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Analysis of Acidic Compounds in Recycle Solvent for Coal Liquefaction

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Recycle solvents were obtained in 50 d of continuous operation of a 1 ton/day coal-liquefaction plant at Kimitsu. Acidic fractions were obtained by base extraction for the starting solvent and final solvent, and their components were analyzed in detail by gas chromatography/mass spectrometry. The application of a selected ion monitoring technique has allowed the assignment of the atomic compositions to practically all compounds despite many of their presence as overlapping peaks on the chromatogram: 327 individual compounds for 142 peaks.

These compounds have been classified into nine of compound types: phenols, indanols/tetrahydronaphthols, naphthols, biphenylols/acenaphthenols, hexahydroacenaphthylenols, fluorenols, phenanthrenols/anthracenols, phenylnaphthols, and pyrenols/fluoranthenols. As compared to the initial solvent, the final solvent contains higher concentrations of indanols/tetrahydronaphthols and hexahydroacenaphthylenols and contains a lower concentration of pyrenols/fluoranthenols.

In the coal-liquefaction process, the recycle solvent plays some important roles in the coal-liquefaction performance: in the yield of coal oil, in the operability of the plant, and on the viscosity during the preheating step, in addition to the role of a coal vehicle. Usually, coal tar or its hydrogenated oil is used as a starting solvent, and its components are substituted for coal-derived compounds according to the cycling of the solvent. However, it is very difficult to obtain a well-substituted recycle solvent because there is no operation of a commercial coal-liquefaction plant now. In 1986, the construction of a pilot supporting unit (PSU), a 1 ton/day coal liquefaction unit, started at Kimitsu, and a study of the unit started in 1989, which made it possible for us to obtain a well-substituted recycle solvent.

The recycle solvent includes oxygen-containing and nitrogen-containing compounds in addition to condensed polycyclic aromatic compounds. In Japan's Sunshine project, a research effect to develop the technology for the separation and utilization of heteroatomic compounds from coal-derived liquids has been carried out in order to improve the cost performance of the coal-liquefaction process by utilizing heteroatomic compounds as chemicals. The research is based on qualitative and quantitative information concerning heteroatomic compounds in coal-derived liquids. However, information about individual heteroatomic compounds has been scarcely available because of the lower content of each compound and an incomplete separation of the peaks on their chromatogram.

Acidic compounds are an important heteroatomic fraction of coal liquid[1—5] because of their minor existence in petroleum fuels. Phenols are one of the most expectant heteroatomic compounds as chemicals.[6] Several phenolic structure types have been reported in hydrotreated anthracene oils,[7,8] in coal liquids,[9,10] and in a coal liquefaction recycle solvent.[1,11] Recently, the authors have developed selected ion-monitoring techniques for peak overlapped compounds[12] in addition to a data base of phenolic compounds.[13] These techniques have also been introduced to identify the individual components in the acidic fraction of the recycle solvent.

In the present work, atomic compositions were studied on the acidic components in the recycle solvents obtained at the initial stage of operation and at the final stage of 50 d of continuous operation by PSU.

Experimental

Materials. Two sample oils, the starting solvent and the final solvent, were provided from PSU after 50 d continuous operation. Liquefaction Australian Wandoan coal, 12.7 wt% of water, 9.9 wt% of ash (dry), 77.09 wt% of C (daf), 15.08 wt% of O (daf), 1.15 wt% of N (daf), and $H/C = 0.999$ (mol) were liquefied at 450 °C and under 17 MPa of hydrogen pressure with the existence of 3 wt% of an iron sulfide catalyst.

Analysis. Acidic fractions were extracted by a 10% NaOH solution and separated from water using benzene as a solvent after neutralization with a 10% H_2SO_4 solution. The same procedure was repeated twice on the original oil to collect the remaining acidic compounds.

The acidic components were analyzed using a Hewlett–Packard 5880A gas chromatograph equipped with a flame-ionization detector (GC/FID). A Hewlett–Packard 5890 gas chromatograph was interfaced with a mass spectrometer (Hewlett–Packard 5970, GC/MS), and each compound was identified by its mass spectrum. A fused-silica capillary column (OV-1, 0.25 mm×50 m) was programmed from 50—300 °C at 2.5 $^{\circ}\mathrm{C\,min^{-1}}$ with a 3 min initial hold. The chromatographic conditions are summarized in Table 1.

The abundance of each compound was calculated from a GC/FID analysis, correcting the existence of the oxygen atom from the molecular weight by a mass analysis. The total concentration of the compounds in an overlapped peak was calculated from the GC/FID value and assigned to individual compounds by using a selected ion-

Table 1. Chromatographic Operating Conditions

Detector	FID
Detector temperature	280 °C
Liquid sample volume	1 μL
Sample injector temperature	260 °C
Column	50 m long, 0.25 mm in diameter OV − 1
Carrier gas flow	Helium 3 mL min^{-1}
Sample split ratio	1 : 200
Initial temperature	50 °C held for 3 min
Programmed temperature	2.5 °C min^{-1}
Final temperature	300 °C held for 60 min
GC/MS interface temperature	260 °C

monitoring technique developed by the authors,[12] the sensitivity of parent ion was measured as a function of concentration for several types of compounds. The sensitivities of other compounds were calculated on the supposition that the sensitivities were equal to the sensitivities of similar types of compounds.

Results and Discussion

Figure 1 shows the total ion chromatogram of the GC/MS analysis for the starting solvent, and Fig. 2 shows some single ion chromatograms eluted between retention times of 80 and 101 min. The peak numbers in Fig. 2 correspond to those in Fig. 1. The overlapped peaks are divided into a few individual peaks by the application of a selected ion-

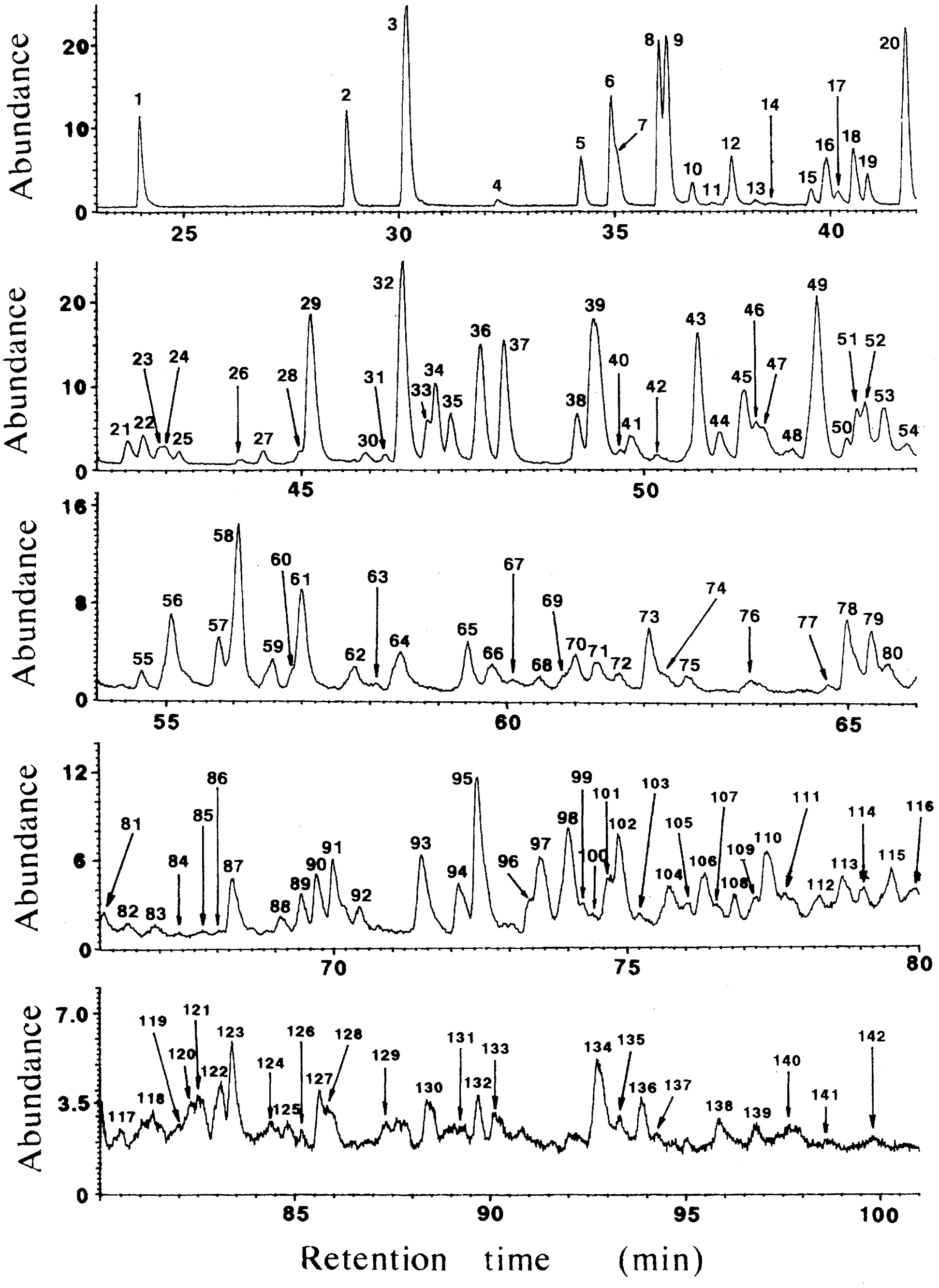

Fig. 1. Total ion chromatogram of initial recycle solvent.

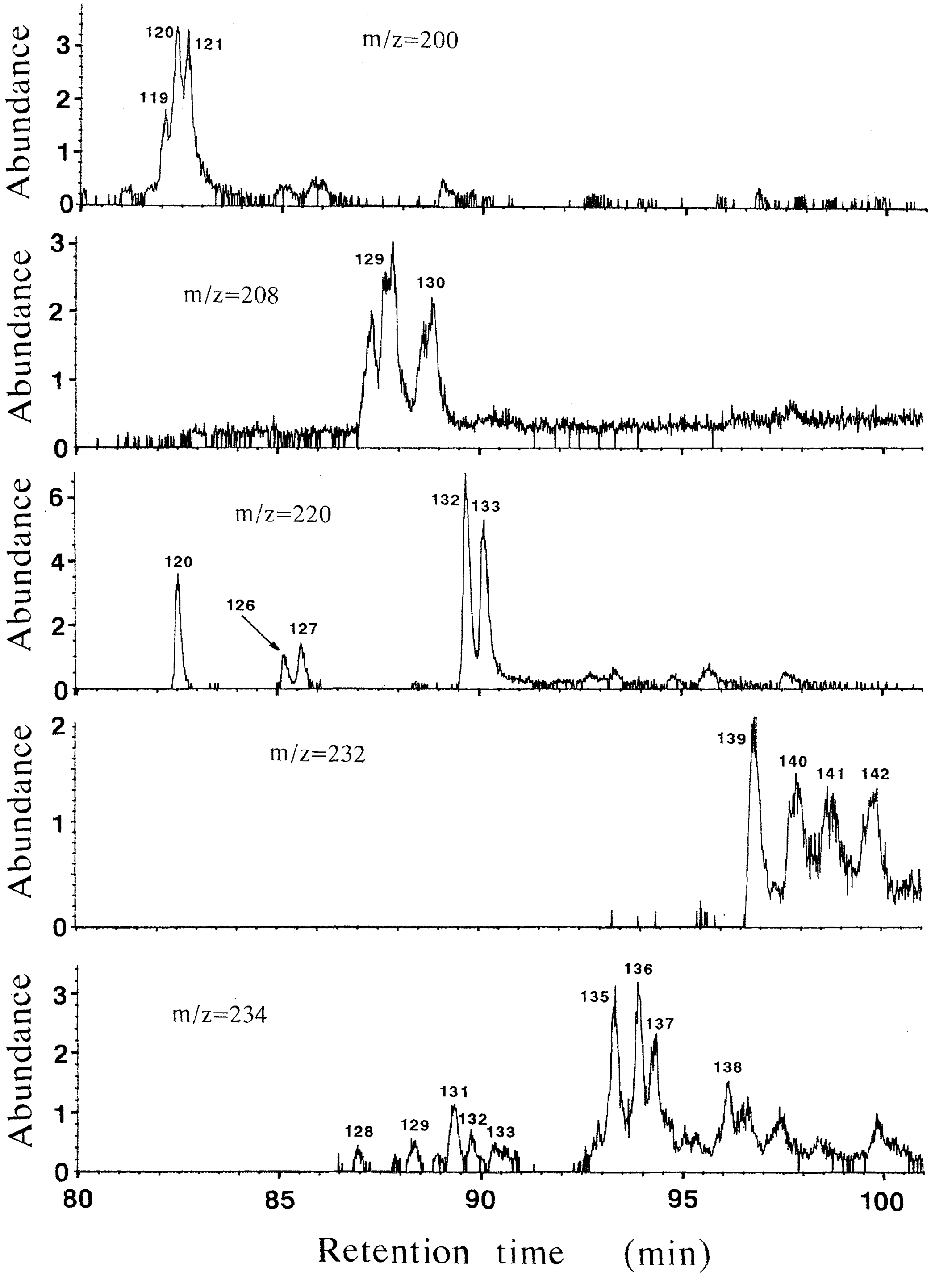

Fig. 2. Single ion chromatograms of initial recycle solvent.

monitoring method. The assignments or postulations to considerable structures are listed in Table 2; the summarized data presented in Table 2 are given in Table 3.

Although there exist 142 peaks on the total ion chromatogram, the selected ion-monitoring data indicate the presence of 325 compounds in this fraction. These 327 compounds can be divided into nine compound types of which the molecular weights were represented by $94+14n$, $134+14n$, $144+14n$, $170+14n$, $174+14n$, $182+14n$, $194+14n$, $218+14n$, and $220+14n$.

The MW $94+14n$ compound type was abundant in this fraction and was assigned as phenols. Many compounds of this type have been identified by comparing the mass spectra and retention times with those of synthesized standard phenols.13) Figure 3 A shows the mass spectrum of the compound with MW of 94 (peak 1 in Fig. 1). The spectrum and retention time of this compound coincided with phenol.

The MW $134+14n$ compound type was also abundant and was assigned as indanols because of the existence of 4- and 5-indanols in this fraction. 12 isomers exist for methylindanols,

Table 2. Acidic Compounds Identified in Recycle Solvent

Peak No.	MW	RT min	Assignment or possible structure	Abundance (wt%) Init.	Abundance (wt%) Final
1	94	23.98	Phenol	0.905	0.243
2	108	28.81	2-Methylphenol	0.293	0.166
3	108	30.17	3-Methylphenol	0.482	0.266
	108	22	4-Methylphenol	0.368	0.375
4	122	32.30	2,6-Dimethylphenol	0.024	0.046
5	122	34.23	2-Ethylphenol	0.120	0.122
6	122	79	2,4-Dimethylphenol	0.260	0.219
7	122	93	2,5-Dimethylphenol	0.128	0.117
8	122	36.03	3-Ethylphenol	0.350	0.146
9	122	20	4-Ethylphenol, 3,5-Dimethylphenol	0.479	0.323
10	122	79	2,3-Dimethylphenol	0.048	0.047
11	136	37.28	2-Ethyl-6-methylphenol	0.005	0.018
12	122	71	3,4-Dimethylphenol	0.103	0.025
13	136	38.28	2-(1-Methylethyl)phenol	0.007	0.101
14	136	62	2,4,6-Trimethylphenol	0.007	—
15	136	39.55	2-Propylphenol	0.027	0.049
16	136	91	2,3,6-Trimethylphenol	0.104	0.078
17	136	40.18	4-(1-Methylethyl)phenol	0.008	0.027
18	136	55	3-(1-Methylethyl)phenol	0.099	0.078
19	136	86	Ethylmethylphenol	0.046	0.036
20	136	41.76	4-Propylphenol	0.467	0.194
21	136	42.43	2,4,5-Trimethylphenol	0.021	0.018
22	136	66	Ethylmethylphenol	0.030	0.014
23	136	91	2,3,5-Trimethylphenol	0.009	0.008
24	136	97	Ethylmethylphenol	0.022	0.016
25	150	43.06	2-(1,1-Dimethylethyl)-phenol	0.001	0.010
26	150	44.09	4-(1,1-Dimethylethyl)-phenol	0.005	0.008
27	136	46	2,3,4-Trimethylphenol	0.008	—
	150	48	2,3-Diethylphenol	0.003	—
28	150	80	3-(1-Methylpropyl)phenol	0.002	0.006
	150	98	4-(1-Methylpropyl)phenol	0.014	0.027
29	134	45.13	4-Indanol	0.362	0.272
	150	20	2-Methyl-5-(1-methylethyl)phenol	0.013	—
	150	29	C_4-Phenol	0.004	—
30	150	94	2-Methyl-4-(1-methylethyl)phenol	0.018	0.034
31	150	46.22	2-Methyl-3-(1-methylethyl)phenol	0.005	0.036
32	134	48	5-Indanol	0.432	0.289
33	150	84	2,3,5,6-Tetramethylphenol	0.052	0.103
34	150	96	2,3,4,6-Tetramethylphenol	0.134	0.342
35	148	47.18	Methylindanol/Tetrahydronaphthol	0.022	0.212
36	148	56	Methylindanol/Tetrahydronaphthol	0.055	0.252
	150	62	4-Butylphenol	0.255	0.327
37	150	97	3-Butylphenol	0.056	0.127
	148		Methylindanol/Tetrahydronaphthol	0.210	0.547
38	164	48.88	C_5-Phenol	0.004	0.025
	148	49.03	Methylindanol	0.078	0.130
	162		C_2-Indanol	—	0.001
39	148	27	Methylindanol	0.171	0.495
	162		C_2-Indanol	0.014	—
	148	31	Methylindanol	0.256	0.370
40	162	66	C_2-Indanol	0.010	0.120
41	164	80	C_5-Phenol	0.050	0.411
42	164	50.17	C_5-Phenol	0.007	0.014
	162	34	C_2-Indanol	—	0.058
	162	67	C_2-Indanol	0.011	0.129
43	148	79	Methylindanol	0.215	0.745
44	148	51.10	Methylindanol	0.031	0.231
	164		C_5-Phenol	—	0.033
45	148	47	Methylindanol	0.091	0.332
	162		C_2-Indanol	0.020	0.088
46	164	65	C_5-Phenol	0.033	0.419
47	162	78	C_2-Indanol	0.041	0.012
	148		Methylindanol	—	0.117
	162	90	C_2-Indanol	0.006	0.004
	164		C_5-Phenol	—	0.008
48	162	52.00	C_2-Indanol	0.020	—
	162	11	C_2-Indanol	—	0.031
	164		C_5-Phenol	—	0.006
49	162		C_2-Indanol	—	0.035
	148	54	Methylindanol	0.318	0.875
	164		C_5-Phenol	—	0.078
	162		C_2-Indanol	0.019	0.056
50	162	98	C_2-Indanol	0.030	0.127
51	162	53.03	C_2-Indanol	—	0.005
	164	13	C_5-Phenol	0.039	0.055
52	162	25	C_2-Indanol	0.069	0.430
53	164	43	C_5-Phenol	0.005	0.026
	148	53	Methylindanol	0.062	0.301
54	162	85	C_2-Indanol	0.016	0.097
	178	54.16	C_6-Phenol	—	0.002
55	162	64	C_2-Indanol	0.015	0.065
	176		C_3-Indanol	—	0.010
56	162	55.07	C_2-Indanol	0.092	0.220
	148		Methylindanol	0.020	0.046
	162	20	C_2-Indanol	—	0.152
	178	28	C_6-Phenol	—	0.001
57	144	66	1-Naphthol	0.009	0.066
	162	78	C_3-Indanol	0.013	0.268
	176		C_3-Indanol	0.003	0.028
58	144	55.99	2-Naphthol	0.106	0.067
	170	56.07	2-Phenylphenol	0.155	0.585
	162	25	C_2-Indanol	—	—
	178		C_6-Phenol	—	0.017
	176		C_3-Indanol	—	0.032
59	162	51	C_2-Indanol	0.007	0.037
	178		C_6-Phenol	0.001	0.004
	184	58	Methyl-2-phenylphenol	0.006	0.160
60	178	82	C_6-Phenol	0.008	0.043
61	162	57.00	C_2-Indanol	0.133	0.180
	176	26	C_3-Indanol	—	0.069
	176	43	C_3-Indanol	—	0.014
62	178	60	C_6-Phenol	—	0.021
	162	65	C_2-Indanol	0.001	0.225
	176		C_3-Indanol	—	0.020
	176	78	C_3-Indanol	0.008	0.038
	162		C_2-Indanol	0.011	0.046
	162		C_2-Indanol	—	—
63	184	58.08	Methyl-2-phenylphenol	—	0.017

Table 2. (Continued).

Peak		RT		Abundance (wt%)	
No.	MW	min	Assignment or possible structure	Init.	Final
	162		C_2-Indanol	—	—
64	176	34	C_3-Indanol	0.006	0.025
	176	44	C_3-Indanol	0.002	0.004
	178		C_6-Phenol	0.024	0.044
	162		C_2-Indanol	0.007	—
	176	54	C_3-Indanol	—	0.012
	178		C_6-Phenol	—	0.006
	176	68	C_3-Indanol	—	0.008
	176	85	C_3-Indanol	—	0.020
65	176	59.23	C_3-Indanol	—	0.023
	176	43	C_3-Indanol	0.024	0.032
	178		C_6-Phenol	0.007	0.008
	177		Dimethylphthalide	—	—
66	176	69	C_3-Indanol	—	0.018
	176	79	C_3-Indanol	0.026	0.071
67	162	60.04	C_2-Indanol	—	0.080
68	174	32	Tetrahydroacenaphthenol	—	0.037
	176	50	C_3-Indanol	0.007	0.026
	190		C_4-Indanol	—	—
69	176	85	C_3-Indanol	—	0.020
	158		Methylnaphthol	—	0.073
70	184	61.01	Methyl-2-phenylphenol	0.023	0.149
	176		C_3-Indanol	—	0.028
	158		Methylnaphthol	0.044	—
	158		Methylnaphthol	—	—
71	158	61.29	Methylnaphthol	0.066	0.056
	176		C_3-Indanol	—	0.004
	174		Tetrahydroacenaphthenol	—	0.007
72	184	65	Methyl-2-phenylphenol	0.018	0.117
	176		C_3-Indanol	0.007	0.062
73	176	62.07	C_3-Indanol	0.058	0.086
74	158	30	Mehthylnaphthol	0.055	0.097
75	174	57	Tetrahydroacenaphthenol	—	0.019
	190	91	C_4-Indanol	—	0.010
	190	63.18	C_4-Indanol	0.002	0.004
	192	44	C_7-Phenol	0.009	—
76	174	69	Tetrahydroacenaphthenol	—	0.005
	188		Tetrahydromethyl-acenaphthenol	—	0.006
	188	88	Tetrahydromethyl-acenaphthenol	—	0.004
	184	64.05	Methyl-2-phenylphenol	—	0.014
	174	39	Tetrahydroacenaphthenol	—	0.013
77	190	68	C_4-Indanol	0.006	0.019
78	170	97	3-Phenylphenol	0.075	0.071
	190		C_4-Indanol	0.006	0.007
	172		C_2-Naphthol	0.005	0.008
	188	65.08	Tetrahydromethyl-acenaphthenol	—	0.015
79	190	17	C_4-Indanol	0.006	0.014
	170	33	4-Phenylphenol	0.084	0.026
80	184	58	Methyl-4-phenylphenol	0.026	0.042
	174		Tetrahydroacenaphthenol	—	0.034
	190		C_4-Indanol	0.009	0.016
	172		C_2-Naphthol	0.005	0.015
	190	78	C_4-Indanol	—	0.006
81	172	66.06	C_2-Naphthol	0.008	0.029
	188		Tetrahydromethyl-acenaphthenol	—	0.012
	184		Methylphenylphenol	0.007	0.010
82	188	34	Tetrahydromethyl-acenaphthenol	—	0.027
	190	42	C_4-Indanol	0.004	0.017
83	172	82	C_2-Naphthol	0.005	0.016
	172	98	C_2-Naphthol	—	0.013
84	172	67.30	C_2-Naphthol	0.005	0.002
85	188	60	Tetrahydromethyl-acenaphthenol	—	0.002
86	188	95	Tetrahydromethyl-acenaphthenol	—	0.001
	172	68.00	C_2-Naphthol	0.003	0.002
87	184	26	Methylphenylphenol	0.042	0.006
	172		C_2-Naphthol	—	0.001
88	184	69.09	Methylphenylphenol	0.017	0.105
89	184	45	Methylphenylphenol	0.020	0.089
90	184	71	Methylphenylphenol	0.036	0.087
	202		Tetrahydro-C_2-acenaphthenol	—	0.019
91	184	69.99	Methylphenylphenol	0.053	0.041
92	184	70.45	Methylphenylphenol	0.008	0.010
93	198	71.28	C_2-Phenylphenol	—	0.002
	186		C_3-Naphthol/Biphenyl-diol	0.019	0.012
	184	50	Methylphenylphenol	0.078	0.016
	186		C_3-Naphthol/Biphenyl-diol	0.024	0.011
	198		C_2-Phenylphenol	—	0.004
94	184	72.13	Methylphenylphenol	0.037	0.006
95	184	46	Methylphenylphenol	0.142	0.032
	186		C_3-Naphthol/Biphenyl-diol	0.006	—
	198	60	C_2-Phenylphenol	0.025	0.008
96	198	73.35	C_2-Phenylphenol	0.025	0.008
97	182	53	Fluorenol	0.037	0.020
	198		C_2-Phenylphenol	0.065	0.029
	196	74	Methylfluorenol	0.003	0.002
98	198	93	C_2-Phenylphenol	0.056	0.038
	198	74.01	C_2-Phenylphenol	0.008	—
	182		Fluorenol	0.077	0.041
99	198	24	C_2-Phenylphenol	0.017	0.011
100	182	38	Fluorenol	0.002	0.018
	198	47	C_2-Phenylphenol	0.007	0.006
	214		C_5-Naphthol/C_2-Biphenyl-diol	0.025	—
101	196	78	Methylfluorenol	0.025	0.011
102	182	86	Fluorenol	0.079	0.028
	198		C_2-Phenylphenol	—	0.002
	198	75.20	C_2-Phenylphenol	—	0.001
103	196	40	Methylfluorenol	0.004	0.003
	212		C_3-Phenylphenol	—	0.002
104	198	74	C_2-Phenylphenol	0.045	0.014
	196		Methylfluorenol	0.010	0.008
	198	82	C_2-Phenylphenol	—	0.010
105	198	76.04	C_2-Phenylphenol	0.007	0.010
	196		Methylfluorenol	0.012	0.002
	212		C_3-Phenylphenol	—	0.002
106	198	33	C_2-Phenylphenol	0.252	0.024
107	198	54	C_2-Phenylphenol	0.024	—
	210	61	C_2-Fluorenol	—	0.002
108	198	83	C_2-Phenylphenol	0.052	0.012
109	212	77.21	C_3-Phenylphenol	0.022	—
	198		C_2-Phenylphenol	—	0.009
110	198	40	C_2-Phenylphenol	0.080	0.029

Table 2. (Continued).

Peak		RT		Abundance (wt%)	
No.	MW	min	Assignment or possible structure	Init.	Final
	212		C$_3$-Phenylphenol	0.043	0.024
111	198	71	C$_2$-Phenylphenol	0.035	0.018
	212	78	C$_3$-Phenylphenol	0.009	—
112	196	78.18	Methylfluorenol	0.012	0.019
	210		C$_2$-Fluorenol	—	0.001
	212	30	C$_3$-Phenylphenol	0.022	0.007
	212	46	C$_3$-Phenylphenol	0.013	—
	186		C$_3$-Naphthol/Biphenyl-diol	0.008	0.008
	214		C$_5$-Naphthol/Biphenyl-diol -Biphenyl-diol	—	0.012
	200		C$_4$-Naphthol/Methyl -biphenyl-diol	—	0.001
113	212	69	C$_3$-Phenylphenol	0.009	0.004
	186		C$_3$-Naphthol/Biphenyl-diol	0.017	0.016
	196		Methylfluorenol	0.018	0.023
	200		C$_4$-Naphthol/Methyl – -biphenyl-diol	—	0.003
114	196	96	Methylfluorenol	—	0.010
	196	79.06	Methylfluorenol	0.018	0.017
	210		C$_2$-Fluorenol	0.007	0.006
115	210	30	C$_2$-Fluorenol	0.005	0.008
	212	40	C$_3$-Phenylphenol	0.006	0.002
	214		C$_5$-Naphthol/C$_2$ -Biphenyl-diol	—	0.010
	196	53	Methylfluorenol	0.012	0.044
116	210	87	C$_2$-Fluorenol	0.011	0.011
	200		C$_4$-Naphthol/Methyl -biphenyl-diol	—	0.004
	212		C$_3$-Phenylphenol	—	0.004
	210	94	C$_2$-Fluorenol	0.010	0.003
	196		Methylfluorenol	0.021	0.016
	210	80.00	C$_2$-Fluorenol	0.004	—
	196	27	Methylfluorenol	0.006	0.004
117	196	47	Methylfluorenol	0.005	0.003
	212	55	C$_3$-Phenylphenol	0.010	0.004
	212	88	C$_3$-Phenylphenol	0.007	0.007
	226		C$_4$-Phenylphenol	0.004	0.003
	212	81.04	C$_3$-Phenylphenol	0.014	—
	210	13	C$_2$-Fluorenol	0.007	0.001
		28		0.019	—
	212		C$_3$-Phenylphenol	—	0.008
	226	33	C$_4$-Phenylphenol	0.007	0.002
118	210	55	C$_2$-Fluorenol	0.003	0.002
	226	90	C$_4$-Phenylphenol	0.007	0.004
	214		C$_5$-Naphthol/C$_2$-Biphenyl -diol	—	0.004
119	210	82.00	C$_2$-Fluorenol	0.002	0.006
	200		C$_4$-Naphthol/Methyl -biphenyl-diol	0.010	0.012
	212	20	C$_3$-Phenylphenol	0.005	0.007
	226		C$_4$-Phenylphenol	0.017	0.009
120	212	32	C$_3$-Phenylphenol	0.003	0.003
	200		C$_4$-Naphthol/Methyl -biphenyl-diol	0.026	0.028
	224	49	C$_3$-Fluorenol	—	0.003
	220		Phenylnaphthalene-ol	0.018	0.007
121	200	82.64	C$_4$-Naphthol/Methyl -biphenyl-diol	0.010	0.012
	214		C$_5$-Naphthol/C$_2$-Biphenyl -diol	0.002	0.003
	210	70	C$_2$-Fluorenol	0.004	0.004
	226	89	C$_4$-Phenylphenol	0.003	—
	224	83.00	C$_3$-Fluorenol	0.002	0.006
122	210	10	C$_2$-Fluorenol	0.013	0.033
123	194	39	Phenanthrenol/Anthracenol	0.039	—
	210	56	C$_2$-Fluorenol	0.003	0.013
	224		C$_3$-Fluorenol	—	0.006
124	210	84.17	C$_2$-Fluorenol	0.015	0.010
	224		C$_3$-Fluorenol	0.008	—
	210		C$_2$-Fluorenol	—	0.004
125	210	76	C$_2$-Fluorenol	0.005	0.006
	224		C$_3$-Fluorenol	0.008	0.011
126	220	85.22	Phenylnaphthalenol	0.004	0.005
	210		C$_2$-Fluorenol	0.001	0.005
127	214	64	C$_5$-Naphthol/C$_2$-Biphenyl -diol	—	0.014
	226		C$_4$-Phenylphenol	—	0.008
	220		Phenylnaphthalenol	0.014	0.005
	210		C$_2$-Fluorenol	—	0.005
128	214	90	C$_5$-Naphthol/C$_2$-Biphenyl -diol	0.034	0.021
	222		C$_2$-Phenanthrenol /Anthracene-ol	—	0.001
	224	86.22	C$_3$-Fluorenol	—	0.003
	222		C$_2$-Phenanthrene-ol /Anthracene-ol	—	0.001
	222		C$_2$-Phenanthrene-ol /Anthracene-ol	—	0.001
	234		C$_1$-Phenylnaphthalenol	0.001	—
		80		—	0.002
	224		C$_3$-Fluorenol	—	0.004
	214	87.08	C$_5$-Naphthol	0.002	—
129	224	20	C$_3$-Fluorenol	0.007	0.005
	224	88.38	C$_3$-Fluorenol	—	0.014
	234		C$_1$-Phenylnaphthalenol	0.003	0.003
130	224	48	C$_3$-Fluorenol	0.021	0.013
	234	86	C$_1$-Phenylnaphthalenol	—	0.002
	222		C$_2$-Phenanthrenol /Anthracenol	—	0.011
131	228	89.15	C$_6$-Naphthol/C$_3$-Biphenyl -diol	0.012	—
	222		C$_2$-Phenanthrene-ol /Anthracene-ol	—	0.008
	234	30	C$_1$-Phenylnaphthalenol	0.007	0.011
132	220	70	Phenylnaphthalenol	0.039	0.039
	234		C$_1$-Phenylnaphthalene-ol	0.002	0.004
133	220	90.14	Phenylnaphthalenol	0.033	0.033
	224		C$_3$-Fluorenol	0.005	0.002
	234		C$_1$-Phenylnaphthalenol	0.002	0.003
	226		C$_4$-Phenylphenol	—	0.009
134	218	92.73	Pyrenol/Fluoranthenol	0.022	—
	234	79	C$_1$-Phenylnaphthalenol	0.004	0.001
135	234	93.28	C$_1$-Phenylnaphthalenol	0.025	0.023
	226	50	C$_4$-Phenylphenol	—	0.008
136	234	86	C$_1$-Phenylnaphthalenol	0.022	0.024
	218		Pyrenol/Fluoranthenol	0.022	—
137	234	94.33	C$_1$-Phenylnaphthalenol	0.015	0.016
138	218	95.87	Pyrenol/Fluoranthenol	0.035	—
	234		C$_1$-Phenylnaphthalenol	0.012	0.003
139	232	96.78	C$_1$-Pyrenol/Fluoranthenol	0.013	0.016

Table 2. (Continued).

Peak No.	MW	RT min	Assignment or possible structure	Abundance (wt%) Init.	Abundance (wt%) Final	Peak No.	MW	RT min	Assignment or possible structure	Abundance (wt%) Init.	Abundance (wt%) Final
	234	97.39	C$_1$-Phenylnaphethalenol	0.001	0.003	141	232	80	C$_1$-Pyrenol/Fluoranthenol	0.008	0.011
	232		C$_1$-Pyrenol/Fluoranthenol	—	0.003		232	99.50	C$_1$-Pyrenol/Fluoranthenol	0.003	0.009
140	232	80	C$_1$-Pyrenol/Fluoranthenol	0.011	0.003	142	232	80	C$_1$-Pyrenol/Fluoranthenol	0.008	0.018
	232	98.50	C$_1$-Pyrenol/Fluoranthenol	0.004	0.008		232	100.24	C$_1$-Pyrenol/Fluoranthenol	—	0.001

Table 3. Structural Summation of Acidic Compounds in Recycle Solvent

Structural type	Abundance (wt%) Init.	Abundance (wt%) Final
C$_1$-Phenols	2.048	1.050
C$_2$-Phenols	1.512	1.069
C$_3$-Phenols	0.902	0.635
C$_4$-Phenols	0.562	1.018
C$_5$-Phenols	0.138	1.074
C$_6$-Phenols	0.040	0.145
C$_7$-Phenol	0.009	—
Total of Phenols	5.211	4.991
Indanols	0.794	0.556
C$_1$-Indanols	1.529	4.650
C$_2$-Indanols/Tetrahydronaphthols	0.522	2.475
C$_3$-Indanols/C$_1$-Tetrahydronaphthols	0.151	0.642
C$_4$-Indanols/C$_2$-Tetrahydronaphthols	0.033	0.090
Total of Indanols/Tetrahydronaphthols	3.209	8.413
Naphthols	0.115	0.132
C$_1$-Naphthols	0.165	0.226
C$_2$-Naphthols	0.031	0.084
C$_3$-Naphthols/Biphenyl-diols	0.073	0.047
C$_4$-Naphthols/C$_1$-Biphenyl-diols	0.046	0.059
C$_5$-Naphthols/C$_2$-Biphenyl-diols	0.063	0.062
C$_6$-Naphthol/C$_3$-Biphenyl-diols	0.012	—
Total of Naphthols/Biphenyl-diols	0.505	0.610
Biphenylols/Acenaphthenols	0.314	0.681
C$_1$-Biphenylols/C$_1$-Acenaphthenols	0.513	0.897
C$_2$-Biphenylols/C$_2$-Acenaphthenols	0.698	0.231
C$_3$-Biphenylols/C$_3$-Acenaphthenols	0.163	0.072
C$_4$-Biphenylols/C$_4$-Acenaphthenols	0.038	0.041
Total of Biphenylols/Acenaphthenols	1.726	1.922
Hexahydroacenaphthylenols	—	0.114
Hexahydro-C$_1$-acenaphthylenols	—	0.065
Hexahydro-C$_2$-acenaphthylenols	—	0.019
Total of Hexahydroacenaphthylenols	—	0.198
Fluorenols	0.195	0.107
C$_1$-Fluorenols	0.146	0.159
C$_2$-Fluorenols	0.071	0.076
C$_3$-Fluorenols	0.051	0.062
Total of Fluorenols	0.463	0.404
Phenylnaphthalenols	0.108	0.088
C$_1$-Phenylnaphthalenols	0.094	0.090
Total of Phenylnaphthalenols	0.202	0.178
Phenanthrene-ols/Anthracenols	0.020	—
C$_1$-Phenanthrenols/Anthracenols	—	—
C$_2$-Phenanthrenols/Anthracenols	—	0.021
Total of Phenanthrenols/Anthracenols	0.020	0.021
Pyrenols/Fluoranthenols	0.079	—
C$_1$-Pyrene-ols/Fluoranthene-ols	0.047	0.068
Total of Pyrenols/Fluoranthenols	0.126	0.068
Total of Acidic Compounds	11.282	16.805

and 12 compounds with MW 148 were also found. However, this compound type was considered to include tetrahydronaphthols in addition to indanols. Figure 3B shows the mass spectrum of a compound with MW of 134 (peak 29 in Fig. 1). The spectrum and retention time of this compound coincided with 4-indanol.

The MW $170+14n$ compound type was present in significant amount and was assigned as biphenylols because of the existence of biphenyl-2-ol, biphenyl-3-ol, and biphenyl-4-ol. This compound type was considered to include acenaphthenols. Figure 3C shows the mass spectrum of a compound with MW of 170 (peak 58 in Fig. 1). The spectrum and retention time coincided with biphenyl-2-ol.

The MW $144+14n$ compound type was present in moderate amount, and was assigned as naphthols because of the existence of 1- and 2-naphthols. However, this compound type was considered to include biphenyl-diols. The authors have previously reported[14] the existence of biphenyl-diols in the acidic fraction from coal and thiolignin by using the reaction with trimethylsilyl. Table 3 shows that the total yield of compounds with MW of 186 is larger than the total yield of compounds with MW of 172 for the initial solvent, which indicates the possibility that the fraction with MW of 186 includes biphenyl-diols in addition to C$_3$-naphthols. Figure 3D shows the mass spectrum of a compound with MW of 144 (peak 58 in Fig. 1). The mass spectrum and retention time of this compound coincided with 2-naphthol. Figure 3E shows the mass spectrum of a compound with a MW of 186 (peak 93 in Fig. 1) as the subtracted spectrum between overlapped compounds. We could not assigned the structure of this compound from its spectrum. The concentration of each compound with MW of $186+14n$ was too low to apply the reaction with trimethylsilyl.

In order to clarify the structures of unknown phenolic compounds, a catalytic dehydroxylation technique has been developed by the authors:[15] a combination of hydrogenation of the aromatic rings of phenolic compounds, subsequent release of the hydroxy groups, dehydrogenation of the naphthenic rings, and structural analysis of the aromatic compounds. Biphenyls, acenaphthenes, fluorenes, phenanthrenes, phenylnaphthalenes, pyrenes, fluoranthenes, and their alkylated compounds were found in the dehydroxylated product of the acidic fraction from coal liquid.[15] The remaining five compound types can be analyzed by considering these results.

The MW $182+14n$ compound type was present in moderate amount and was considered to be fluorenols. Fluorenol contains four isomers and four compounds with MW, of

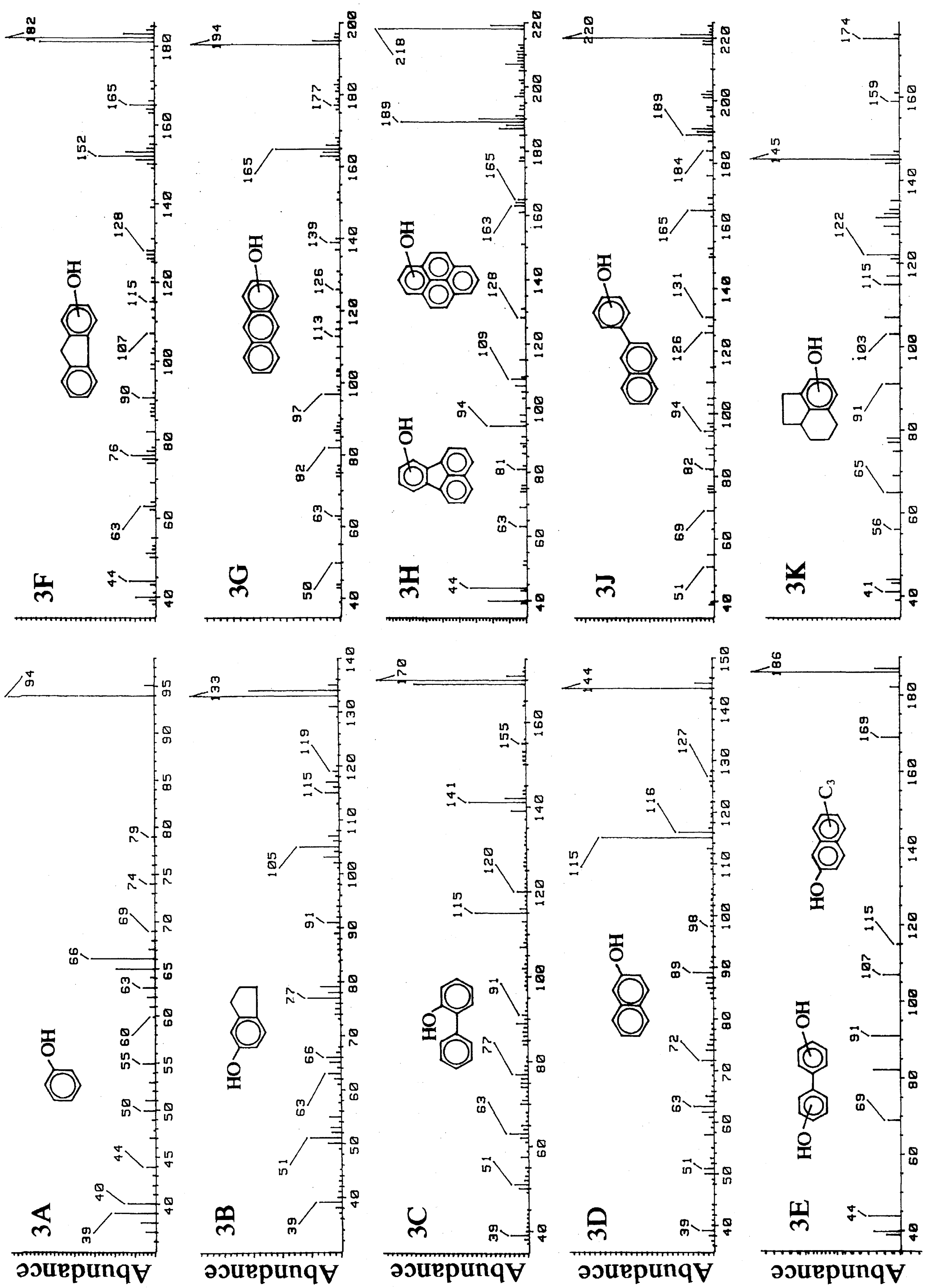

Fig. 3. Mass spectra of typical compound of each type.

which 182 were also found in this fraction. Figure 3F shows the mass spectrum of a compound with MW of 182 (peak 102 in Fig. 1). This spectrum includes a sub-peak with m/z of 152, smaller by 29 than the parent ion, which accord with phenol (Fig. 3A), biphenyl-2-ol (Fig. 3C), and 2-naphthol (Fig. 3D) and indicates that this compound is fluorenol.

The MW $194+14n$ compound type was present in a very small amount and was considered to be phenanthrenols/anthracenols. Figure 3G shows the mass spectrum of a compound with a MW of 194 (peak 123 in Fig. 1). Although the mass spectrum of this compound was very similar to that of anthracene-9-ol, the retention time did not agreed with these two compounds, which suggests that this compound is an isomer of anthracene-9-ol.

The MW $218+14n$ compound type is present in a small amount and is considered to be pyrenols/fluoranthenols. Figure 3H shows the mass spectrum of a compound with a MW of 218 (peak 134 in Fig. 1). This spectrum also includes a main peak with a m/z of 189, smaller by 29 than parent ion, indicating that this compound is pyrenol or fluoranthenol.

The MW $220+14n$ compound type was present in a small amount and was considered to be phenylnaphthalenols. This compound type has been rarely found in a liquid derived from coal liquefied with toluene as the solvent, suggesting that it is formed by the condensation of naphthalene, i.e., tetralin deprived of hydrogen, and phenols.[15] Figure 3J shows the mass spectrum of a compound with a MW of 220 (peak 132 in Fig. 1). Because the concentration of an individual compound of this type was very low, a clear mass spectrum was not obtained.

The MW $174+14n$ compound type was present only in the final solvent in a small amount, and was considered to be hexahydroacenaphthylenols. Figure 3K show the mass spectrum of a compound with a MW of 174 (peak 75 in Fig. 1). This spectrum also includes a main peak with a m/z of 145, smaller by 29 than the parent ion.

In addition to the mass spectrum, the retention time is sometimes useful to consider regarding whether the structural assignment is correct or not. Figure 4 shows the relation between the compound type and the retention time. When compared on the similar range of MW, the retention time increases in the following order: (1) monocyclic and monoaromatic compounds [Phenols], (2) condenced bicyclic and monoaromatic compounds [Indanols], (3) condenced tricyclic and monoaromatic compounds [Hexahydroacenaphthenols], (4) bicyclic and biaromatic compounds [Phenylphenols], (5) condenced bicyclic and biaromatic compounds [Naphthols], and (6) condenced tricyclic and biaromatic compounds [Fluorenols], which accords with the structural assignment in this paper. Figure 4 also indicates that the retention-time range of MW 186 for the compounds in naphthols is fairly broad compared to the ranges of MW 144, 158, and 172 for compounds which support the consideration that the fraction of MW 186 contains C_3-naphthols and biphenyldiols.

The results of this assignment are given in Table 2. Phenolic compounds are rarely found in the conventional oil-base fuels, and are characteristic of a coal-derived liquid. White et al.[16] analyzed the acidic fraction in the recycle stream of the SRC II process to identify a total of 29 types of phenolic compounds. The authors[15] have measured 99 components in the acidic fraction from coal-derived oil. In this study, 327 components in the acidic fraction from recycle solvent were measured by introducing the selected ion-monitoring technique.

In this study a recycle solvent well substituted with coal-

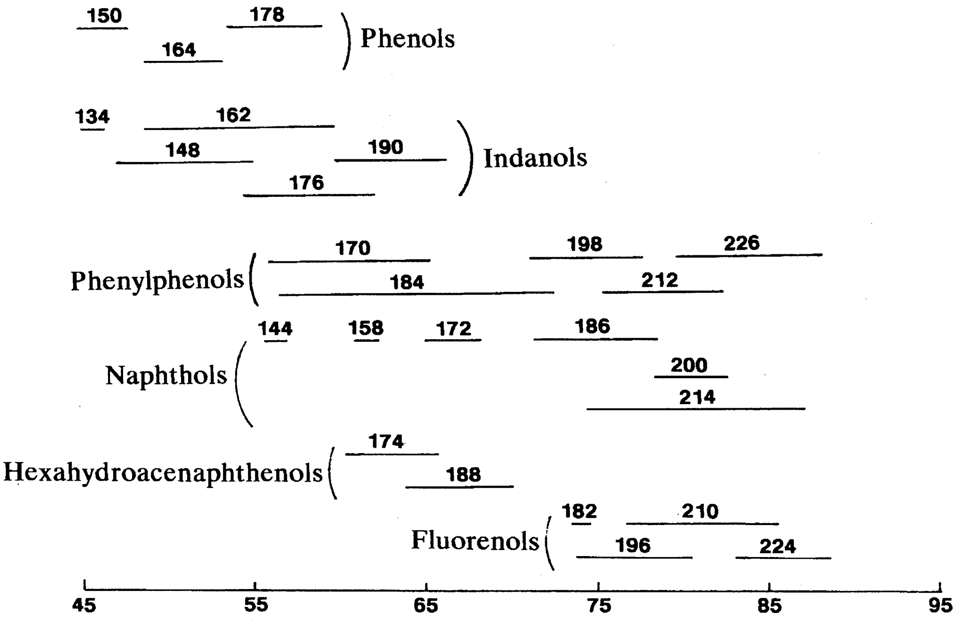

Fig. 4. The relation between compound type and retention time.

derived compounds was utilized in addition to a starting solvent, which made it possible to compare the composition of these two solvents. Table 2 indicates that a larger number of acidic compounds are included in the final solvent (coal liquid) than in the initial solvent (carbonization tar). Table 3 indicates that larger amounts of indanols/tetrahydronaphthols and hexahydroacenaphthylenols are included in the final solvent than in the initial solvent, while the amounts of other compounds, such as phenols, naphthols, biphenylols/acenaphthenols, fluorenols, phenylnaphthalenols, phenanthrenols/anthracenols, are considerably equal between these two solvents. Table 3 also indicates that the final solvent includes greater amounts of multisubstituted compounds or compounds with large alkyl group. These data suggest that coal liquid is more difficult to separate the acidic compounds as chemicals than carbonization tar.

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