatus for gaseous products and on a GC-4BPTF apparatus for liquid and solid products. The GC-MS spectra were taken with a Hitachi RMU-6MG spectrometer at 20 eV connected with a Hitachi M 5201 apparatus using a 3 m×3 mm column of 5% Silicone OV-1 on Uniport KS. The average molecular weights were determined with a Hitachi-Perkin Elmer 115 vapour-pressure osmometer in chloroform, with bibenzyl as the calibration standard. The zinc chloride and copper(I) chloride were obtained from Nakarai Chemicals, Ltd.

Preparation of SRC. The experiments were carried out in a 500 ml SUS 32 autoclave; 50 g of Yūbari coal (−200 mesh) and 100 ml of tetralin were placed in it, and hydrogen was added up to a pressure of 80 kg/cm^2. The rate of the temperature rise was controlled to about 3 °C/min up to 400 °C, after which the temperature was held for 3 h. The autoclave was shaken in a horizontal direction (70 strokes/min). No attempts were made to maintain the hydrogen pressure at a constant level during the reaction. After the system had been cooled to room temperature, the gases were collected in a gas holder and analyzed by GLC (60—80 mesh silica-gel column, 3 m×3 mm, TCD, 120 °C, N_2 carrier). The product was filtered, and the residue was extracted with benzene by means of a Soxhlet extractor. The above procedure was repeated 3 times. The benzene and tetralin were then removed from the combined mixture of filtrates and extracted solutions. The yield of Yūbari SRC was 90 g. In the case of the Tempoku coal, the reaction time was 30 min and the autoclave experiment was repeated 4 times. The yield of Tempoku SRC was 70 g. All the properties of coals and their SRC are shown in Table 1.

Hydrocracking of SRC. A stainless-steel vessel containing 8 g of SRC and the catalyst was placed in a SUS 32 autoclave with a capacity of 200 ml. The air in the autoclave was replaced by hydrogen, and then the system was filled with hydrogen to 100 kg/cm^2; thereafter, the autoclave was heated up to the desired temperature. The time taken to reach the stage was from 60—70 min. The reaction system shaken in a horizontal direction (68 strokes/min) was maintained at the reaction temperature for 3 h. No attempts were made to maintain the hydrogen pressure at a constant level during the reaction. After the system had been cooled to room temperature, the gases were collected in a gas holder and analyzed by GC. The liquid and solid products were extracted with pentane by means of a Soxhlet extractor, and the residues were subjected to benzene extraction. Moreover, the pentane extracts were separated into two fractions (PSL and PSH) by means of vacuum distillation (−190 °C/3 mmHg). The lighter fraction (PSL) was analyzed by GC (4.5 m×3 mm packed with 20% SE-30 on Uniport B 60—80 mesh, programmed from 30—270 °C, 5 °C/min, TCD, H_2 carrier).

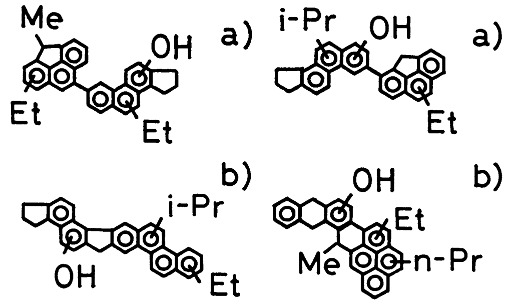
TABLE 1. PROPERTIES OF COAL AND SRC

	Ultimate analyses$^{a)}$				Structural parameters$^{b)}$			
	H	C	N	O$^{c)}$	f_a	σ	Hau/Ca	mol wt$^{d)}$
Yūbari coal	6.0	86.1	2.1	5.8	—	—	—	—
Yūbari SRC	6.4	88.9	2.2	2.6	0.73	0.28	0.63	506
Tempoku coal	5.4	69.8	1.9	22.9	—	—	—	—
Tempoku SRC	6.3	87.2	1.7	4.8	0.76	0.26	0.69	340

a) D.a.f. b) By Brown-Ladner's method.[5)] c) Difference. d) In $CHCl_3$.

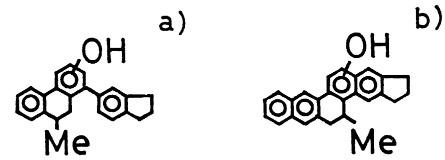
Results and Discussion

Average Structure of SRC. The SRC consists of large numbers of compounds possessing different molecular weights; moreover, the constituents cannot be determined. However, as these compounds may be supposed to consist of similar types of compounds, the concept of the average structure has been employed for a variety of structural analyses. In this investigation, the average structure of the SRC was estimated according to the CAMSC method proposed by Oka *et al.*[4] This CAMSC method attempts to represent the average structure as a combination of aromatic and aliphatic groups, in accordance with the input data represented as integral numbers based on the experimental data from the elemental, NMR, and molecular-weight analyses. The oxygen atoms were considered as a phenolic OH, as an ether, or as a carbonyl group; on the other hand, the sulfur and nitrogen atoms were not considered. The determination of the average structures has been carried out by means of a computer program prepared according to the flow chart and the classification method of Oka *et al.* The results for Yūbari SRC and Tempoku SRC are shown in Figs. 1 and 2 respectively. It may be supposed to be unreasonable to represent the average structure by a single structure. It is preferable to divide the average structures obtained by the CAMSC method broadly into two types, that is, the type containing a direct bond between two aromatic rings (a) and the type containing a large ring structure (b).



Experimental result: $H_\alpha=9.4$, $H_0=10.5$, $H_{al}=19.9$, $H_{ar}=12.2$, $C_{ar}=28.0$, $C_{al}=9.4$, (OH=0.82).
Input data for CAMSC: $H_\alpha=9$, $H_0=11$, $H_{al}=20$, $H_{ar}=12$, $C_{ar}=28$, $C_{al}=9$, (OH=1).

Fig. 1. Average structure of Yūbari SRC by CAMSC.



Experimental result: $H_\alpha=6.9$, $H_0=5.0$, $H_{al}=11.9$, $H_{ar}=9.6$, $C_{ar}=19.0$, $C_{al}=5.7$, (OH=0.79).
Input data for CAMSC: a) $H_\alpha=7$, $H_0=5$, $H_{al}=12$, $H_{ar}=10$, $C_{ar}=18$, $C_{al}=6$, (OH=1). b) $C_{ar}=20$.

Fig. 2. Average structure of Tempoku SRC by CAMSC.

Hydrocracking of SRC. The SRC, which underwent a thermal scission of the bonds between structural units and stabilization by hydrogen transfer from tetralin, is the primary hydrocracked product of coal and may be regarded as representative some of the structural units of coal. The difference in the structural parameters calculated using Brown-Ladner's method[5] and the average molecular weight between Yūbari SRC and Tempoku SRC suggest that the original structure of coal considerably influences the structure of SRC. On the other hand, as the SRC is molten at this reaction temperature and becomes a homogeneous liquid, the catalytic action of the molten salts on the SRC may be expected to be similar to that on polynuclear aromatic hydrocarbons (PAH). With these facts in view, the SRC was selected as a kind of model substance of coal.

The results of the hydrocracking of the SRC are shown in Table 2. The products were classified into Gas, PSL, PSH, and BS. The GC charts of the hydrocracked products (PSL) of Yūbari SRC are shown in Figs. 3 and 4. The products listed in Figs. 3 and 4 were identified by means of GC-MS and by reference to the GC charts of the hydrocracked products of PAH.[3] The structural parameters, the average molecular weight, and the nitrogen content of the hydrocracked products of Yūbari SRC are shown in Table 3. The catalytic action of molten salts will now be discussed on the basis of the product distribution shown in Table 2 and the properties shown in Table 3.

TABLE 2. HYDROCRACKING OF YŪBARI SRC[a)]

	Run No.								
	1	2	3	4	5	6	7	8	9[b)]
Catalyst	$ZnCl_2$	$ZnCl_2$/CuCl	—	$ZnCl_2$	$ZnCl_2$/CuCl	$ZnCl_2$	$ZnCl_2$/CuCl	$ZnCl_2$/CuCl	$ZnCl_2$/CuCl
(mol: mol)		(60:40)			(60:40)		(90:10)	(60:40)	(60:40)
Catalyst/Feed (wt/wt)	0.1	0.1	—	0.1	0.1	1	1	1	1
Reaction temp (°C)	350	350	400	400	400	400	400	400	400
Gas	2	3	9	13	14	25	29	36	40
PSL	2	2	7	16	19	32	32	24	34
PSH	25	34	19	39	41	28	22	13	8
BS	48	42	61	17	14	1	1	1	1

Reaction conditions: initial hydrogen pressure, 100 kg/cm^2; reaction time, 3h; a) Yūbari SRC consists of 22% of PS, 61% of BS, and 17% of BIS. b) Tempoku SRC.

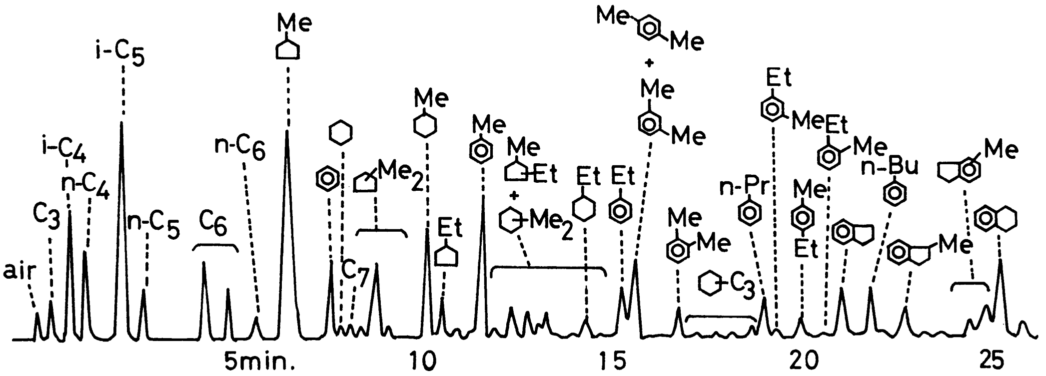


Fig. 3. Gas chromatogram of hydrocracked products of Yūbari SRC (Part 1).

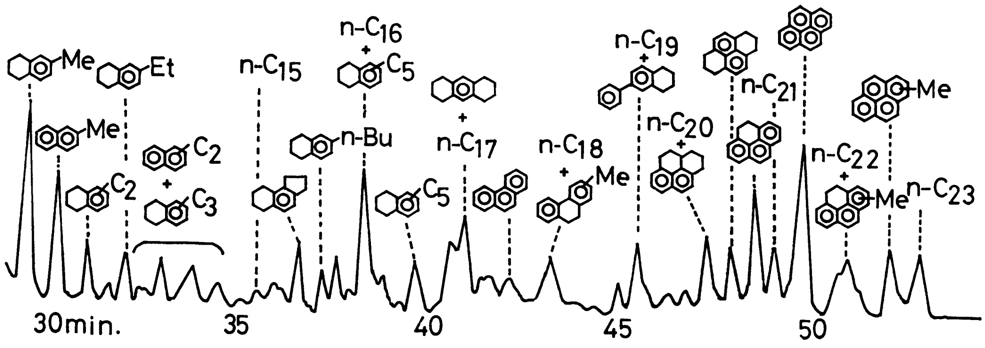


Fig. 4. Gas chromatogram of hydrocracked products of Yūbari SRC (Part 2).

TABLE 3. PROPERTIES OF HYDROCRACKED PRODUCTS OF YŪBARI SRC

Sample	f_a	Hau/Ca	mol wt	N(%)
SRC-PS	0.61	0.78	284	2.12
1-PSH[a]	0.55	0.82	275	0.85
2-PSH	0.52	0.82	299	0.71
3-PSH	0.59	0.79	288	1.66
4-PSH	0.57	0.79	285	0.57
5-PSH	0.57	0.79	283	0.64
6-PSH	0.61	0.71	273	—
7-PSH	0.63	0.73	257	—
8-PSH	0.60	0.70	268	—
SRC-BS	0.76	0.63	511	2.40
1-BS	0.66	0.66	521	1.44
2-BS	0.65	0.69	537	1.14
3-BS	0.75	0.57	487	2.29
4-BS	0.74	0.58	376	1.05
5-BS	0.75	0.57	403	0.98

a) 1-PSH represents PSH of Run 1.

The reaction conditions of Runs 6—8 were established by considering the case of PAH.[3] As the yield of gas increases with an increase in the content of CuCl, the cracking ability of the catalyst is considered to be increased by addition of CuCl; however, the undesirable recombination of fragments also seems to be accelerated.[6] Accordingly, milder conditions than the conditions in Runs 6—8 are considered to be necessary for the hydrocracking of SRC. The quantity of the catalyst was decreased in Runs 3—5, and the reaction temperature was lowered in Runs 1 and 2.

The average molecular weights and the structural parameters of PSH in Runs 4 and 5 are similar to those in Run 3. On the other hand, the average molecular weights of BS in Runs 4 and 5 are less than that in Run 3. In a comparison of the product distributions in Runs 3—5, the increase in the amounts of Gas, PSL, and PSH, the decrease in the amounts of BS, and the lowering of the average molecular weight of BS strongly demonstrate that these molten salts are remarkably effective for the hydrocracking of Yūbari SRC. In addition, denitrogenation was found to be accelerated by the catalytic action of the molten salts.

In the hydrocracking of PAH at 400 °C, the catalytic activity of $ZnCl_2/CuCl$ molten salt had been found to be greatly higher than that of $ZnCl_2$ molten salt.[3] However, in the hydrocracking of SRC at 400 °C over these molten salt catalysts, the difference in the catalytic activity was not so remarkable. In comparison with the PAH examined in a previous paper,[3] SRC possesses a higher average molecular weight and hetero atoms. These factors may be supposed to reduce the difference in the catalytic activity of these two catalyst systems. Morita *et al.*[8] has reported that the hydroxyl group attached to the aromatic ring facilitates the hydrocracking of the aromatic ring. The results of the hydrocracking of naphthalene and 2-naphthol over the molten salts shown in Table 4 support this consideration, and the hydroxyl group[9] existing in SRC are supposed to facilitate the hydrocracking of SRC. Accordingly, hydroxyl groups are anticipated to be important in reducing the difference in the catalytic activity of these two catalysts.

Table 4. Influence of OH substituent on the product distribution

Feed		Naphthalene		2-Naphthol	
Catalyst (mol: mol)		$ZnCl_2$	$ZnCl_2/CuCl$ (60:40)	$ZnCl_2$	$ZnCl_2/CuCl$ (60:40)
Products (wt %)	C_1–C_4 gases	3.4	45.7	26.3	56.0
	C_5–C_7 alkanes	—	3.7	1.1	2.9
	cycloalkanes	0.1	1.5	3.2	3.1
	monocyclic aromatics	2.0	46.4	18.7	33.7
	indans and tetralins	16.0	1.7	31.2	3.0
	naphthalene	77.9	0.5	9.3	0.7
	higher boiling products	0.7	—	10.3	0.6

Reaction conditions: initial hydrogen pressure, 100 kg/cm^2; reaction time, 3h; reaction temperature, 400 °C. *Catalyst/Feed = 1 (mol/mol).*

At 350 °C (Runs 1 and 2), a difference in these two catalysts was observed in the yields of PSH and BS.

In the hydrocracking of PAH, it was clarified that the product distribution is dependent upon the original structure and that the methyl groups in the feed remarkably affect the compositions of monocyclic aromatics and of gases.[10] Based on the results obtained in the hydrocracking of SRC under conditions similar to those in the hydrocracking of PAH,[3] the structure of SRC will be discussed.

Table 5. Influence of ring size on the product distribution

Substance used for hydrocracking	Cycloalkanes/monocyclic aromatics[a]
Bicyclic compounds[b]	0.03—0.04
Tricyclic compounds[c]	0.14—0.42
Chrysene	0.70
Tempoku SRC[d]	0.82
Yūbari SRC[e]	1.11

a) wt/wt. b) Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene. c) Anthracene, 2-methylanthracene, 9-methylanthracene, 9-propylanthracene, 9,10-dihydroanthracene, 9,10-dihydro-9-methylanthracene, 9,10-dihydro-9,10-dimethylanthracene, phenanthrene, 9-methylphenanthrene, 9,10-dihydro-9-methylphenanthrene, fluorene. d) Run 9. e) Run 8.

Monocyclic aromatics are relatively stable under these reaction conditions. On the other hand, cycloalkanes are mainly formed *via* highly hydrogenated compounds (for example, *unsym*-octahydrophenanthrene in the hydrocracking of phenanthrene[3]), and so the yield of cycloalkanes can be expected to increase as the size of the original ring structure increases. The ratio of the amounts of cycloalkanes to those of monocyclic aromatics in the hydrocracked products shown in Table 5 is considered to be a measure of the size of the ring structure. If the SRC consists of alkyl-substituted PAH, they are supposed to have larger a ring structure than chrysene, on the average. This finding suggests that the type containing a large ring structure (b) is more important than that containing a direct bond between two aromatic rings (a) in the average structures as determined by the CAMSC method. Table 5 also indicates that the average ring size of Yūbari SRC is larger than that of Tempoku SRC. The values shown in Table 5 are supposed to reflect the difference in the average structures, shown in Figs. 1 and 2, between these two SRC.

Table 6. Composition of monocyclic aromatics (mol %)

	Yūbari SRC[a]	Tempoku SRC[b]
A[c]	14.2	27.0
B[d]	25.0	27.7
C[e]	28.7	26.8
D[f]	20.2	12.3
E[g]	12.0	6.2
R[h]	0.57	0.97

a) Run 8. b) Run 9. c) Benzene. d) Toluene. e) Ethylbenzene and xylenes (C_2 alkylbenzenes). f) C_3 alkylbenzenes. g) Alkylbenzenes containing more than C_4. h) R = benzene/toluene (mol/mol).

Table 7. Composition of gases (mol %)

	Yūbari SRC[a]	Tempoku SRC[b]
C1[c]	40.0	39.1
C2[d]	17.7	17.7
C3[e]	19.3	20.7
C4[f]	22.9	22.5

a) Run 8. b) Run 9. c) Methane. d) Ethane. e) Propane. f) Butanes and butenes.

In the hydrocracking of alkyl-substituted PAH,[10] the behavior of the alkyl group attached to the condensed ring has been found to be different. The methyl group was not completely dealkylated in the initial stage, but remained in the products as monocyclic aromatics; the extent of dealkylation had been found to be dependent upon the type of starting materials. Table 6 suggests that Yūbari SRC possesses many more alkyl groups as substituents than does Tempoku SRC. On the other hand, Table 7 indicates that the extent of dealkylation is similar to that in the case of Tempoku SRC. These results seem to support the idea that the average structures shown in Figs. 1 and 2 reflect quite well the characteristics of the real structures of these two SRC.

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6) In the isomerization of cyclohexene at 400 °C over the molten salts,7) the yield of isomerized products was found to be remarkably dependent upon the composition between $ZnCl_2$ and CuCl. The catalytic activity for the isomerization displayed its maximum in a ratio of 2: 1 ($ZnCl_2$: CuCl).

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