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Close Similarities of Chemical Structures between Light (Hexane-Soluble) and Heavy (Hexane-Insoluble and Benzene-Soluble) Fractions of Solvent-Refined Coal

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Curie-point pyrolysis-GC analyses were applied for structural analyses of hexane-soluble (HS) and hexane-insoluble and benzene-soluble (HI-BS) fractions from two SRC samples. Pyrograms of HS and HI-BS fractions are strikingly similar, indicating that they are composed of similar aromatic constituents, although the molecular weight distributions between the two fractions are different. The difference in coal rank for the two SRC samples was reflected as the profiles of pyrograms.

Although many works1-3) have been carried out on the characterization of coal-derived liquids, however, most of which give only averaged, partly detailed, structural information about the constituents in these complex samples. Recently, FI- and FD-MS measurements have been applied to the characterization of coal-derived liquids4-8) because these techniques provide fragment-free mass spectra and, subsequently, simplified compound-type distribution of complex organic materials. Another powerful method is Curie-point pyrolysis combined with gas chromatography and mass spectrometry (Py-GC-MS), which is now widely used in the characterization of complex organic materials, such as oil shales,9) coals10-11), and coal-tar pitches.12)

In the present study, constituents in Solvent-Refined Coal (SRC) were elucidated by Py-GC-MS analyses. Furthermore, the results were assessed by the comparison with those obtained by FI- and FD-MS measurements.

Akabira and Wandoan SRC were provided by Sumitomo Metal Mining Co., Ltd. SRC was further fractioned as follows: 10 g of SRC was extracted with boiling benzene (300 ml) for 3 h being separated to benzene-soluble (BS) and benzene-insoluble (BI) fractions, respectively. The BS fraction, concentrated to about 20 ml by evaporating benzene, was poured into hexane (1000 ml) to precipitate hexane-insolubles (HI-BS). Hexane-soluble (HS) was obtained by evaporating hexane from the filtrate. The HS and HI-BS fractions were subjected to analyses. The elemental

Table 1. Elemental analyses of SRC fractions

		C	H	N	S+O(diff.)
Akabira SRC	HS	89.6	7.3	1.0	2.1
	HI-BS	84.1	6.4	2.0	7.5
Wandoan SRC	HS	87.5	8.8	0.3	3.4
	HI-BS	82.2	6.7	1.0	10.1

analyses of the HS and HI-BS fractions are listed in Table 1.

Curie-point pyrolysis was performed with an equipment of Japan Analytical Industry Co., Ltd (Model JHP-2 or JHP-3). In order to perform efficient pyrolysis of the sample, ferro-magnetic foil (pyro-foil) was used with Curie-point temperature at 690 $^{\circ}$C. Structural analyses were performed using a JEOL DX303 double focusing mass spectrometer combined with a Hewlett-Packard 5970 GC and a JHP-3 pyrolyser. Conditions used were: 0.25 mm i.d. X 25 m OV-101 Fused Silica column; 50 $^{\circ}$C for 2 min and 10 $^{\circ}$C/min to 300 $^{\circ}$C; ionization potential 70 eV; scan speed 0.5 sec from m/z 35 to 500. For compositional determination, a Shimadzu 7A GC equipped with 0.32 mm i.d. X 25 m ULBONHR-101 Bonded Fused Silica column (equivalent to OV-101 column; Chromato Packing Co., Ltd.) was combined with JHP-2 pyrolyser. Conditions were: 50 $^{\circ}$C for 2 min and 10 $^{\circ}$C/min to 300 $^{\circ}$C. FI- and FD-MS spectra were recorded for HS and HI-BS fractions using a JEOL DX300 double focusing mass spectrometer. The conditions for FI-MS measurements were as follows: cathode potential -5.5 kV, emitter current 10 mA. Scanning (2 s/cycle) was repeated 600-700 times (FI-MS) or 230 times (FD-MS). For FD-MS analysis, emitter current was elevated at a rate of 4.2 mA/min.

Figures 1**a** and **b** show the FI-MS spectra of HS fractions from Akabira and Wandoan SRC, respectively. The compound-type distributions are also indicated in these figures as z numbers which refer to the formula C_nH_{2n+z}. Most of the ions were assigned to the series of z=-12 (+2), -14, -16, -18, and -22, which could correspond to the homologues of naphthalene (alkane), biphenyl, fluorene, phenanthrene, and pyrene, respectively. In comparison with the spectra of Akabira HS, the components of Wandoan HS have relatively higher m/z number and the homologues of z=+2 series appear in the range of higher m/z, which could correspond to alkanes.

Figure 2 shows the FD-MS spectrum of Akabira HI-BS, which indicates the complexity of

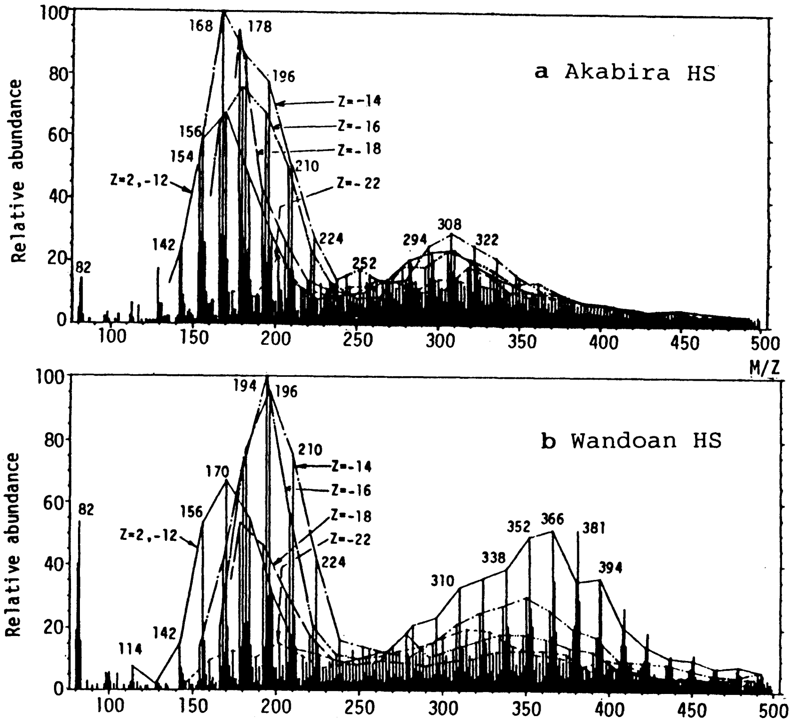

Fig. 1. FI-MS spectra of HS fractions

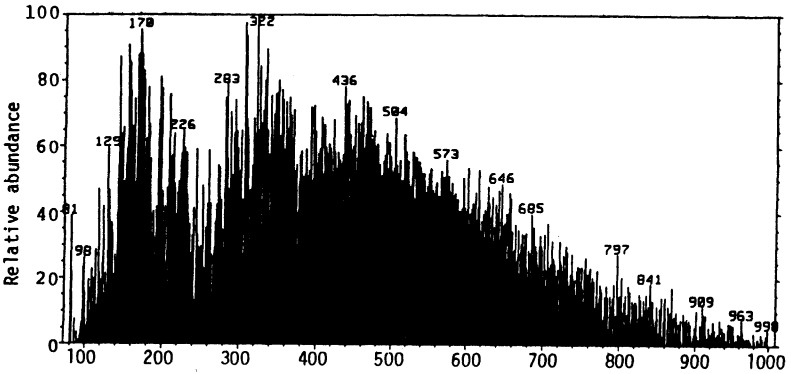

Fig. 2. FD-MS of Akabira HI-BS fraction

chemical composition of the HI-BS fraction. In case of Wandoan HI-BS fraction, no reproducible spectra were obtained by FD- and FI-MS analyses, probably due to thermal lability or non-volatility.

Thus, FI-MS analyses give information about the molecular-mass distribution of constituents with different compound-types. However, it is impossible to distinguish compounds with the same molecular-mass but different structures; for example, distinction between phenanthrene and anthracene (m/z=178). Furthermore, it is difficult to assess compound-type distributions for very complex FD-MS spectrum of Akabira HI-BS (Fig. 2). Therefore, it seems to be very difficult to assign the chemical structures of constituents in HS and HI-BS fractions by measuring only FI- and FD-MS spectra.

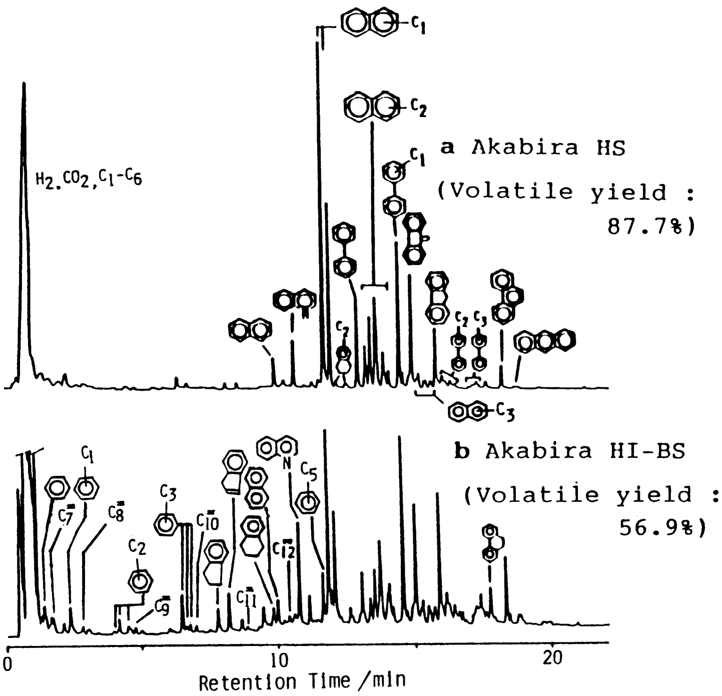

Fig. 3. Pyrograms of Akabira HS and HI-BS.

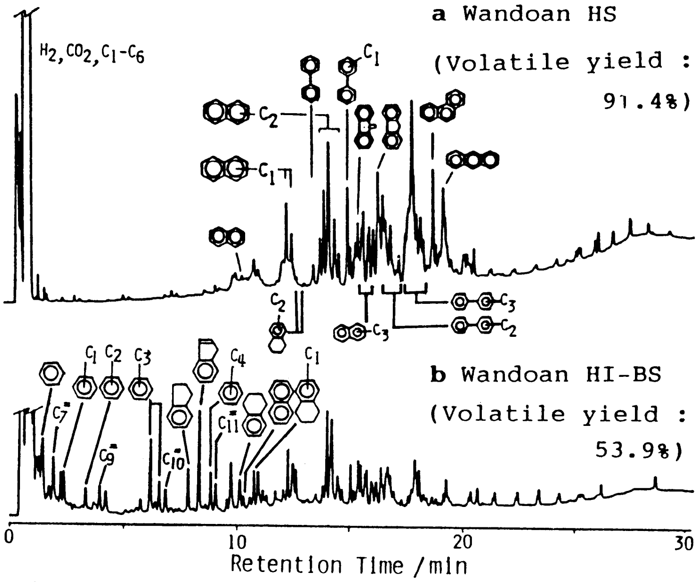

Fig. 4. Pyrograms of Wandoan HS and HI-BS.

Figures 3**a** and **b** show the pyrograms of HS and HI-BS fractions of Akabira SRC, respectively. It should be noted that these pyrograms are strikingly similar after 11 min of the retention time. Figures 4**a** and **b** show the pyrograms of HS and HI-BS fractions of Wandoan SRC, respectively. A close similarity between two fractions also established. These similarities refer not only to the profiles of pyrograms, but also to the relative abundances of the dominant peaks. Accordingly both HS and HI-BS fractions are composed of very similar aromatic components, as regard to GC-analyzed volatile materials. Larger amounts of gas, alkylbenzenes, and hydroaromatics, such as tetralin and dihydrophenanthrene, were detected in the pyrogram of the HS than that of the HI-BS. This would suggest that constituents in HI-BS is more complex, having more substituents and more bridging groups.

Although the original Akabira and Wandoan coals are of different ranks, the major components in their pyrograms are very similar, in the way that compounds detected have simple aromatic skeletons, such as naphthalene, biphenyl, fluorene, dibenzofuran, phenanthrene, anthracene, and their homologues. The differences in coal rank appeared in the relative concentrations of these compounds on pyrograms: (i) Naphthalenes and biphenyls had C_2-C_3 substituents in the pyrograms of Wandoan whereas C_1-naphthalenes were dominant in that of Akabira. (ii) Several peaks appeared with a certain regularity on the pyrograms of Wandoan at retention time longer than 20 min. These peaks would be assigned to n-alkane homologous series because these compounds were also observed on the FI-MS spectrum (Fig. 1**a**).

The yields of GC-analyzed volatile materials were estimated by the weight difference between the charged sample and the pyrolysis residue. The HI-BS fraction showed low yield than the HS fraction for both Wandoan and Akabira samples. This result indicates that the HI-BS fractions are composed of larger molecules than the HS fractions. By considering the similarity of the pyrograms between the HS and HI-BS fractions mentioned above, it is suggested that constituents in both the HS and HI-BS fractions have similar aromatic structural units, however, the number of structural units per one molecule would be different.

The nature of Curie-point Pyrolysis technique, quick and reproducible heating[13,14] and rapid removal of the pyrolyzed products from the heated zone, ensure that the products observed are primary products, and not secondary or rearrangement products.

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References

1) J. E. Farcasiu, Ann. Chem., 49, 2292 (1977).
2) M. M. Boduszynski, R. J. Hurtubise, T. W. Allen, and H. F., Silver, Ann. Chem., 55, 225, 232 (1983).
3) R. S. Brown and L. T. Taylor, Ann. Chem., 55, 723 (1983).
4) R. Yoshida, T. Yoshida, H. Narita, and Y. Maekawa, Fuel, 65, 425 (1986).
5) T. Yoshida, Y. Maekawa, T. Higuchi, E. Kubota, Y. Itagaki, and S. Yokoyama, Bull. Chem. Soc. Jpn., 54, 1171 (1981).
6) T. Yoshida, Y. Maekawa, and T. Shimada, Anal. Chem., 54, 967 (1982).
7) M. W. Boduzynski, R. J. Hurtubise, T. W. Allen, and H. F. Silver, Anal. Chem., 55, 225, 232 (1983).
8) S. A. Qian, Y. X. Xiuo, and Y. D. Gu, Fuel, 66, 242 (1987).
9) M. V. Robillard, S. Siggia, and P. C. Uden, Ann. Chem., 51, 435 (1979).
10) E. J. Gallegos, Ann. Chem., 47, 1524 (1975).
11) A. L. Chaffee, G. J. Perry, and R. B. John, Fuel, 62, 303, 311 (1983).
12) J. L. Glajch, J. A. Lubkowitz, and L. B. Rogers, J. Chromatogr., 168, 355 (1979).
13) H. L. C. Meuzelaar, A. M. Harper, G. R. Hill, and P. H. Given, Fuel, 63 ,640 (1984).
14) P. J. J. Tomp, J. A. Moulijn, and J. J. Boon, Fuel, 65, 960 (1986).

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