

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 [CS₂-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 (g) was extracted with 200 ml of CS₂-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). CS₂-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 evaporated in vacuo. The CS₂-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

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 (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-Packard 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

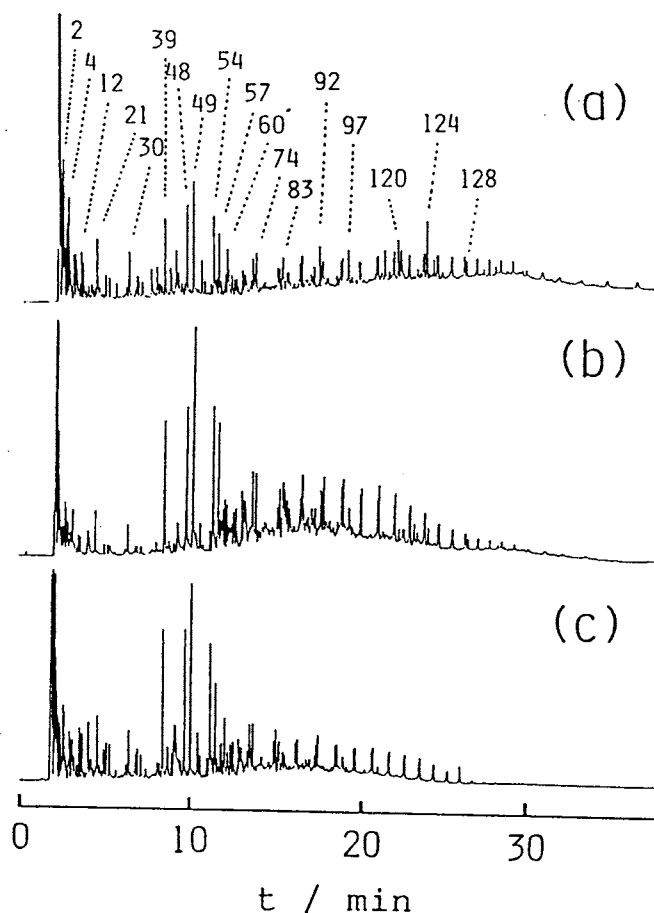


Fig. 1. Pyrograms of each fraction, (a); AS, (b); PS, (c); Residue

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 work⁷⁾ 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	46 indene
2	propane	47 indan
3	butane	48 cresol
4	pentane	49 cresol
5	dihydrofuran	50 dimethylphenol
6	furan	51 n-undecene
7	C6-alkane	52 n-undecane
8	n-hexene	53 ethylphenol
9	n-hexane	54 dimethylphenol
10	C1-cyclopentane	55 tetralin
11	cyclohexane	56 ethoxybenzene
12	benzene	57 dimethylphenol
13	pyridine	58 dimethylphenol
14	branched heptane	59 naphthalene
15	n-heptene	60 quinoline
16	n-heptane	61 trimethylphenol
17	C1-cyclohexane	62 n-dodecene
18	C1-cyclohexadiene	63 n-dodecane
19	C1-cyclohexadiene	64 ethylmethylphenol
20	C1-cyclohexadiene	65 ethylmethylphenol
21	toluene	66 trimethylphenol
22	branched octane	67 C12-cycloalkane(?)
23	branched octane	68 ethylmethylphenol
24	branched octene	69 ethylmethylphenol
25	n-octene	70 trimethylphenol
26	n-octane	71 trimethylphenol
27	C2-cyclohexane	72 2-methylnaphthalene
28	C2-cyclohexene	73 n-tridecene
29	p-xylene	74 1-methylnaphthalene
30	m-xylene	75 n-tridecane
31	styrene	76 C1-benzofuran
32	o-xylene	77 C1-benzofuran
33	n-nonene	78 tetradecadiene
34	n-nonane	79 C2-naphthalene
35	C9-cycloalkane	80 n-tetradecene
36	thiophenol	81 C2-naphthalene
37	C3-benzene	82 n-tetradecane
38	C3-benzene	83 C2-naphthalene
39	phenol	84 C2-naphthalene
40	C3-benzene	85 C2-naphthalene
41	C3-benzene	86 C2-naphthalene
42	n-decene	87 C14-cycloalkane
43	C3-benzene	or branched alkene(?)
44	n-decane	88 2-naphthol
45	C3-benzene	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 h61d 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 workers⁹⁻¹⁰) 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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