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Flash Pyrolytic Study on Chemical Structures of Akabira Coal Extracts and Residue

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Akabira coal extracts [Pyridine soluble fraction (PS) and Acetone soluble fraction (AS)] and residue [CS_2-N-methyl-2-pyrrolidone (NMP) insoluble fraction (Residue)] were analyzed to get detailed information about components contained in three fractions using Curie-Point Pyrolyser-GC (Py-GC) and -GC-MS (Py-GC-MS). The pyrograms obtained from these fractions by Py-GC showed close similarities among them. The examination by Py-GC-MS resulted in the identification of 130 compounds.

Structural estimation of coal organic materials has been approached from different angles over the last thirty or forty years, however, most of these analyses of coal were usually carried out after the chemical degradation: hydrogenation,1) oxidation,2) or alkylation. Although these methods are useful to make coal organic materials soluble in common organic solvents, from a point of view to get intrinsic structural information of original coal, these chemical degradations are not appropriate. Solvent extraction under mild conditions can provide valuable information on coal structures through characterization of the extracts and the residue because such extraction is believed not to accompany any chemical reactions. Py-GC and Py-GC-MS are regarded as one of the most powerful methods to evaluate chemical structures of solid organic materials, on molecular level, such as oil shale,3) coals,4) and many natural and synthetic polymers.5)

In the present work, the extracts and the residue obtained from Akabira coal by solvent extraction were analyzed by means of Py-GC and Py-GC-MS.

Akabira coal was ground under 200 mesh and subjected to solvent extraction after drying in vacuo at 110 °C for 24 h. Coal (8 g) was extracted with 200 ml of CS_2-NMP mixed solvent (1:1) under ultrasonic irradiation for 30 min at room temperature because, at present time, this binary solvent system6) is known very powerful for extracting coal organic materials. After centrifugation for 60 min the supernatant was separated by decantation. These procedures repeated until the supernatant became almost colorless (7 times). CS_2-NMP insoluble (Residue) fraction was then washed with acetone three times under ultrasonic irradiation (30 min). The above supernatant was filtered and the solvent was evapolated in vacuo. The CS_2-NMP wet extract was put into a thimble in a Soxhlet extractor and subsequently extracted with 200 ml of acetone for 24 h, and then with 200 ml of pyridine for 48 h. After stripping of the solvents, the acetone-soluble fraction and the pyridine-soluble (PS) fraction were obtained. The small amount of residue in the thimble was designated MS fraction. The acetone extract was, further, washed with 8:2 water-acetone solution, then the water-acetone soluble (WS) and water-acetone insoluble (AS) fraction was obtained. The AS (14 wt%), PS (15 wt%) and Residue (67 wt%) fractions were subjected to analyses after dealing with hot water (100 °C) for 5, 10, and 15 days, respectively, to remove NMP completely. The ultimate analyses of raw coal, Residue, PS and AS were shown in Table 1.

Table 1. Ultimate analyses (wt% daf)

	C	H	N	O+S(diff.)
Akabira Coal	81.1	5.7	2.0	11.2
Residue	78.9	5.4	2.2	13.5
PS	78.5	4.7	2.5	14.3
AS	81.6	6.6	1.8	10.0

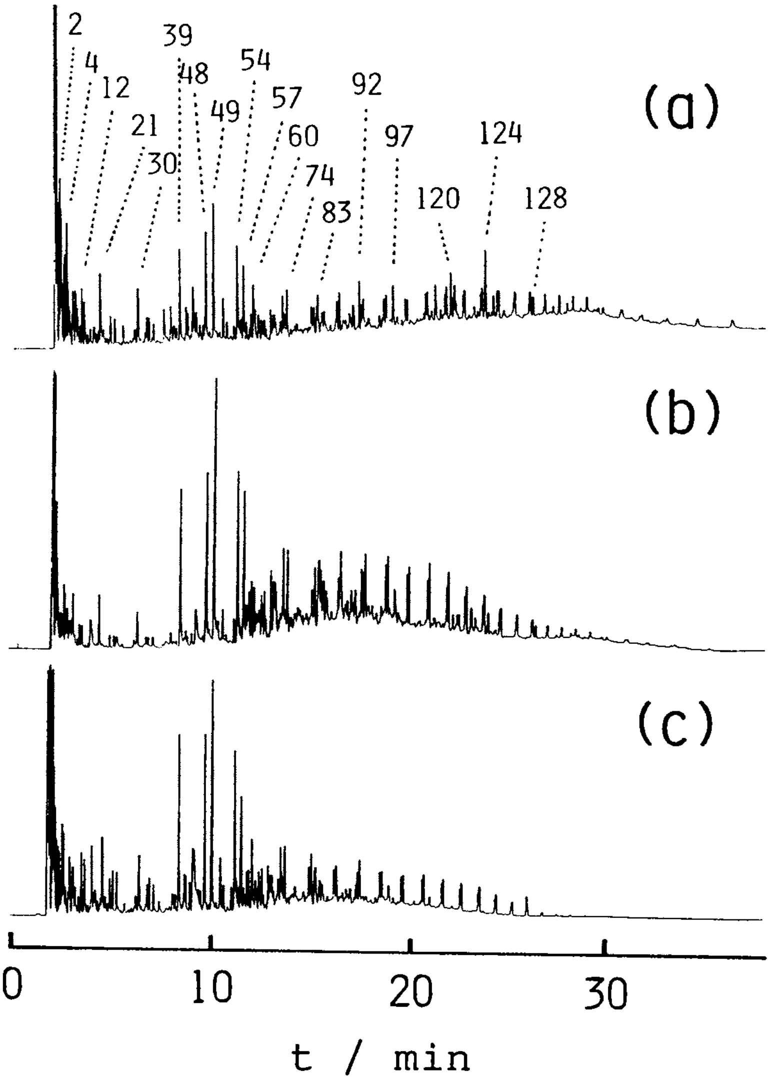

Fig. 1. Pyrograms of each fraction, (a);AS, (b);PS, (c);Residue

Curie-Point Pyrolysis was performed with an equipment of Japan Analytical Industry Co. , Ltd. (Model JHP-2 or JHP-3). The Curie-point temperature and pyrolytic time were selected 670 °C (heating rate 3350 °C/s) and 3 s, respectively. Structural analyses were performed using a JEOL DX303 double focusing mass spectrometer combined with a Hewlett-Packerd 5970 GC and a JHP-3 pyrolyser. For compositional determination, a Shimadzu GC-8APF equipped with fused silica capillary column was combined with JHP-2 pyrolyser. Conditions were described in detail elsewhere.7)

The pyrograms of three fractions are presented in Fig. 1 and the corresponding compounds of AS, which were identified by mass spectroscopy, are listed in Table 2. In these pyrolysates, benzene, phenol, naphthalene, and their series of alkyl homologues were observed in addition to alkanes/alkenes (C1 - C22). Relatively smaller nuclei such as benzene and naphthalene were most abundant and over three-ring aromatics were present only in small amount. The remarkable peaks of phenol derivatives found are seemed to be connected with lignin structure.[8]

Figures 1a, b, and c show the pyrograms of AS, PS, and Residue fractions of Akabira coal, respectively. It should be noteworthy that these pyrograms are roughly the same except peaks appeared after retention time of 22 min on the pyrogram of AS fraction, which considered to be isoprenoid derivatives. Therefore, as to GC-analyzed volatile materials, the close similarity of chemical structure among the coal extracts and the residue could be strongly supported. This similarity was also found in the previous work[7] about Akabira SRC. The volatile materials were evaluated quantitatively by weighting, carefully, both the pyro-tube and the pyro-foil before and after pyrolysis, respectively. The amount of volatile materials to be analyzed directly by GC and GC-MS were established as 34% (AS), 29% (PS), and 31% (Residue) from each fraction.

Table 2. Compounds identified by GC-MS in AS fraction [Fig.1.(a)]

Peak No.	Proposed Compounds
1	carbon dioxide
2	propane
3	butane
4	pentane
5	dihydrofuran
6	furan
7	C6-alkane
8	n-hexene
9	n-hexane
10	C1-cyclopentane
11	cyclohexane
12	benzene
13	pyridine
14	branched heptane
15	n-heptene
16	n-heptane
17	C1-cyclohexane
18	C1-cyclohexadiene
19	C1-cyclohexadiene
20	C1-cyclohexadiene
21	toluene
22	branched octane
23	branched octane
24	branched octene
25	n-octene
26	n-octane
27	C2-cyclohexane
28	C2-cyclohexene
29	p-xylene
30	m-xylene
31	stylene
32	o-xylene
33	n-nonene
34	n-nonane
35	C9-cycloalkane
36	thiophenol
37	C3-benzene
38	C3-benzene
39	phenol
40	C3-benzene
41	C3-benzene
42	n-decene
43	C3-benzene
44	n-decane
45	C3-benzene
46	indene
47	indan
48	cresol
49	cresol
50	dimehtylphenol
51	n-undecene
52	n-undecane
53	ethylphenol
54	dimethylphenol
55	tetralin
56	ethoxybenzene
57	dimethylphenol
58	dimethylphenol
59	naphthalene
60	quinoline
61	trimethylphenol
62	n-dodecene
63	n-dodecane
64	ethylmethylphenol
65	ethylmethylphenol
66	trimethylphenol
67	C12-cycloalkane(?)
68	ethylmethylphenol
69	ethylmethylphenol
70	trimethylphenol
71	trimethylphenol
72	2-methylnaphthalene
73	n-tridecene
74	1-methylnaphthalene
75	n-tridecane
76	C1-benzofuran
77	C1-benzofuran
78	tetradecadiene
79	C2-naphthalene
80	n-tetradecene
81	C2-naphthalene
82	n-tetradecane
83	C2-naphthalene
84	C2-naphthalene
85	C2-naphthalene
86	C2-naphthalene
87	C14-cycloalkane or branched alkene(?)
88	2-naphthol
89	1-naphthol
90	n-pentadecene
91	n-pentadecane
92	C3-naphthalene
93	C3-naphthalene
94	C3-naphthalene
95	C3-naphthalene
96	C3-naphthalene
97	C3-naphthalene
98	$C3^{=}$-naphthalene
99	n-hexadecene
100	n-hexadecane
101	C1-dibenzofuran
102	C1-dibenzofuran
103	C4-naphthalene
104	C5-naphthalene
105	C5-naphthalene
106	C5-naphthalene
107	n-heptadecene
108	n-heptadecane
109	C5-naphthalene
110	C2-dibenzofuran
111	C2-dibenzofuran
112	phenanthrene
113	anthracene
114	n-octadecene
115	n-octadecane
116	C3-dibenzofuran
117	n-nonadecene
118	n-nonadecane
119	C1-phenanthrene
120	C19-cycloalkane or branched alkene(?)
121	C19-cycloalkane or branched alkene(?)
122	n-eicosene
123	n-eicosane
124	C20-cycloalkane or branched alkene(?)
125	C20-cycloalkane or branched alkene(?)
126	C20-cycloalkane(?)
127	n-heneicosene
128	n-heneicosane
129	n-docosene
130	n-docosane

? = identification uncertain

This observation that the volatile materials were obtained almost same amount, also, seems to indicate the structural similarities among the extracts and the residue.

The results obtained here using Curie-Point Pyrolyser may be interpreted by the following two ways: (i) All of the compounds on the pyrograms arose from pyrolysis of coal macro-molecule. (ii) These had been trapped in the coal physically or held by weak-bond like hydrogen-bonding were released by activated diffusion or some breakdown of the network due to shock heating. The former assumption means that the similarity of pyrograms reflects the three fractions are composed of similar unit skeletons, and the latter means that the similar kinds and quantities of low-molecular-weight materials are held in the three fractions by some interactions. However, these arguments need to await further clarification to be concluded. Some workers[9-10)] found that small compounds; aromatic hydrocarbons and phenols were trapped in the coal network as clathrates and were not extractable with common organic solvents at their normal boiling point. Therefore, present authors consider that most of the compounds observed on pyrograms originated from the collapse of physical or weak-chemical bond rather than covalent bond. Now, the relationship between the low-molecular-weight materials obtained by Py-GC and "mobile phase"[11)] which is discussed on the basis of coal-two-component model are, also, under investigation.

By application of this analytical system, ca. 30% of the coal extracts (AS, PS) and the residue (Residue) composed high-molecular-weight materials (over m/z = 2000) could be analyzed by GC and GC-MS, and it is found that the pyrograms obtained by the method described above revealed almost same appearance. There have been few reports being related to comparison of chemical structure among coal extracts and residue. Consequently, these structural information among them seem to be of great importance.

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