CHEMICAL STRUCTURE ANALYSIS OF COAL HYDROGENATION PRODUCTS —— DISTRIBUTION OF STRUCTURAL PARAMETERS AND APPLICATION OF ^{13}C NMR TO STRUCTURAL ANALYSIS

Y. Maekawa, S. Ueda, Y. Hasegawa, Y. Nakata,
S. Yokoyama and Y. Yoshida

Government Industrial Development Laboratory, Hokkaido, Agency of Industrial Science and Technology, MITI, Japan
41-2, Higashi-Tsukisamu, Toyohiraku, Sapporo, Japan —— 061-01

In order to study the chemical structure of coal, Yubari coal (C : 86.1, H : 6.2, N : 1.5, S : 0.3, O : 5.9) was subjected to mild hydrogenation with red mud catalyst under a reaction temperature of 400°C and 200 atm. of hydrogen pressure[1]. Under these conditions, it was found from previous studies[2] that the main reaction of decrease of the molecular weight is the cleavage of linkages of the structural units and the decomposition of structural units is limited.

The hydrogenation was conducted in a 5L rotating autoclave with an inner vessel set at a uniform temperature zone. The reaction time was changed 8 times from 26 to 206 min. (exp. No. 502 - 509). The solvent soluble products were extracted with n-haxane, benzene and pyridine successively, which resulted in 5 fractions; oil-1 (n-hexane solubles at room temperature), oil-2 (n-hexane solubles extracted by Soxhlet extractor), asphaltene (benzene solubles), Py-1 (pyridine solubles at room temperature), Py-2 (pyridine solubles extracted by Soxhlet extractor). Regarding these hydrogenation reaction products, ultimate analysis, high resolution proton NMR spectroscopy and molecular weight measurement were carried out and the chemical reaction in Yubari coal in the course of hydrogenation was followed. From the above, structural analysis of the average structural unit of Yubari coal was conducted and reported[3].

This was followed by fractionation of the oil-2 (Exp. No. 503, reaction time : 206 min.) which corresponds to the mixture mainly consists of monomers of structural units[3], by GPC and each fraction was measured for ^{1}H-NMR, ^{13}C-NMR spectra, molecular weight and ultimate compositions. The structural parameters determined from the above fractions and the distribution of the structure of structural units were studied. At the same time, attempts to apply ^{13}C-NMR spectroscopy to the structural analysis of coal hydrogenation products was carried out in this work.

RESULTS AND DISCUSSION

DISTRIBUTION OF STRUCTURAL PARAMETERS OF COAL HYDROGENATION PRODUCTS

For the fractionation of No. 503, oil-2 (503-O-2), 100 cm respectively of SG -1 (theoretical plates / foot-T.P.F. = 1250) (Shimadzu Seisakusho Ltd) and SG-2 (T.P.F = 1360) column were applied. $CHCl_3$ was used as the solvent, and the eluent flow rate was set at 1.5 ml. / min.. The eluted sample was divided into 15 fractions and the respective elution volume, yield (against total eluted), ultimate composition and molecular weight were shown in Table 1. Elution after 440 ml was colorless and it was recognized that elution was completed.

The ^{1}H-NMR spectra of 503-O-2 and fractions separated from 503-O-2 were obtained on a GEOL JNM-PFT-100 spectrometer and shown in figure 1. The determination of chemical shifts of various functional hydrogens was carried out after the method of Bartle et al[4] and hydrogen distribution was calculated from figure 1. The percentage distribution of Ho, Hα, Ha in fractions separated from 503-O-2 by GPC were shown in figure 2. Based on the values of Table 1 and from the hydrogen

TABLE 1. - Yield, ultimate composition and molecular weight of fractions separated from 503-0-2 by GPC

Fractionated sample No.	Range of elution volume ml.	Yield wt. %	Ultimate analysis C	H	N	O	S	M.W. (Mv)
503-0-2	-	-	87.5	7.1	2.0	3.2	0.8	390
Fr. 3	92 - 96	0.75	87.5	8.1	1.3	4.2	-	540
Fr. 4	97 - 100	2.51	88.4	8.2	1.1	3.9	-	930
Fr. 5	101 - 104	4.27	87.4	7.5	1.2	3.6	-	490
Fr. 6	105 - 108	7.54	87.8	8.2	1.3	3.6	-	670
Fr. 7	109 - 112	7.04	87.5	7.5	1.7	3.5	-	620
Fr. 8	113 - 116	8.54	86.7	7.6	1.7	4.1	-	540
Fr. 9	117 - 120	8.29	86.8	7.4	1.8	4.6	-	510
Fr.10	121 - 128	17.84	86.8	7.1	1.8	3.8	-	360
Fr.11	129 - 148	26.38	87.6	6.8	1.8	4.0	-	340
Fr.12	149 - 168	7.29	85.8	6.5	2.4	5.8	-	270
Fr.13	169 - 200	2.76	80.1	8.8	3.0	-	-	250
Fr.14	201 - 252	1.76	-	-	-	17.0	-	310
Fr.15	253 - 440	5.03	72.5	8.2	0.0	21.0	-	380

TABLE 2. - Structural parameters of fractions separated from 503-0-2 by GPC

Samples	fa	Hau/ca	Ho/Hα	σT	σCH3*1	σal'*2	σCH2*3	σo*4
503-0-2	0.69	0.75	1.2	0.40	0.04	0.23	0.08	0.05
Fr. 4	0.57	0.61	2.8	0.45		0.32	0.03	0.10
Fr. 5	0.64	0.64	2.8	0.43	0.07	0.20	0.08	0.08
Fr. 6	0.59	0.66	3.4	0.45	0.08	0.22	0.08	0.08
Fr. 7	0.64	0.69	1.8	0.47	0.06	0.26	0.08	0.07
Fr. 8	0.63	0.71	2.0	0.47	0.06	0.24	0.10	0.08
Fr. 9	0.65	0.72	1.6	0.47	0.05	0.26	0.07	0.09
Fr.10	0.68	0.68	1.6	0.43	0.05	0.24	0.06	0.07
Fr.11	0.72	0.72	1.1	0.39	0.05	0.23	0.05	0.07
Fr.12	0.76	0.75	1.1	0.34	0.06	0.16	0.04	0.09

*1 Substitution by CH_3 groups α to rings
*2 Substitution by aliphatic chain (except*1)
*3 Substitution by CH_2 groups α to two rings
*4 Substitution by oxygene containing groups

distribution calculated from figure 1, the structural parameters were calculated by partially modified Brown-Ladner method[3]) and shown in Table 2. Regarding elution by GPC, as seen in theoretical work and experimental results conducted hitherto, it was recognized roughly that elution occurred in the order of high molecule to lower molecules. Thus from the parameter Hau/ca which is inversely proportional to the number of aromatic rings, a decrease of the number of aromatic rings in the order

of Fr. 4, 5, 6 of the initial elution is seen whereas in Fr.7 - 11 an approximately similar Hau/ca value is seen, namely, in Fr.7 - 11 which comprises the majority of 503-0-2 (approx. 70%) the aromatic ring size is approximately the same. Therefore, while the aromatic rings of structural units of 503-0-2 show a slightly sporadic presence, the majority is approximately the same and it may be surmized that the aromatic rings of the original Yubari coal are unified.

APPLICATION OF ^{13}C-NMR TO COAL HYDROGENATION PRODUCTS STRUCTURAL ANALYSIS

The ^{13}C-NMR spectra of 503-0-2 and part of fractions which gave comparatively large yield are shown in Fig. 3. For the measurement of these spectra a JEOL, JNM-PFT 100 NMR spectrometer was applied. Decoupling of the protons was achieved with decoupler and spectra was accumulated by repetition of scanning (10000 - 30000 times) to improve the signal to noise ratio.

^{13}C-NMR spectra are greatly simplified a signal enhancement due to the operation of ^{13}C-^{1}H overhauser effect is possible. The magnitude of the overhauser enhancement ordinarily differs for different ^{13}C-Nuclei, and the spectra as is, generally can not be applied to quantitative analysis. Further the value of spin-latice relaxation time (T_1) shows different values with different ^{13}C-Nuclei, and in a quantitative analysis, it is necessary to take sufficient longer pulse repetition time. In order to clarify the influense of the above two on the spectra, the ^{13}C-NMR spectra in measured by changing the repetition time of the pulse and the ratio of Ca (aromatic carbon) against Cp (aliphatic carbon) is calculated from the intensity of the spectra. This is shown in Table 3.

TABLE 3. - Ca/Cp ratio of Yubari coal hydrogenation products under various pulse repetition times

Samples	Pulse repetition time, sec.	Ca%	Cp%	Ca/Cp
Fr.11	0.8	0.668	0.332	2.0
Fr.11	2.0	0.655	0.345	1.9
503-0-2	1.0	0.615	0.385	1.6
503-0-2	1.5	0.649	0.351	1.9
503-0-2	2.0	0.635	0.365	1.7
503-A	1.0	0.689	0.311	2.2
503-A	1.5	0.689	0.311	2.2

From the esults in Table 3, with regard to the sample used in the present work, no influence of the pulse repetition time was recognized or the Ca/Cp ratio, and at 0.8 sec of pulse repetition time already a quantitative spectra was obtained.

Regarding this it has been stated that this ^{13}C-^{1}H overhauser polarization might be eliminated by the presence of a paramagnetic species[5]. Inasmuch as a free radical exsists in the sample used in the present work, it is surmized that a similar effect exsists.

Based on this, it is possible to make a direct calculation of aromaticity (fa') using the spectra of Fig. 3. When this value and the fa value of Table 2 calculated from the assumption of x=y=2 lead from ^{1}H-NMR are compared the fa/fa' value in Table 4 are both in the vicinity of 1.2, this indicated that the assumption x=y=2 is an over estimation. In the case of Fr.10, if the following is taken namely if x=y=1.5, fa is calculated as fa=0.60, which resembles fa' to a considerable extent.

In Fig. 3, the peaks are clearly identified the aromatic carbon (Ca) may be

subdivided into 4 species namely Ca_1, Da_2, Ca_3 and Ca_4 while the aliphatic carbon (Cp) may be subdivided into 9 species namely Cp_1, Cp_2, Cp_3, Cp_4, Cp_5, Cp_6, Cp_7, Cp_8 and Cp_9, while the data of the chemical shift in ^{13}C-NMR is still insufficient, it may be surmized from the data collection[6]) that Cp_4, Cp_5, Cp_6 are intimately related to the carbon of the chain β or father from ring Cp_1, Cp_2, Cp_3,are closely related to the α carbon atoms Cp_8, Cp_9 is closely related to the end methyl carbon atoms of the chains and Cp_7 is closely related to the α methyl carbon atoms.

TABLE 4. - Aromaticities of fractions separated from 503-0-2 by GPC

Samples	fa*1	fa'*2	fa/fa'
503-0-2	0.69	0.63	1.1
Fr. 8	0.63	0.63	1.0
Fr. 9	0.65	0.53	1.2
Fr.10	0.68	0.57	1.2
Fr.11	0.72	0.67	1.1
Fr.12	0.76	0.65	1.2

fa*1 Calculated from ^{1}H-NMR spectra
fa*2 Calculated from ^{13}C-NMR spectra

From the ratio of Cp_1 - Cp_3 and Cp_4 - Cp_6, Cp_8, Cp_9 the mean chain length is obtained. This was compared with Ho/Hα + 1 and presented in Table 5 as shown a fairly good coincidence is seen. Further based on the above it may be surmized that the assumption x=y is feasible. Still further since x and y have a value close to 1.5 in the present sample, on the chain including the substitution on the naphthenic ring there would be a considerable branching of the chain.

TABLE 5. - Average carbon numbers of chains on fractions separated from 503-0-2 by GPC

Samples	503-0-2	Fr.8	Fr.9	Fr.10	Fr.11	Fr.12
Ho/Hα + 1	2.2	3.0	2.6	2.6	2.1	2.1
$\frac{Cp_4\text{-}Cp_6,\ Cp_8,\ Cp_9}{Cp_1\text{-}Cp_3} + 1$	1.8	2.0	2.0	1.5	1.9	2.2

For a still further detailed study of the chemical shift of the ^{13}C-NMR spectra, it is the intent of the author to continue work along this line.

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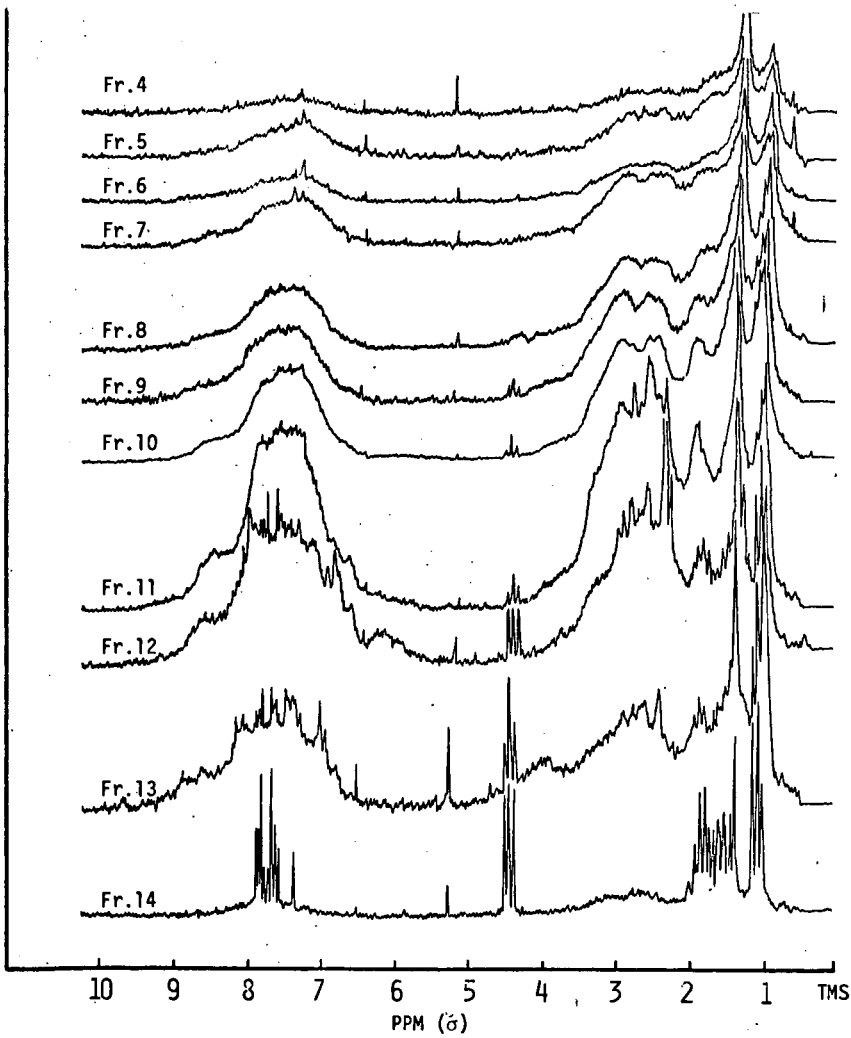

FIGURE 1 - ^{1}H-NMR spectra of fractions separated from 503-0-2 by GPC

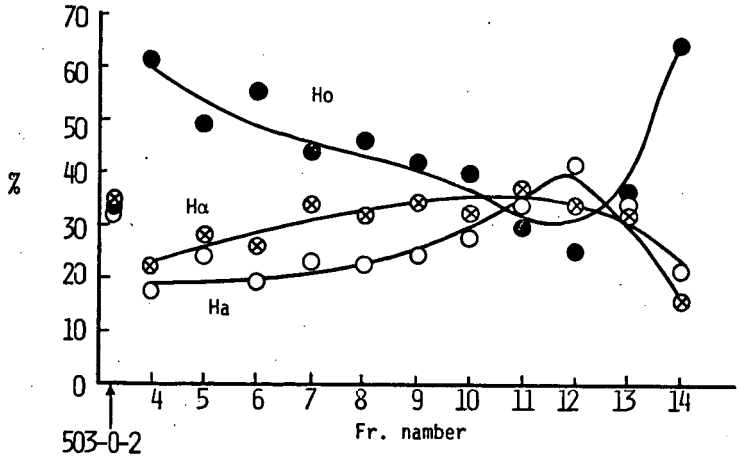

FIGURE 2 - Percentage hydrogen distribution in fractions separated from 503-0-2 by GPC

Ho : Hydrogen on β or farther from ring carbon
Hα : Hydrogen on α-carbon atoms
Ha : Aromatic hydrogen

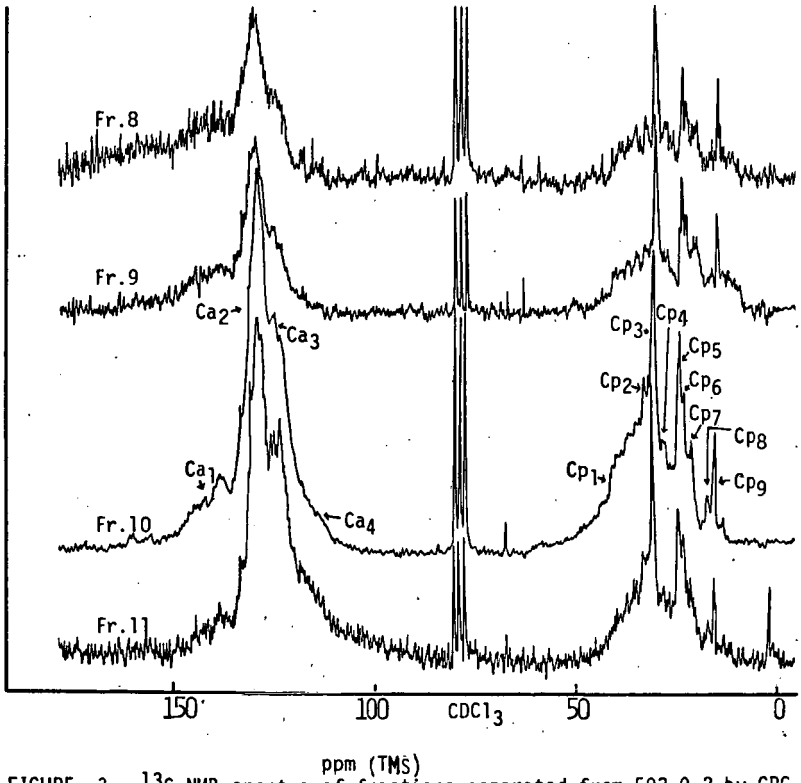

FIGURE 3 - ^{13}C NMR spectra of fractions separated from 503-0-2 by GPC