

PYROLYSIS OF SOLVENT-REFINED COALS

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Introduction

Solvent-refined coals (SRC) are usually characterized or analyzed after solvent fractionation. The present study demonstrates that a newly developed pyrolysis technique (1) can provide valuable insights to the chemical structure of SRC without fractionation and it allows direct comparison of SRC with raw coal. In addition, the technique can also offer critical evaluation for the process potential of SRC.

Experimental

A Chemical Data Systems Pyroprobe 100 solids pyrolyzer was interfaced to the conventional capillary chromatographic injection port of a Hewlett-Packard 5993 (GC)/MS/DS system, using glass-lined metal tubing. An Alltech 50-meter SCOT SE-30 glass capillary column with 0.5 mm internal diameter was installed in-line with the pyrolysis interface. Volatile degradation products were cold trapped on the head of the capillary column by maintaining the column oven at either 0°C or 10°C. During analysis, the chromatographic oven was programmed using either a 6°C/min or 8°C/min heating rate from the starting temperature to 260°C. The pyrolyzer interface and gas chromatographic injection port were maintained at 240°C and 260°C, respectively. Solid coal samples (about 1 mg) were placed in 3 mm i.d. quartz tubes and these tubes inserted in the pyrolyzer coil. The coil was heated at a rate of 20,000°C/sec and maintained at 1000°C for 10 sec. More detailed information on the experimental arrangement can be found in a previous publication (1).

The three SRC samples, Illinois No. 6, Wyodak, and Kentucky No. 9 were produced from the SRC-I process at the Wilsonville pilot plant. They were ground to -80 U.S. mesh under nitrogen and dried at 100°C under vacuum before the experiment.

Results and Discussion

Total weight loss and the product distribution of Illinois No. 6 and Wyodak solvent-refined coals were compared with that of their parent coals. Wyodak SRC lost the same weight (about 54%) as the untreated coal. Illinois No. 6 SRC had a lower weight loss (about 27%) than its parent coal (about 44%). Kentucky No. 9 SRC produced about 54% volatiles.

Figure 1 shows the total ion chromatograms, for masses 35-450, of the two raw coals. The chromatograms of the three SRCs are shown in Figure 2 over the same mass range as Figure 1. Major components in these figures are identified and they are listed in Table 1. Also included in Table 1 are the retention time, characteristic mass of each component, and the relative peak area to naphthalene. Typical mass spectrometric operating conditions resulted in complete 70 eV mass spectra being obtained every 2 seconds. Since 70 eV electron ionization cross sections of most compounds is constant, the yield given in Table 1 as area relative to naphthalene, should be approximately equivalent to the yield in weight relative to naphthalene. The naphthalene yields of the two raw coals were about 1 µg/mg of coal, and are assumed to be constant for the purposes of this study.

Both Illinois No. 6 and Wyodak SRC show significantly higher alkane and alkene yields. This implies that the SRC process provides a hydrogen-enriched fraction for its product, and this enriched fraction tends to convert to aliphatics during pyrolysis. The conversion of raw coal to these fractions may depend on the severity of

the solvent-refining process. In a recent study on hydropyrolysis of short contact time SRC (2), methane yields were found to be the same as for their parent coals and ethane yields increased considerably.

By comparing Figure 1 and 2, or the data reported in Table 1, it is interesting to note that SRC samples produce higher alkane/alkene ratios, for each C_n , than their parent coals. Again, this may indicate that part of the coal was hydrogenated, at least during a certain period of time, in the cause of the solvent refining reaction.

The three sharp peaks of polynuclear aromatics (No. 45, 46, 47) in Figure 1 marked another significant difference between SRC and its parent coal. The higher conversion to anthracene, phenanthrene, fluoranthene and pyrene confirms an earlier cross-polarization ^{13}C -NMR report (3) that the aromaticity of SRC increases with coal conversion and reaction severity. In addition, the three distinct peaks may also imply that the 3 and 4 fused aromatic rings comprise the basic SRC skeleton and that SRC has more uniform aromatic structure than its parent coal. In Figure 2, the chromatograms of raw coals do not show such distinct PNA peaks. The number of condensed rings in coal is usually estimated based on various NMR techniques and assumptions. The results vary from 2 to 5 fused rings, and the theoretical arguments behind the different 2 results were recently reviewed by Davidson (4). Our study indicates that $Py/(GC)^2/MS$ technique can provide at least complementary information on the aromatic structure of coal and its derivatives.

Our study cannot offer a direct explanation of the fact that aromaticity increases while another part of the coal was hydrogenated during solvent-refining. It should be noted that the technique $Py/(GC)^2/MS$ analyzes only the volatile portion of the sample, and about 50% of the sample remains as char.

Table 1 also indicates that the SRC pyrolysis product contains only a very small amount of sulfur-containing species. This is expected since the solvent-refining process usually removes most sulfur in the coal; Kentucky No. 9, however, still produces significant H_2S and thiophenes. No comparison of this SRC with its parent coal was made in this study.

The SRCs show a notable reduction in CO_2 yield, but the CO and phenol yields are still significant. Other researchers have offered evidence that, while all oxygen functionalities decrease with increasing conversion during solvent-refining, the oxygen remaining in SRC's becomes more and more phenolic (3, 5). In a study of the distribution of oxygen-containing functional groups in SRC, Szladow and Given (6) claimed that ether cleavage was an important step in the early stages of the liquefaction of a bituminous coal with tetralin, and concluded that such ethers would not include diaryl ethers, since these would be too unreactive. The CO and phenol yields in the pyrolysis of SRC indicate (Table 1) that SRC's contain both strong ether linkages and phenolic groups.

Acknowledgement

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References

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TABLE 1. CHARACTERISTIC ION RATIOS MEASURED FOR THE MAJOR DEGRADATION PRODUCTS

Peak Number	Degradation Product	Retention Time (min)	Characteristic Mass Range (m/e)	Degradation Product Yields Relative to Naphthalene				
				Illinois #6	Illinois SRC	Wyodak	Wyodak SRC	Kentucky #9 SRC
1	Methane	3.1	15-16	38.8	78.4	48.5	67.5	164.7
2	Carbon Monoxide	3.1	28	25.2	33.4	63.2	32.4	66.5
3	Carbon Dioxide	3.1	44	7.8	2.22	32.7	3.79	4.15
4	Catbenyl Sulfide	3.2	60	0.46	0.026	0.09	--	0.033
5	Hydrogen Sulfide	3.1	34	0.36	0.038	--	--	0.511
6	Carbon Disulfide	5.4	32, 76	0.38	0.009	--	--	--
7	Benzene	8.3	77-79	2.34	1.40	2.62	1.36	2.64
8	Thiophene	8.5	45, 58, 84	0.32	0.053	--	--	--
9	Toluene	11.2	91-93	2.91	2.02	3.16	1.82	3.87
	<u>Methyl Thiophene</u>		97-99					
10	Isomer #1	11.3		0.341	0.018	0.062	--	0.039
11	Isomer #2	11.6		0.210	0.013	0.035	--	0.020
	<u>Dimethyl Benzene</u>		91-92, 105-106					
12	Isomer #1	13.9		0.193	0.242	0.259	0.235	0.403
13	Isomer #2	14.1		1.063	1.037	1.175	0.939	1.97
14	Isomer #3	14.7		0.396	0.421	0.486	0.418	0.760
	<u>Dimethyl Thiophene</u>		111-113					
15	Isomer #1	14.1		0.108	0.009	0.012	--	--
16	Isomer #2	14.3		0.130	0.005	0.017	--	0.012
17	Isomer #3	14.6		0.085	--	0.011	--	0.006
18	Phenol	16.8	65-66, 94-95	1.14	2.17	1.87	2.59	3.77
19	Naphthalene	21.5		1.00	1.00	1.00	1.00	1.00
20	Benzothiophene	21.7		0.229	--	0.057	--	--
21	C-8 Alkene	12.3	41-43, 55-57	0.105	0.209	0.229	0.616	0.623
22	C-8 Alkene	12.6	41-43, 55-57	0.271	0.128	0.128	0.509	0.758
23	C-9 Alkene	14.9	41-43, 55-57	0.091	0.153	0.214	0.644	0.609
24	C-9 Alkene	15.2	41-43, 55-57	0.088	0.231	0.127	0.560	0.739
25	C-10 Alkene	17.4	41-43, 55-57	0.088	0.201	0.235	0.776	0.609
26	C-10 Alkene	17.7	41-43, 55-57	0.073	0.263	0.119	0.575	0.737
27	C-11 Alkene	19.7	41-43, 55-57	0.075	0.200	0.187	0.716	0.680
28	C-11 Alkene	19.9	41-43, 55-57	0.068	0.235	0.116	0.587	0.754
29	C-12 Alkene	21.8	41-43, 55-57	0.056	0.175	0.132	0.663	0.602
30	C-12 Alkene	21.0	41-43, 55-57	0.094	0.231	0.106	0.588	0.716

Table 1. (continued)

Peak Number	Degradation Product	Retention Time (min)	Characteristic Mass Range (m/e)	Degradation Product Yields Relative to Naphthalene						
				Illinois #6	Illinois SRC	Wyodak	Wyodak SRC	Kentucky #9 SRC		
	<u>Methyl Benzo thiophene</u>		147-148							
31	Isomer #1	23.6		0.060	0.029	0.010	--	0.035		
32	Isomer #2	23.8		0.125	--	0.018	--	0.009		
33	Isomer #3	23.9		0.094	0.051	0.018	--	0.032		
34	Isomer #4	24.0		0.100	--	0.016	--	0.493		
35	Isomer #5	24.2		0.017	--	0.003	--	--		
	<u>Dimethyl Benzo thiophene</u>		161-163							
36	Isomer #1	25.6		0.061	0.016	0.004	--	0.009		
37	Isomer #2	25.7		0.024	--	0.016	--	0.008		
38	Isomer #3	25.8		0.100	--	0.007	--	--		
39	Isomer #4	25.9		0.050	--	0.003	--	0.053		
40	Isomer #5	26.1		0.039	--	0.004	--	--		
41	Isomer #6	26.3		0.022	--	0.009	--	0.024		
42	Dibenzothiophene		184-186	0.091	0.169	--	0.121	0.043		
	<u>Trimethyl thiophene</u>		111, 125-126							
43	Isomer #1			0.094	--	--	--	0.005		
44	Isomer #2			0.034	--	--	--	--		
45	Anthracene & Phenanthrene	32.5	176-179	0.583	5.35	0.345	5.75	2.63		
46	Fluoranthene	36.6	200-203	--	3.73	--	3.55	1.91		
47	Pyrene	37.8	200-203	--	5.83	--	4.42	3.84		

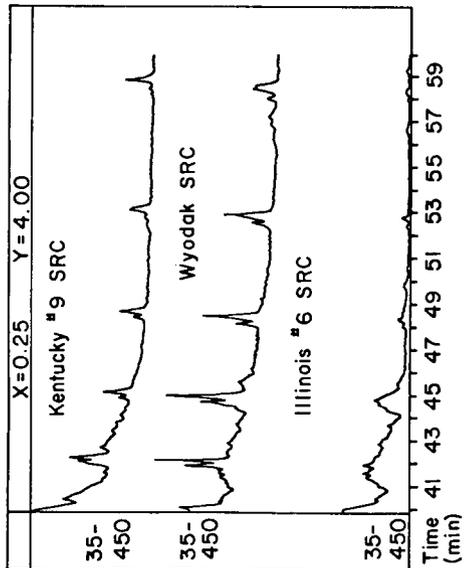
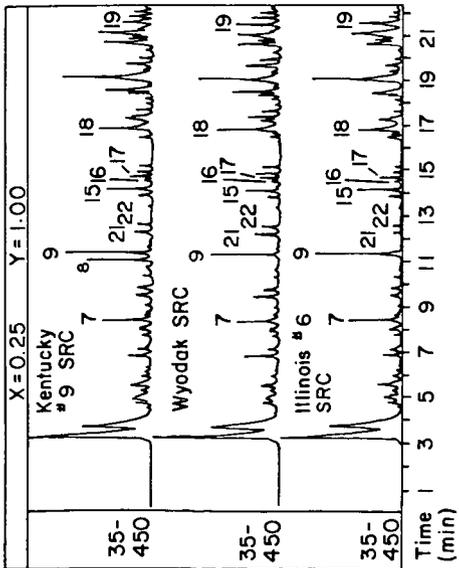
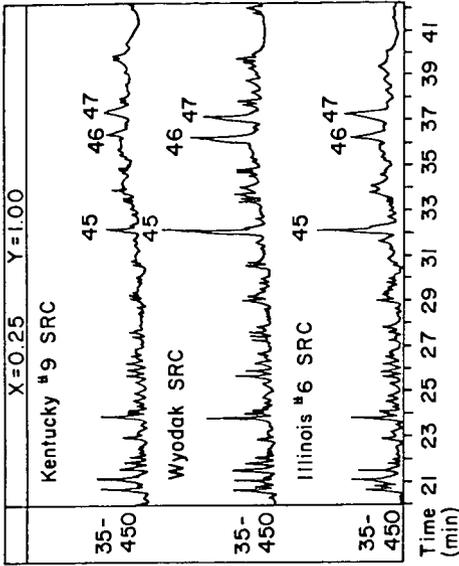


Figure 1. Chromatograms of the three SRC samples.

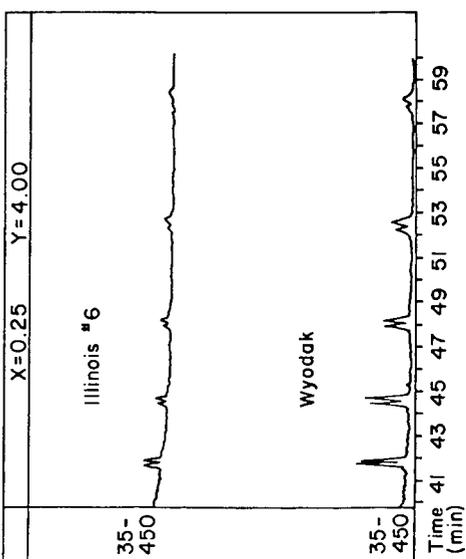
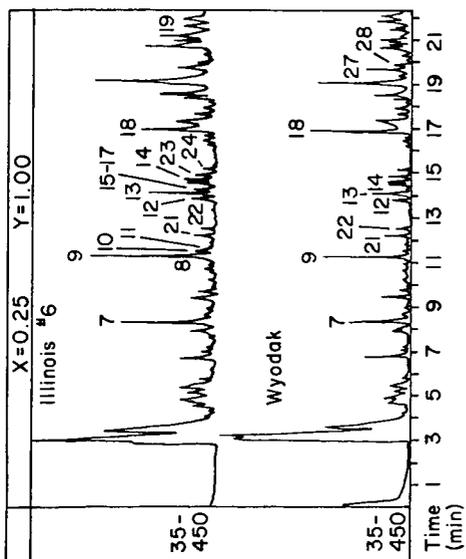
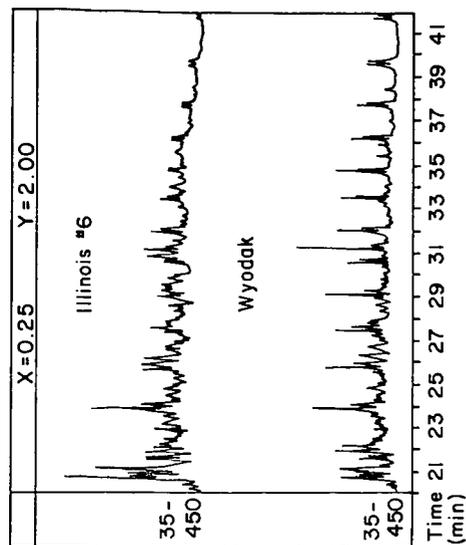


Figure 2. Chromatograms of the Two Raw Coals.