

## ORGANIC VOLATILE MATTER AND ITS SULFUR-CONTAINING COMPOUNDS PRODUCED BY COAL PYROLYSIS

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### INTRODUCTION

The types and distributions of the major components in the volatile matter produced from two types of coal pyrolysis were examined. Batch pyrolysis was used to produce coal tars for fractionation and characterization. Flash pyrolysis, in combination with gas chromatography (GC) analysis, showed a broad distribution of the volatile organics, including sulfur-containing compounds. Further characterization of these volatile sulfur compounds should provide the understanding needed of coal's behavior during thermal processing, an understanding critical for cleaning coal through flash pyrolysis or thermal pre-treatment processes.

### EXPERIMENTAL

**Tar Collection, Separation, and Characterization - Batch Pyrolysis:** About 100 g of coal was pyrolyzed at 450 °C or 600 °C in a Parr reactor (1). The tar was delivered through a heated quartz tube to a collection flask containing a mixture of tetrahydrofuran and dimethoxypropane at -30 °C. After evaporation of the solvents, the tar was fractionated into acid, base, neutral-nitrogen, saturates, and aromatic fractions by ion-exchange, coordination, and adsorption chromatography (SARA) (2). The *n*-paraffins, separated from the saturates by a molecular sieve method (3), were analyzed by GC. Three solvents (5% benzene in pentane, 15% benzene in pentane, and 20% benzene/20% ethyl ether/60% methanol) were used to separate aromatic fractions into three subfraction by column chromatography on alumina. The fractions were designated monoaromatics, diaromatics and polyaromatics, and identified as SAF-1, SAF-2, and SAF-3, respectively (4). Elemental analyses were performed on each subfraction.

**On-line Analysis of Volatile Matter from Flash Pyrolysis:** A Perkin-Elmer 3920B gas chromatograph (GC) with a flame photometric detector (FPD) and a flame ionization detector (FID) and a Dexsil-300 column (programmed for 8 °C/min from 50 °C to 280 °C) was used. Coal volatile matter was produced by a Chemical Data System pyroprobe 190 pyrolyzer in the GC's injection port. Pulverized coal (5 mg to 15 mg) in a 25 mm by 2.4 mm quartz tube was heated at 75 °C/msec in the GC's helium carrier gas flowing at 30 mL/min. Samples were preheated at 100 °C for 30 seconds prior to the first analysis. A given sample was analyzed at 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, and 800 °C. The pyroprobe temperature was held at each temperature for 20 seconds and then it was allowed to return to the injection port temperature during the 37 minutes required for the GC analysis of the volatile matter from each step using the FID. A new coal sample was analyzed at 600 °C with FPD for sulfur compounds.

### RESULTS AND DISCUSSION

**Batch Pyrolysis Products:** The amount of tar obtained from the pyrolysis of six coals (Table 1) varied from 3 to 15 weight percent of the raw coal and the yields were approximately proportional to the H/C atomic ratio of the raw coal. Yields of fractions separated from each coal by the SARA method are also listed in Table 1. The aromatic fraction was generally the largest fraction in the tars. Elemental analysis of the SARA fractions from one coal sample (Table 2) showed most of the nitrogen to be in the base fraction. Sulfur was more evenly distributed but it too was highest in the base fraction.

The C, H, N, and S contents of the three aromatic subfractions are listed in Table 3. The H/C ratio decreased as expected for a progression of increasing aromaticity from monoaromatics (SAF-1) to the polyaromatics (SAF-3). Sulfur in the aromatic fractions was detected only in the polyaromatic subfractions, and this trend was observed both at 450 °C and 600 °C. The nitrogen content within the aromatic subfractions varied in a similar fashion, especially at 600 °C. The lack of sulfur and nitrogen in the monoaromatics and diaromatics fractions may be due a higher ratio of the functional group(s) to carbon atoms in the hydrocarbon portion of the molecule, or to having both sulfur and nitrogen in the same small molecule. Either factor might result in the partitioning of these aromatics into earlier SARA fractions,

possibly the basic fraction. Further study is needed to identify the S and N functional groups and learn more about their positions in the structure of molecules in order to understand the solvent partitioning properties seen in this study and other studies (3, 5). GC/FPD chromatograms of two SAF-3 fractions show most of the sulfur-containing compounds to be in the GC retention time range starting with dibenzothiophene and beyond as expected of a polyaromatic fraction. They also indicated that the distribution of sulfur-containing compounds of the high-sulfur Illinois coal (Figure 1, B) was much more complex than those of the low-sulfur Alabama coal (Figure 1, A).

Patterns among tars for the distribution of  $n$ -paraffins are indicated in Figure 2. The effect of different pyrolysis temperatures (450 and 600 °C) on  $n$ -paraffins distribution of the same coal sample was minor. Calkins et al. (6) who studied flash pyrolysis of pure  $n$ -paraffins and also low-temperature tar showed that  $n$ -paraffins in low temperature tar (<600 °C) were the precursors of light hydrocarbon gases, such as ethylene and propylene, that were produced when the low temperature tar was further subjected to a much higher temperature (700-800 °C) heating. The current results indicated that there was not much more cracking of  $n$ -paraffins at 600 °C than at 450 °C. The distribution of chain lengths appeared to be related to coal rank. As indicated in Figure 2, the major  $n$ -paraffins from lignite were distributed between C<sub>14</sub> and C<sub>21</sub>. The distributions of the major  $n$ -paraffins produced from high volatile bituminous (hvCb) and medium volatile bituminous (mvb) coals were in a relatively narrow carbon number band compared to the broad band obtained from the lignite sample, and they peaked at C<sub>17</sub>. The two pyrolysis temperatures (450 and 600 °C) appeared to induce a similar thermal extraction of  $n$ -paraffins in coal (7,8). The lower rank, less mature LigA contains more longer chain  $n$ -paraffins than the higher rank, relatively more mature hvCb and mvb coals.

Cross Polarization/Magic Angle Spinning (CP/MAS) solid state <sup>13</sup>C NMR has been used to determine the aliphatic and aromatic compositions of the raw coals (9). In this study, three raw coals were analyzed by the CP/MAS NMR. The analysis condition and peak assignment are described elsewhere (10). The percent of total carbon in aliphatic positions was 48% for LigA coal, 54% for the hvCb, and 34% for the mvb coal. Comparison of the NMR data with the  $n$ -paraffins data from batch pyrolysis suggests that more paraffin, algae/resins-derived material (11) is found during the relatively early stages of coalification, and perhaps more branch/cyclic or aromatic associated aliphatic material occurs in coal at later stages of coalification. The NMR analysis does not distinguish among these aliphatic types.

**Flash Pyrolysis Products:** Typical step wise pyrolysis GC/FID chromatograms of LigA, hvCb and mvb coals are shown in Figure 3. The chromatograms of these coals indicated that volatilization of heavy hydrocarbons in coal took place mainly between 500 °C and 700 °C. The maximum production appears to be rank dependent. The maximum volatility appears to be lower than 600 °C for lignite, at 600 °C for hvCb coal, and higher than 600 °C for mvb coal (Figures 3a, 3b, and 3c, respectively). These observations are consistent with those of Barker (12) on programmed-temperature pyrolysis of vitrinite of various rank coals. His programs, showing the GC detector response as a function of temperature, indicated a single maximum at 660 °C for higher rank samples and 420 °C for lignite samples.

In the present study, through GC fingerprint analysis, volatile organics were examined in more detail in the C<sub>15</sub>+ region. The components in this region appeared to be less branched for the lignite. The proportion of the long straight chain aliphatic components decreased as the rank of the coal increased from ligA, hvCb, to mvb. These results are consistent with the earlier suggestion that the low-rank coal contained a greater degree of longer chain aliphatic hydrocarbons.

GC chromatograms of volatile organic sulfur compounds produced from flash pyrolysis of three coals at 600 °C were compared. As indicated in Figure 4, the GC fingerprint of products from the high-sulfur Illinois coal (hvCb) was much more complex than those of the low-sulfur Alabama coal (mvb) and the low-sulfur North Dakota lignite (LigA). The GC chromatogram of sulfur compounds from high sulfur Illinois hvBb coal has material with retention times expected of aliphatic sulfides, thiophene, and alkylthiophene isomers. The large envelop fraction at 15 minutes to 40 minutes retention time corresponds to retention times expected of benzothiophene and dibenzothiophene having an array of side chains. Additional high-sulfur Illinois coals were analyzed. Their fingerprints (not shown) indicate that the types of volatile organic sulfur compounds in other Illinois coals were quite similar. They were present in a much greater variety and in larger quantities than those of either the Alabama coal or the North Dakota lignite. The GC/FPD chromatograms obtained from the flash pyrolysis of raw coal were consistent with those of SAF-3 fractions

(Figure 1). They indicated that the distribution of sulfur-containing compounds of the high-sulfur Illinois coal was much more complex than that of the low-sulfur coal. Flash pyrolysis of raw coal with on-line GC/FPD analysis of sulfur volatile matter (Figure 4) showed sulfur-containing compounds as a broad peak in the region corresponding to retention times for benzothiophene (two aromatic rings) and dibenzothiophene (three aromatic rings). The sulfur compounds in the SAF-3 fractions (Figure 1) are better resolved. The absence of sulfur in SAF-1 and SAF-2 (Table 3), despite the presence sulfur compounds in pyroprobe products corresponding to their molecular weight range (Figure 1), suggests that sulfur in this molecular weight range may be in basic nitrogen molecules separated by the SARA method into another fraction.

### SUMMARY AND CONCLUSION

With one exception, the aromatic fraction was the largest fraction isolated. The sulfur-containing compounds were observed to concentrate in the polyaromatic subfraction of the three aromatic subfractions, and this tendency was observed for both 450°C and 600°C samples. This study indicated that the distribution of sulfur-containing organic compounds in the tar produced from the high-sulfur Illinois coal was much more complex than that of the low-sulfur coal. Although there are numerous sulfur compounds in flash pyrolysis products having molecular weights up through those of benzothiophene and dibenzothiophene, sulfur compounds did not appear in the monoaromatics and diaromatics subfractions. We postulate that sulfur in the molecular weight compounds below dibenzothiophene may be in compounds having a basic nitrogen as well. Sulfur as well as nitrogen were the highest in the SARA base fractions as would be expected by this postulate. This would account for the absence of this molecular weight range of sulfur compounds in the SARA aromatic fraction. The nitrogen compounds in batch pyrolysis tars partitioned mainly into the base fraction of the tar, whereas the sulfur-containing compounds were more evenly distributed between the base, neutral-nitrogen, and aromatic fractions. This study also indicated that flash pyrolysis in a pyroprobe is a fast method to screen and compare sulfur-containing compounds produced during thermal treatment of coals of different rank.

The observation that the distributions of *n*-paraffins in tars produced at 450°C or 600°C from a given coal were essentially the same supports the view that these *n*-paraffins are thermal extraction products, not cracking products. The variations in the distributions of the *n*-paraffins from coals of different rank show that the lower rank, less mature LigA contained more longer chain *n*-paraffins than the higher ranks. The NMR spectra of raw coal together with the batch pyrolysis *n*-paraffins GC analysis support the view that algae/resins-derived *n*-paraffinic material occurring during the relatively early stages of coalification may have been converted to branched/cyclic material and ultimately either eliminated as light hydrocarbons or converted to aromatics as coalification progressed toward anthracite. The preponderance of relatively long chain aliphatic hydrocarbons in low-rank coal was also seen in the GC spectra of flash pyrolysis products.

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Table 1. Yields of pyrolysis products from six coal samples

Coal	(seam)	Blue Creek	Herrin (No. 6)	Herrin (No. 6)	Herrin (No. 6)	Springfield (No. 5)	Ft. Union Formation
Coal Sample Number		C-18848	C-18857	C-16501	C-18560	C-16264	C-18440
State		Alabama	Illinois	Illinois	Illinois	Illinois	N. Dakota
Rank		mvb	hvBb	hvBb	hvCb	hvCb	ligA
H/C Atom Ratio (mf)		0.67	1.05	0.85	0.85	0.85	0.78
Type of sample		composite face channel	face channel	composite face channel	column	composite face channel	face channel
Tar Yield (wt %)	450°C	3.2	14.5	10.4	12.1	11.9	7.3
	600°C	3.1	14.6	15.8	12.2	13.8	8.3
Tar Sample No.	450°C	T-18848	T-18857	T-16501	T-18560	T-16264	T-18440
Tar fraction recovered from chromatography (wt%)							
	Acid	10.4	11.7	26.0	11.1	52.2	10.4
	Base	2.5	2.7	1.0	8.6	2.3	5.1
	Neutral-Nitrogen	--	2.4	2.0	10.5	--	3.4
	Saturate	3.9	5.4	9.0	5.7	8.6	8.2
	Aromatic	57.1	24.9	35.0	46.9	27.6	29.9
Tar Sample No.	600°C	T-18848	T-18557	T-16501	T-18560	T-16264	T-18440
Tar fraction recovered from chromatography (wt%)							
	Acid	27.5	10.3	--	9.3	47.9	12.2
	Base	2.0	5.2	--	7.4	4.0	5.1
	Neutral-Nitrogen	--	5.4	--	0.5	--	3.9
	Saturate	3.5	5.6	--	6.1	7.5	14.5
	Aromatic	57.6	39.1	--	49.0	27.6	46.8

-- not determined

Table 2. Elemental analyses acid, base, and neutral-nitrogen, saturate, and aromatic fractions derived from coal sample C18440.

Fraction	Carbon	Hydrogen	Nitrogen	Sulfur	H/C Atom Ratio
Acid	78.75	7.81	0.12	0.56	1.18
Base	77.29	7.73	3.85	1.13	1.21
Neutral-Nitrogen	78.42	8.18	0.38	0.90	1.25
Saturate	79.75	12.22	--	--	1.84
Aromatic	79.50	9.22	0.30	1.05	1.39

-- not determined

Table 3. Elemental analysis of aromatic subfractions

Coal (seam)		Blue Creek	Herrin (No.6)	Springfield (No. 5)
Tar Sample Number		T-18848-450 °C	T-16501-450 °C	T-16264-450 °C
Aromatic Subfraction 1 monoaromatics (eluted with 5% benzene in n-pentane)	Carbon	89.64	87.06	84.24
	Hydrogen	9.77	10.70	11.60
	Nitrogen	trace	0.18	0.21
	Sulfur	--	--	--
	H/C Atom Ratio	1.30	1.46	1.64
Aromatic Subfraction 2 diaromatics (eluted with 15% benzene in n-pentane)	Carbon	89.97	87.26	84.91
	Hydrogen	8.02	8.21	9.03
	Nitrogen	0.23	0.07	0.25
	Sulfur	--	--	--
	H/C Atom Ratio	1.14	1.12	1.27
Aromatic Subfraction 3 polyaromatics (eluted with mixed solvent: 20% benzene, 20% ethyl ether and 60% methanol)	Carbon	85.81	82.48	84.41
	Hydrogen	7.30	7.32	7.44
	Nitrogen	0.53	0.14	0.24
	Sulfur	1.10	2.37	2.37
	H/C Atom Ratio	0.97	1.06	1.05
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Tar Sample Number		T-18848-600 °C	T-16501-600 °C	T-16264-600 °C
Aromatic Subfraction 1 monoaromatics (eluted with 5% benzene in n-pentane)	Carbon	87.25	87.74	86.71
	Hydrogen	9.55	10.20	10.70
	Nitrogen	--	--	--
	Sulfur	--	--	--
	H/C Atom Ratio	1.30	1.39	1.47
Aromatic Subfraction 2 diaromatics (eluted with 15% benzene in n-pentane)	Carbon	90.55	86.14	85.45
	Hydrogen	7.71	7.25	8.01
	Nitrogen	--	--	--
	Sulfur	--	--	--
	H/C Atom Ratio	1.01	1.01	1.12
Aromatic Subfraction 3 polyaromatics (eluted with mixed solvent: 20% benzene, 20% ethyl ether and 60% methanol)	Carbon	86.88	81.90	80.92
	Hydrogen	7.04	6.90	7.81
	Nitrogen	0.35	0.34	0.90
	Sulfur	0.80	3.93	4.29
	H/C Atom Ratio	0.97	1.01	1.15
-- not detectable				

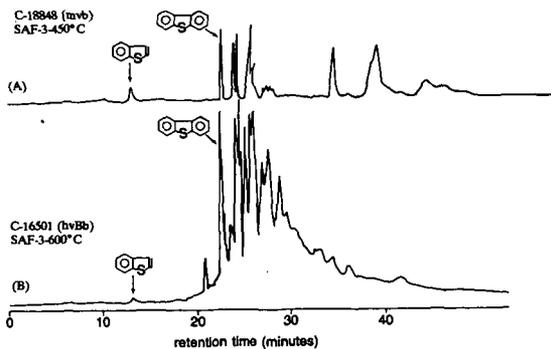


Figure 1. Typical GC/FPD chromatogram of SAF-3 fraction from a low-sulfur Alabama coal (A) and a high-sulfur Illinois coal (B).

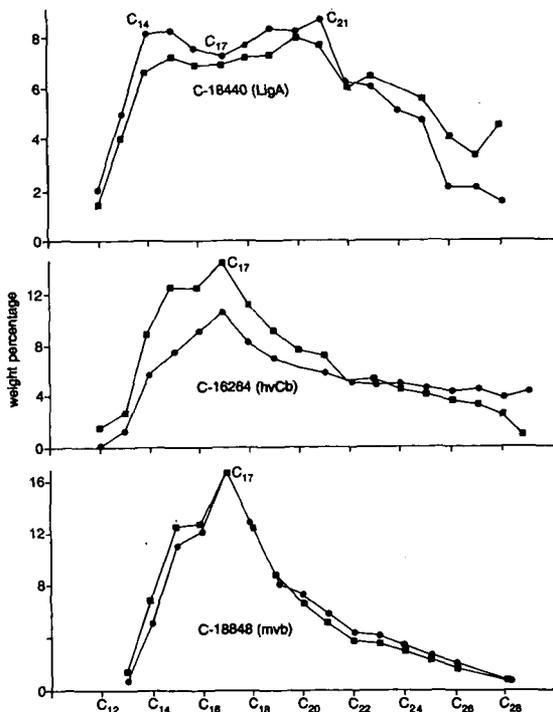


Figure 2. Distribution of n-paraffins obtained from batch pyrolysis three different ranks of coal at 450°C (●) and 600°C (■).

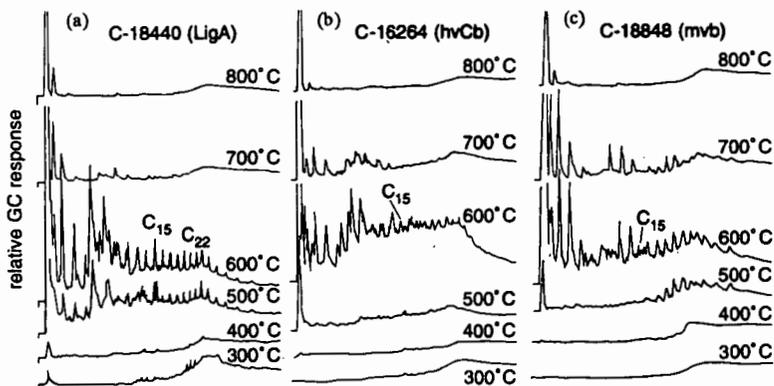


Figure 3. GC/FID chromatogram of organic compounds produced from stepwise flash pyrolysis of three different ranks of coal.

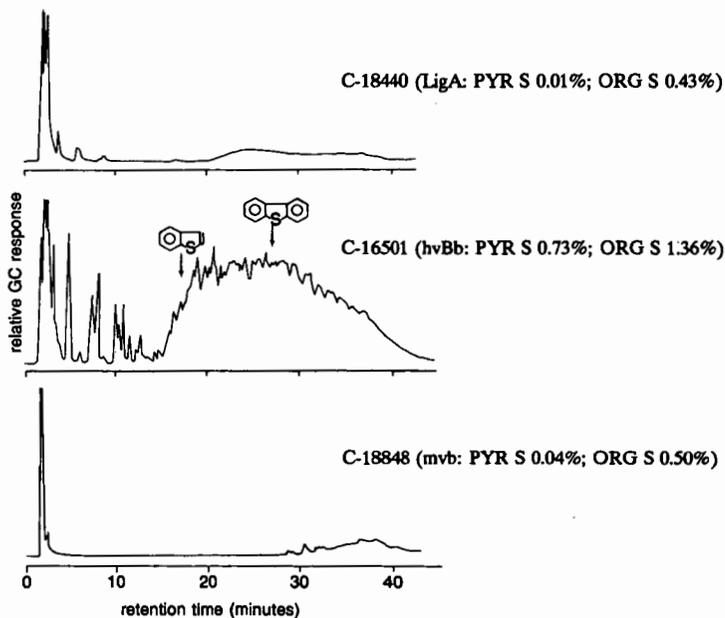


Figure 4. GC/FPD chromatogram of volatile sulfur compounds produced from flash pyrolysis of three different ranks of coal at 600°C.