

## AROMATIC STRUCTURES IN WHOLE COALS AND COAL MACERALS

Randall E. Winans, Ryoichi Hayatsu, Robert L. McBeth,  
Robert G. Scott and Robert E. Botto  
Chemistry Division, Argonne National Laboratory,  
9700 South Cass Avenue, Argonne, IL 60439 USA

### ABSTRACT

New information on the chemical and physical structure of coals and separated coal macerals strongly suggests that polycyclic aromatics do not dominate the aromatic structure except in the very high-rank coals and in inertinites. Two very different approaches have led to these conclusions. First, a very mild, selective oxidation method has been used to break down the coal macromolecular structure into molecules which can be readily characterized. The products are dominated by single ring aromatics. Second, small-angle neutron scattering has been used to study solvent swollen coals. There is no evidence from the scattering data for the existence of a layered structure, instead long tubular pores are being formed apparently as a result of changes in the hydrogen-bonding in the matrix.

### INTRODUCTION

In the past, coal scientists have thought that coal consists mainly of polycyclic aromatic structures. Figure 1 depicts an extreme example. Even recently, three ring aromatics have been proposed as an average aromatic structural unit on the basis of NMR spectroscopic evidence. Our recent findings strongly suggest that polycyclic aromatics are not the most abundant structures in the lower rank bituminous coals as has been previously thought. Our results have significant implications for the development of mild coal-solubilization processes.

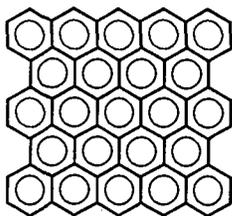


Figure 1. Early thoughts on the aromatic structure of coals.

A major problem in coal characterization and in coal utilization is the intractability of the coal macromolecular network. High temperature treatments yield smaller, volatile and soluble molecules, which can be greatly altered

from their original structures, along with a significant amount of a non-volatile char. Mild oxidation should provide a soluble mixture of compounds in higher yields and with structural characteristics more like the original coal. The approach described here oxidatively cleaves activated benzylic sites which are activated by the formation of pyridinium salts at that carbon from the reaction with pyridine and iodine. This reaction sequence has been described in an initial communication for whole coals (1) and the results of the first reaction step on the macerals have been published (2). This report summarizes the results on the yields of the oxidation step and the characterization of the products (3). Also, a solvent refined coal (SRC) has been reacted to test the selectivity of the method.

A few oxidative degradation studies on separated coal macerals have been published (4-6). In these studies there was extensive oxidation and only small molecules were identified. In this study, both smaller and higher molecular weight fractions, which were separated on the basis of solubility, have been characterized by using gel permeation chromatography (GPC), GCMS, Pyrolysis MS (PyMS) in the precise mass measurement mode, and NMR. Compounds in the higher molecular weight range are not volatile enough for GCMS and are broken down into smaller fragments by PyMS. While rearrangements may occur in PyMS, their likelihood is reduced when pyrolysing the oxidation products in comparison to the whole coals or maceral concentrates. It is interesting to note the remarkable lack of large polycyclic aromatics in the soluble products. The significance of this result will be discussed.

Coal porosity has been studied by SANS in the dry state (7,8,9) and in non-swelling deuterated solvents (7,9). These studies suggested that this technique can be useful for examining pore structure. In the second part of this study, changes in the physical structure of coals upon swelling in an organic solvent have been examined. It is known that bituminous coals will swell in solvents such as pyridine (10). The phenomenon of coal solvent swelling is being used to characterize coal structure, especially in determining molecular sizes between crosslinks. Swelling can affect coal reactivity in thermolysis reactions. Also, it is important to note that swelling increases reagent accessibility in chemical modification of coals (11). SANS is being used in this study to examine the changes in pore structure in a Pittsburgh seam hvA bituminous coal, Argonne Premium Coal Sample #4 (12,13). Two perdeuterated solvents are used, benzene for non-swelling and pyridine for swelling conditions. The deuterated solvent provides a large contrast between the solvent and the solid coal for neutron scattering.

#### EXPERIMENTAL

A description of the coals and SRC is given in Table 1. The Argonne Premium Coal Samples (APCS) have been recently mined and have been stored under nitrogen in sealed glass ampules (14).

The pyridine salts of the samples were prepared by refluxing 1 g of the coal, maceral or polymer in 60 ml of pyridine with 4 g of iodine for 70 hrs (2). The reaction mixture was poured into 10% aqueous NaHSO<sub>3</sub> and the solution filtered. The derivatized coal was washed free of pyridine, dried and analyzed. In a typical oxidation, fresh Ag<sub>2</sub>O prepared from 9.5 g of AgNO<sub>3</sub> and sodium hydroxide, was refluxed with 1.0 g of the substrate in 50 ml of 10% aqueous NaOH

TABLE 1. Characteristics of Coal and Maceral Samples.

Sample	Source	Rank	%C	Empirical Formula	Py <sup>+</sup> /100°C	Ag <sub>2</sub> O Oxidation Yields*	
						Organic Soluble, %	Humic Acid, %
APCS #1	Upper Freeport	mv Bituminous	85.5	C <sub>100</sub> H <sub>66</sub> <sup>N</sup> <sub>1.5</sub> S <sub>0.3</sub> O <sub>6.6</sub>	2.8	27	5
APCS #2	Wyodak-Anderson	Subbituminous	75.0	C <sub>100</sub> H <sub>86</sub> <sup>N</sup> <sub>1.3</sub> S <sub>0.2</sub> O <sub>18.0</sub>	4.1	40	26
APCS #3	Illinois Herrin	hvc Bituminous	77.7	C <sub>100</sub> H <sub>77</sub> <sup>N</sup> <sub>1.5</sub> S <sub>1.1</sub> O <sub>13.0</sub>	3.7	25	34
APCS #4	Pittsburgh	hva Bituminous	83.2	C <sub>100</sub> H <sub>77</sub> <sup>N</sup> <sub>1.7</sub> S <sub>0.4</sub> O <sub>8.0</sub>	3.3	30	30
APCS #8	Beulah-Zap	Lignite	72.9	C <sub>100</sub> H <sub>80</sub> <sup>N</sup> <sub>1.3</sub> S <sub>0.4</sub> O <sub>20.9</sub>	3.6	39	21
SRC	Wilsonville (Pittsburgh coal)		86.9	C <sub>100</sub> H <sub>76</sub> <sup>N</sup> <sub>1.8</sub> S <sub>0.5</sub> O <sub>3.8</sub>	2.6	21	9

\*Based on carbon composition.

for 20 hrs. The silver and unoxidized samples were removed by filtration and the filtrate acidified with aqueous HCl. Products which were alkaline soluble but insoluble in the slightly acidic solution are termed humic acids. The solubles were extracted with Et<sub>2</sub>O-MeOH. Yields were determined by analyzing the products for carbon. The products were methylated with diazomethane for further analysis.

GCMS and PyMS data were obtained on a Kratos MS-25 mass spectrometer. A 60 m x 0.25 mm DB-1701 fused silica column was used in GCMS analysis. The details of the PyMS experiment have been reported (2). The samples were all heated at 50°/min on a platinum screen and the instrument was operated in the precise mass measurement mode.

For the very high resolution experiments, the samples were inserted into an all glass heated inlet system (300°C) and leaked into the source of a Kratos MS 50 ultra high resolution mass spectrometer. A dynamic resolution of 80,000 was obtained for the low voltage (11 eV) electron impact LVHRMS experiment with a scan rate of 1000 seconds/decade. The 70 eV EI spectra were obtained with 50,000 dynamic resolution with a scan rate of 100 seconds/decade. Both spectrometers were operated with a Kratos DS 90 data system. Data were transferred to a Micro VAX II for final analysis.

## RESULTS AND DISCUSSIONS

The yields for the oxidation step are very sample dependent, as is shown in Table 1. The yields are calculated on the basis of carbon content of the starting material and of the products, with the values given being an average of at least two experiments.

Proton NMR data lends support to the observation of the lack of polycyclic aromatics in the products. Since even the solvent-soluble fractions contained compounds which were too large and nonvolatile for GCMS, the proton NMR spectra were taken. The methyl ester region is the most informative and is shown for several coal samples and the SRC sample in Figure 2. From the spectra of a number of known methyl esters, three regions can be assigned: 3.6-3.8 aliphatic, 3.8-4.0 single-ring aromatics and heteroaromatics, and 4.0-4.2 polycyclic aromatics and heteroaromatics. Single-ring aromatics and aliphatics are the most abundant species in these samples, except in the SRC. A general trend is observed in which the relative amount of polycyclic aromatics increases with rank. This observation is important in that it shows that the procedure does not destroy many of the polycyclic aromatics.

Compounds that can be separated by GCMS are mostly benzene and hydroxybenzene carboxylic acids. The total ion chromatograms for subbituminous and Pittsburgh Seam coals are shown in Figure 3. Although this is a fairly mild oxidant, tetra-, penta-, and hexa-carboxylic acids are still formed. Also note that even the hydroxybenzene tetra- and penta-carboxylic acids are formed. More model compounds are being examined to understand this result better. In addition to benzene and hydroxybenzene carboxylic acids, significant amounts of furan carboxylic acids are found in the subbituminous coal.

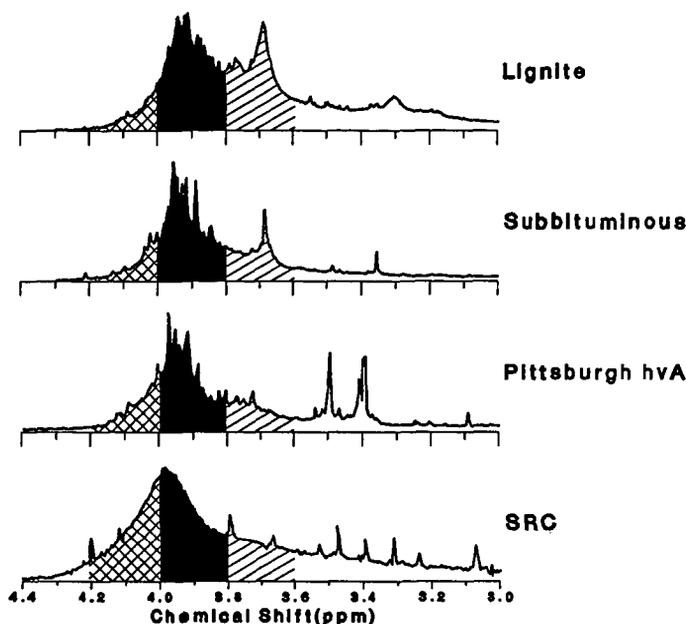
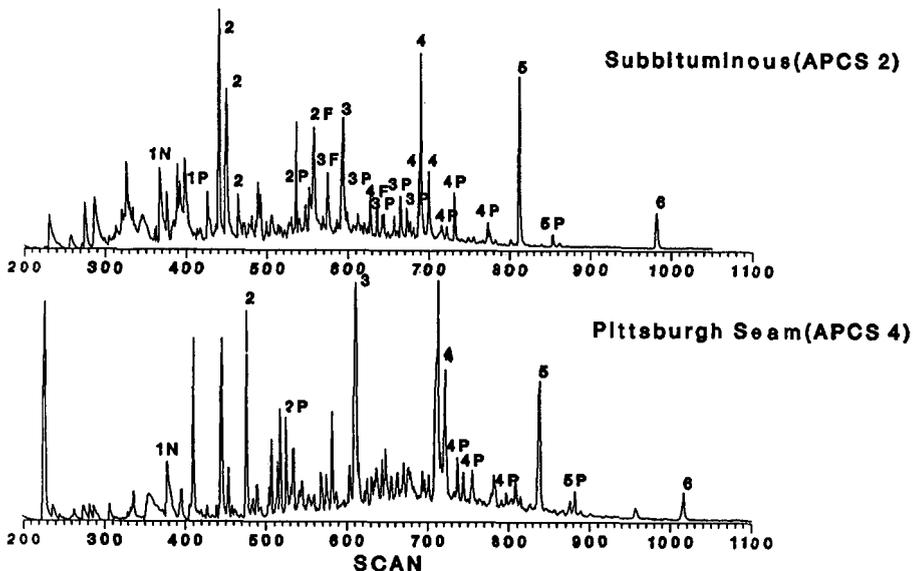


Figure 2. Methyl ester region of the  $^1\text{H}$  NMR spectra of the methylated solvent-soluble fractions from the  $\text{Ag}_2\text{O}$  oxidation recorded on a Nicolet 200 MHz instrument with  $\text{CDCl}_3$  as the solvent. ( / / -aliphatic, ■ -single ring aromatic, ⊗ -polycyclic aromatic.)

Fragments found by PyMS with the premium coal samples and the vitrinites (3) are dominated by aliphatics, single-ring aromatics, and hydroxylated aromatics. PyMS of the humic products results in volatilization at lower temperatures than with the coal. Comparing the pyrolysis products between the two samples, the most striking difference is the reduction in aliphatics in the humic acid fraction. All of these results strongly suggest that, for our vitrinite samples and the coals with a carbon content of less than 83%, the single-ring aromatics dominate. Unlike many other experiments, most of the carbon is characterized with this approach.

From preliminary small-angle neutron scattering results, we conclude that in a good swelling solvent the tertiary structure of this bituminous coal undergoes major rearrangement (12,13). Whereas the original coal contains a broad size range of roughly spherical pores, the swollen coal contains elongated pores with several distinct sizes. The pyridine appears to be determining the new

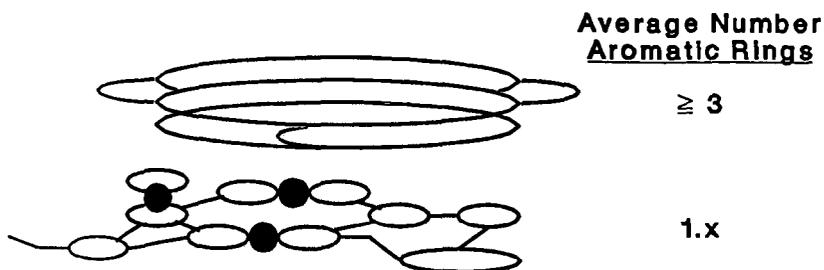


**Figure 3.** Total ion chromatograms of solvent soluble fractions from the Ag<sub>2</sub>O oxidation of two premium coals. Major peaks: 2-6 number of methyl carboxylates on benzene; 1P-5P, on phenol; 1N, on pyridine; 2F-4F, on furan.

pore dimension. Exactly five pyridines can be fitted into a 9 Å radius circle. The size of the pyridine molecule has been estimated from space-filling computer models based on the van der Waals radii of the individual atoms. It is important to note that we are observing relatively narrow elongated pores. These results could be explained by invoking hydrogen bonding between the pyridines and the phenols or other acidic hydroxyls on the surface of the tubular pores. In addition, it is thought from the NMR and ESR experiments that the motion of pyridine in a coal is restricted (15). Our SANS data argues against a layered, polycyclic aromatic structure for this coal.

In summary, the results from both oxidation and SANS strongly suggest that polycyclic aromatics do not dominate the structures of hv bituminous, subbituminous, and lignite coals. These can be contrasted with the calculations made by NMR spectroscopists (16,17) which suggest that the average aromatic ring size is three. This number does not seem to be rank dependent (16) which is a little difficult to rationalize. We know that for vitrinites the starting material is mostly lignin (18) which does not contain polycyclic aromatics. Therefore, one would expect a gradual increase in the amount of polycyclic aromatics in vitrinites with increasing rank. The remnants of lignin are easily identified in low rank coals (19). Our results do not rule out the possibility of microdomains of layered structure, but they do suggest

that stacking of planar polycyclics is unlikely. Figure 4 displays two generalized structural arrangements for coals. The lower one appears to be more likely with hydrogen bonding, represented by the filled circles, playing a critical role in determining the overall structure.



**Figure 4.** Possible coal structural arrangements. Top-stacked polycyclic aromatics, bottom-single ring aromatics with hydrogen bonding.

#### ACKNOWLEDGMENTS

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

#### REFERENCES

1. R. Hayatsu, R. G. Scott, R. E. Winans, R. L. McBeth, and R. E. Botto, Proceedings International Conference on Coal Science, p. 322 (1983).
2. R. E. Winans, R. Hayatsu, R. G. Scott, and R. L. McBeth, in "Chemistry and Characterization of Coal Macerals", Winans, R. E.; Crelling, J. C., Eds., ACS Symposium Series No. 252, ACS:Washington, p. 137 (1984).
3. R. E. Winans, R. Hayatsu, R. L. McBeth, R. G. Scott, and R. E. Botto, Preprints, Div. Fuel Chem., ACS, 31(4), 94 (1986).
4. R. E. Winans, G. R. Dyrkacz, R. L. McBeth, R. G. Scott, and R. Hayatsu, Proceedings International Conference on Coal Science, p. 22 (1981).
5. J. Allan and S. R. Larter, "Advances in Organic Geochemistry 1981", M. Bjoroby, Ed., Wiley:Chichester, U.K., p. 534 (1983).
6. C.-Y. Choi, S. H. Wang and L. M. Stock, *Energy & Fuels*, 2, 37 (1988).

7. H. Kaiser and J. S. Gethner, Proceedings International Conference on Coal Science, p. 300 (1981).
8. M. J. Tricker, A. Grint, G. J. Audley, S. M. Church, V. S. Rainey and C. J. Wright, *Fuel*, **62**, 1092 (1983).
9. J. S. Gethner, *J. Appl. Phys.*, **59**, 1068 (1986).
10. T. Green, J. Kovac, D. Brenner, and J. W. Larsen, in "Coal Structure", R. A. Meyers, Ed., Academic Press, p. 199 (1982).
11. R. Liotta, *Fuel*, **58**, 724 (1979).
12. R. E. Winans and P. Thiyagarajan, Preprints, Div. Fuel Chem., ACS, **32(4)**, 227 (1987).
13. R. E. Winans and P. Thiyagarajan, *Energy & Fuels* (in press).
14. K. S. Vorres and S. K. Janikowski, Preprints, Div. Fuel Chem., ACS, **32(1)**, 492 (1987).
15. B. G. Silbernagel, L. B. Ebert, R. H. Schlosberg, and R. B. Long, in "Coal Structure", M. L. Gorbaty and K. Ouchi, Eds., ACS Adv. Chem. Series, **182**, 23 (1981).
16. B. C. Gerstein, P. D. Murphy, and L. M. Ryan, in "Coal Structure", R. A. Meyers, Ed., Academic Press, p. 87 (1982).
17. M. Solum, R. J. Pugmire, and D. M. Grant, Preprints, Div. Fuel Chem., ACS, **32(4)**, 273 (1987).
18. R. Hayatsu, R. E. Botto, R. G. Scott, R. L. McBeth, and R. E. Winans, *Fuel*, **65**, 821 (1986).
19. R. Hayatsu, R. E. Winans, R. L. McBeth, R. G. Scott, L. P. Moore, and M. H. Studier, in "Coal Structure", Adv. in Chem. Series, No. 192, M. L. Gorbaty and K. Ouchi, Eds., ACS, p. 133 (1981).