

The Macromolecular Structure of Coal- Its Relationship to Diffusion and Reaction Processes in Coals

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INTRODUCTION

Recently, a considerable amount of attention has been directed at understanding how the macromolecular structure of coal influences its reaction behavior. The fact that coal must have a macromolecular structure has been recognized for some time, and has been embodied in many of the "classic" models of coal structure (e.g. refs. 1-5). The recognition that coals will behave accordingly naturally accompanied the development of these models. Van Krevelen² and Kreulen⁶ recognized the colloidal nature of coals and used this to explain many important features of their behavior. Wolfs et al.⁷ demonstrated that certain polymeric substances were good analogs for coal, with respect to pyrolysis behavior. This work remains the cornerstone for many of the sophisticated models of coal pyrolysis behavior today. The development of models of fluidity has long been based on "depolymerization" as a key step (e.g. ref.8). And of course extraction of soluble material from coal has been understood for many years as the segregation of small soluble components from an insoluble matrix which can also be broken down to some extent by thermal decomposition.⁹

What has changed in recent years is mainly the level of understanding of the macromolecular structure of coal, and the number of tools (mostly borrowed from the polymer field) used to study that structure. The review by Green et al.¹⁰ has summarized much of the historical development of the coal macromolecular concept, as it exists today, and discusses many of the tools that have been applied in studying the problem.

The present paper is concerned mainly with some rather specific aspects of the problem of characterization of the macromolecular structure of coals, and their relationship to key reaction processes and physical properties. The main characterization technique used throughout this work is solvent swelling¹¹, as has been used extensively in recent years to characterize the extent of crosslinking in coals¹²⁻¹⁶. This classic technique was originally developed for examination of extents of crosslinking in polymers. The simplest relationship that embodies the essence of the technique is the Flory-Rehner equation, a relationship between the molecular weight between crosslinks in a polymer (M) and the extent to which the polymer is volumetrically swollen by a particular solvent (Q):

$$M = - \left[\frac{\rho_c M_s}{\rho_s} \right] \left[\frac{(1/Q)^{1/3}}{\ln [1-(1/Q)] + (1/Q) + \chi(1/Q)^2} \right]$$

where ρ_c is the density of the original coal, ρ_s is the density of the solvent, M_s is the molecular weight of the solvent and χ is the solvent-network interaction parameter. The measurement of χ is difficult, as is its estimation for specifically interacting solvents such as pyridine. Values range between 0.3 and 0.6 for typical pairs of solvents and coals. It has been suggested that the Flory-Rehner equation does not hold particularly well for coals, which are highly crosslinked rigid networks^{12,13}. Its use here is only illustrative, and more sophisticated approaches have been developed^{17,18}; unfortunately these other approaches require more information about the structure of the coal- namely, the molecular weight of repeat units within the coal structure. Since such information is not readily available at present, this will tend to restrict somewhat the use of these more sophisticated approaches. For the purposes of modeling transport and reaction processes in coals, detailed information about the structure will not always be necessary, and progress can be made without having the exact form of the structure-swelling relationship available. It is in this light that the

present results are presented.

The present paper considers two entirely different aspects of the relationship between macromolecular structure and reactivity and transport in coals. The first aspect concerns the reactions of crosslinking in coals during thermal treatment. This topic has been previously explored using the solvent swelling methodology^{15,16}. Here the work is extended to consider how the colloidal structure of coal is affected by moisture removal, and by further heating. The second aspect concerns the diffusive transport of solvent species in coals, and the activation energies for such processes.

EXPERIMENTAL

The analyses of the coals examined in this study are provided in Table 1. Except where otherwise noted, the coals were ground and sieved to the size range 53-88 μ m. Special care was given to the lignites to avoid any more drying than necessary while processing. The first four samples in Table 1 were judged to have dried to only a limited extent since mining, and all were crushed in-house from large lumps. To prevent drying, these four samples were stored at 100% relative humidity conditions, at room temperature, by suspending the samples above a large reservoir of clean water, in a sealed container. It is of course difficult in practice to maintain truly 100% relative humidity conditions in such a manner, particularly if the chamber must be occasionally opened for sample removal. There was consequently a small difference in measured moisture contents between bed-moist samples (which are effectively immersed storage samples) and those used in this study. The difficulty in characterizing the initial moisture contents of immersed samples was what prompted us to use this slightly different storage method. Related sample storage and characterization information concerning these lignites can be found elsewhere¹⁹.

Thermal treatments of the samples were always performed under inert gas (high purity helium or nitrogen), to avoid any possible role of oxidation in the results. The thermal treatments were performed in either standard tube furnaces, in which the samples were normally heated at low heating rates (a few tens to hundreds of degrees per minute) or in a wire mesh type of apparatus, in which small amounts of sample are contained in the folds of a stainless steel wire grid that is heated at rates of order 1000K/sec.

Solvent swelling measurements were performed largely as described in other studies²⁰. In the present case, however, the measurements were performed in small tubes of a few millimeters inner diameter and less than 5 cm in length. This technique permitted such measurements to be made with modest quantities of sample, provided that the sample and solvent is frequently stirred during the first phases of the swelling process. This technique gives reproducibility comparable to that for the standard technique with large tubes. A major reason for the difference between the standard solvent swelling techniques and those employed here stems from a concern about measuring accurately rates of swelling. In the second part of this paper, results will be given for activation energies of diffusion processes in coals, which were determined from timed swelling experiments. In the cases in which rate data were of interest, the swelling experiments were performed in thermostatted baths. The small diameter of the tubes and the frequent mixing of the contents with a small stirrer assured good heat transfer between the environment and the sample. In order to determine the height of the column of coal at any particular time (and thus the volumetric swelling ratio), the samples were "quenched" by immersion in an ice bath, and were quickly centrifuged in a high speed centrifuge, with cooling. The centrifugation takes only about ten minutes, during which time, because they are cooled, the samples swell negligibly.

RESULTS AND DISCUSSION

THE CROSSLINKING BEHAVIOR OF COALS DURING DRYING AND PYROLYSIS

Some aspects of this problem have been discussed previously, both in connection with the drying behavior of lignites¹⁹ and the pyrolysis behavior of various ranks of coal^{15,16}. This work has been extended in order to understand more fully how the macromolecular structure is altered during these processes.

At the outset, it is important to note that all ranks of coal have a colloidal structure, that will shrink and swell in response to imbibation of a solvent. The most common "solvent" is water, in that it is naturally present in all ranks of coal at the time of mining. The shrinkage and swelling behavior of lignites and brown coals in response to moisture loss and gain, respectively, has been quantitatively studied^{19,21}. In these earlier studies, it was noted that the extent of shrinkage was closely related to the amount of moisture lost from the lignite-- to a crude approximation, the extent of shrinkage was calculable assuming the the water lost from the coal had a specific volume of 1 cc/g. This is why measurements of BET surface area (or any of the other usual measurements of porosity) often reveal so little micro- and transitional porosity in lignites-- the porosity essentially collapses as the samples are being dried for examination by the usual porosity determination methods.

More recently, we have extended the examination of drying phenomena to include a much wider range of ranks. Figure 1 shows the volumetric shrinkage of coals ranging from lignite up to bituminous in rank, and surprisingly, a very good linear correlation exists between the volumetric shrinkage and moisture content throughout the entire range. The actual correlation is:

$$\% \text{Shrinkage} = 0.94(\% \text{Moisture Loss}) - 0.6$$

Thus it is apparent that colloidal swelling behavior is observed with water as a "solvent" even in ranks up to bituminous. This means that this entire range of ranks is subject to the same qualitative kinds of uncertainty in porosity characterizations as are lignites. To be sure, the effects are not nearly as large in bituminous coals, but there is no question that porosity does collapse upon drying.

It has been shown that the shrinkage that accompanies drying of lignites is to some extent irreversible. Typically, only about 80% of the shrinkage is recoverable¹⁹. The question is, what determines the extent of irreversibility of shrinkage? There are apparently some processes that occur, presumably on a molecular level, that prevent full reswelling of the coal, once it is rewet. This raises a general question of how coals crosslink during thermal treatments of any kind. We have explored some aspects of this problem by performing solvent swelling measurements on thermally treated coals. The results on one set which was heated slowly in a tube furnace is shown in Table 2. Several features may be noted in Table 2. First, coals that are still wet generally do not swell to as great an extent in pyridine as do coals that are dried at ordinary conditions. This is easily understood in terms of the network having already swollen to a significant extent in water. The fact that pyridine is able to swell it as much as it does is evidence of its stronger interaction with the lignites, relative to water with the lignites. Tetrahydrofuran (THF), on the other hand, is only a marginally better solvent for these lignites than water itself, as indicated by the modest swelling of wet coals in this solvent. There appears to be no constant ratio of swelling in pyridine to swelling in THF, nor is there a constant ratio of swelling in THF compared to that in water; this makes the point that even in fairly similar coals of identical rank, such as in this set of North Dakota lignites, the individual interactions of solvent and coal are rather important in determining swelling behavior.

The swelling ratio of a wet coal in pyridine is related to the swelling ratios of room temperature dried coals in pyridine. If the pyridine swelling ratio of a wet sample is multiplied by the ratio of (water) wet to dry volume of the lignite, the actual swelling ratio of the dry sample in pyridine may be estimated, i.e. there is no evidence of co-operative swelling effects involving pyridine and water.

The samples that are heated directly to 373K from a wet state obviously crosslink to a much lesser degree than do the samples that were first dried, and then heated. This is evidence that there are crosslinking processes that must occur at temperatures at least as low as 373K, and in the absence of oxygen from the atmosphere. Further, the processes are apparently strongly promoted by the absence of moisture during heating. The carboxyl contents of the lignites have been measured directly by barium exchange after reaction under these conditions, and in no case was a reduction greater than 10% seen in increasing the drying temperature from 373K to 473K. Together, this information suggests that the decarboxylation reactions that have been postulated to determine crosslinking in high temperature processes¹⁵ (and which has received support from modeling work²²), may be supplemented by another process that is promoted by the absence of water during the initial phases of the heating process. For comparison, high heating rate pyrolysis

behavior is shown in Figure 2. The illustrated behavior is fairly typical of all of the lignites, whether dried or undried, except as noted below. The experiment in this case consisted of heating a wet lignite at a rate of roughly 1000K/sec to a peak temperature, shown as the abscissa value, and then immediately cooling at a rate of about 300K/sec. It can be seen that the extent of crosslinking remains much lower at much higher temperatures in these rapid heating experiments. There is, however, still a slight tendency to crosslink at temperatures below about 625K. Above about 650K, all the lignites show a tendency to depolymerize, shown as an increase in solvent swelling tendency, and coinciding with the onset of the tar formation process. A similar observation has recently been independently reported²³. The swelling ratio decreases rapidly beyond about 700K, as the crosslinking reactions occur rapidly in this temperature range. It was in this temperature range that the decarboxylation reactions were thought to dominate. The directly determined decrease in carboxyl content did, in the one case studied, exactly equal the amount of CO₂ formed in the temperature range up to 900K. The mechanism of the decarboxylation, and more importantly, how it participates in the crosslinking process remains unknown. Again, the absence or presence of water had no effect on these higher temperature mechanisms, except in one sample. This may not be surprising in view of the fact that the water should have evaporated by the time these high temperatures are attained. However, earlier pyrolysis results for the Beulah lignite did show an effect of predrying even at high heating rates¹⁵.

In addition to the effects of thermal treatment noted above, 373K drying was also noted to considerably decrease the rate of diffusion into coals, compared to the rate of diffusion into room temperature air-dried samples. The rate of swelling of even a low moisture bituminous coal, such as Powhatan was decreased by a factor of two by 373K drying (i.e. standard ASTM conditions). The ultimate swelling ratio was however unaffected by the drying. This suggests that physical crosslinking of some kind is promoted by the drying procedure, but may be reversed if the solvent is strong enough. This reversible crosslinking is also noted in the lignite samples, and is distinct from the irreversible crosslinking that occurs above 373K, or in some cases, even at 373K.

ACTIVATION ENERGIES FOR DIFFUSION

The above discussion of the effects of crosslinking has pointed up how crosslinking may affect the diffusion process in coals. As part of an effort to characterize better the diffusion of solvents and large molecules through the bulk of the coal (as opposed to through pores), we have made measurements of diffusion rates of various solvents by tracking solvent swelling as a function of time. The process of diffusion in the bulk of a crosslinked macromolecular material is generally an activated process, meaning that the diffusion coefficient varies according to: $D=D_0\exp(-E/RT)$. Very good recent studies of the diffusion process, under conditions similar to those of interest here have shown the process to actually be of the "Case II" type; i.e. relaxation controlled^{14,18}. There is not space here to go into the details of the process.

The process of diffusion has been studied at temperatures from 298K up to 318K, with pyridine, tetrahydrofuran and water as diffusants. Various ranks of coal, and heat treated coals have been examined. Selected results are given in Table 3. Several features are important to note. First, there is a large difference in activation energies between the different ranks of coal, and between different solvents. Heat treatment seems to have the expected effect - not only does the diffusion become slower at all temperatures, but the activation energy increases, presumably as the structure becomes more rigid, and the vibrational conformations necessary to allow for solvent molecules to pass become ever less probable. The value of activation energy is felt to depend more upon the size of the penetrant species, and less upon the specific interactions of the coal and the solvent molecule. Note that the activation energy for THF is considerably lower than that for pyridine, however the rate of swelling in pyridine is more than an order of magnitude higher than in THF at room temperature, and the extent of swelling is also much higher in pyridine.

CONCLUSIONS

This paper has, in a very brief manner, touched upon two different aspects of how the macromolecular structure of coal relates to important physical and chemical phenomena. The studies continue as of this writing, on both of the above topics. The utility of straightforward techniques of characterization of macromolecular structures, such as solvent swelling, cannot be underestimated as important contributors to the more complete understanding of complex processes and phenomena in coals.

ACKNOWLEDGEMENT

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Table 1-Coals Studied

SAMPLE	C	H	N	S	ASH	O	Moisture
Beulah lignite ^a	65.6	3.6	1.1	0.8	11.0	17.9	26.0
Freedom lignite ^a	63.5	3.8	0.9	1.4	6.1	24.3	27.9
Glenn Harold lignite ^a	61.1	4.4	0.8	0.4	7.4	25.9	28.9
Gascoyne lignite ^a	60.9	4.2	0.6	1.4	8.2	24.7	30.7
Beulah lignite ^b	65.9	4.4	1.0	0.8	9.7	18.2	32.2
Texas lignite (PSOC1036) ^c	61.5	4.7	1.4	1.3	12.5	18.5	31.8
Belle Ayr Subbit.	69.3	4.4	1.0	0.5	10.3	14.5	30.3
Big Brown Subbit.(PSOC785) ^c	62.8	4.6	1.1	1.1	12.6	17.8	27.8
Montana Subbit.(PSOC837) ^c	57.8	4.3	0.8	0.7	11.9	24.6	17.0
Pittsburgh No.8 (HVBIt.) ^b	74.2	4.1	1.4	2.3	13.2	4.8	1.7
Bruceton HVBit. ^d	80.4	5.3	1.6	1.0	4.6	6.7	1.7
Powhatan HVBit.	72.3	5.1	1.5	3.6	9.7	7.8	1.1

*All results on a dry weight percent basis, except moisture which is ASTM value on an as-received, bed moist basis.

*Oxygen by difference.

a- Grand Forks Energy Research Center lignite sample bank.

b- Argonne National Laboratory Premium Coal Samples.

c- Pennsylvania State University Coal Sample Bank.

d- U.S. Bureau of Mines Standard Sample.

Table 2- Effect of Drying and Thermal Treatments on Solvent Swelling of Lignites

Condition	Beulah	Freedom	Gascoyne	Glenn Harold
Wet	1.48/1.08	1.62/1.00	1.33/1.07	1.60/1.18
0% R.H.,300K,24hrs	2.20/-	2.01/-	1.90/-	2.10/-
0%R.H.,300K, 30days	2.22/1.28	2.06/1.33	2.10/1.32	2.14/1.32
Wet, dried at 373K,1hr	2.34/-	2.50/-	2.05/-	2.47/-
Dry, then 373K,1hr	2.0/1.34	1.70/1.35	1.68/1.38	1.81/1.33
" , then 473K, 1hr	1.43/1.25	1.66/1.28	1.54/1.29	1.75/1.22
" , then 573K, 1 hr	1.22/1.16	1.45/1.15	1.50/1.06	1.50/1.15
" , then 573K, 2 hr	1.14/1.10	1.30/1.12	1.42/1.06	1.45/1.13

*All values are volumetric swelling ratios, given as:

(pyridine volumetric swelling ratio/tetrahydrofuran volumetric swelling ratio).

*0% R.H. refers to drying over concentrated sulfuric acid, a 0% relative humidity environment. Samples marked "dry" were initially dried in this manner at room temperature, prior to thermal treatment.

Table 3- Activation Energies for Diffusion in Coals

<u>Coal</u>	<u>Treatment</u>	<u>Activation Energy (kcal/mol)</u>
Beulah (Argonne Sample)	Air dried, 1day	18.0
" "	Air dried, 3days	17.9
" "	Vacuum dried, 298K	19.4
" "	Vacuum dried, 373K	21.5
Montana Subbit.	Air dried	18.1
Pitts. No. 8	Vacuum dried, 373K	12.6
Bruceton HVBit.	Vacuum dried, 373K	13.
Bruceton HVBit.	Vacuum dried, 373K	8.8 (THF)

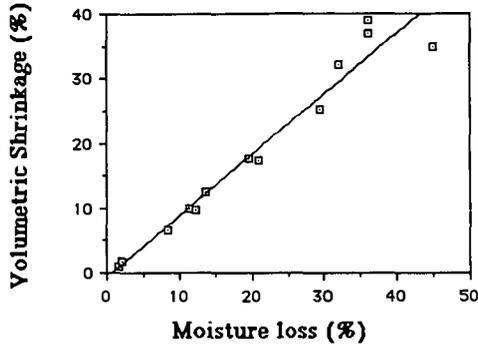


Figure 1. Volumetric Shrinkage of coals during room temperature drying.

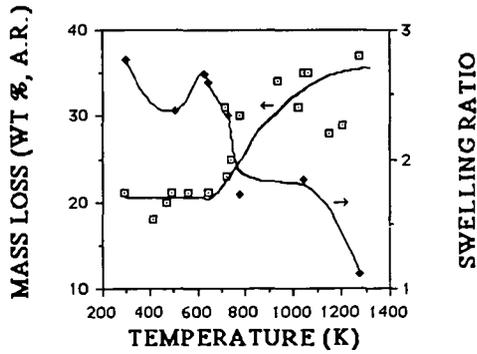


Figure 2. Mass loss and pyridine solvent swelling behavior of "wet" Freedom lignite, rapidly pyrolyzed under non-isothermal conditions to indicated peak temperatures.

INTERRELATIONSHIPS BETWEEN COAL ANALYSIS, COAL CONVERSION
AND COAL STRUCTURE

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Models for the average structure of a coal and for its chemistry both rely heavily on analyses that are subject to considerable errors. In addition to these analytical problems, it is often true that our notions concerning the "reasonableness" of a chemical reaction of a coal are influenced by our conception of what an average structure for that coal looks like. This picture of an average structure for a coal was in turn probably influenced by analytical results obtained for extracts and/or products of "mild" reaction conditions. These two factors -- the weakness of analytical techniques for solid coal, and the somewhat circular dependence of our concept of coal structure on coal chemistry -- present problems for studies of both coal structure and coal chemistry. The development of improved analytical techniques for solid coal as well as for characterization of coal chemistry, is very important to any improvement in our real knowledge of coal and its significant fuel-processing chemistry. Several projects at PETC have focused on improvement of our ability to characterize solid coal and its fundamental chemistry during direct liquefaction.

A large number of average structural models for specific coals have been published, and many describe in some detail how the structure was derived (1). The input data include elemental analyses (C,H,N,O,S), possibly an aromaticity from ¹³C NMR, and often some characterization data on extracts or mild-reaction products. It is emphasized by everyone who publishes an average structure that the structure is only a statistical entity and is not meant to represent the organic structure of a coal on a molecular scale. Although we are repeatedly cautioned, it is easy to let our thought processes concerning chemistry be influenced by such attractive (seductive) visual representations. It is worthwhile to look at the potential errors in the data used for generation of an average structure or for describing a chemical reaction of coal.

Determination of the elemental composition of coal is routinely accepted as a starting point for describing a coal's structure; however, the distinction between organic and inorganic forms can lead to problems. The recent paper by Ehmann et al. (2) reviews the well-documented problems associated with determination of organic oxygen in coals. This problem is in part related to the lack of an accurate analytical method for the determination of water. Because of the sequence of steps in a total elemental analysis of coal, residual water remaining after drying translates directly into errors in both organic oxygen and organic hydrogen. Similarly, the accepted method for determination of organic sulfur is by difference (3) and thus contains a significant coal-specific uncertainty related to the dispersion of pyritic sulfur in the coal. The rather bleak picture is that there is significant uncertainty in three of the five major elements in the organic structure of coal.

The composition of coal extracts is a very important input to construction of coal models; however, this extract rarely appears explicitly in average structural models that focus on representing the insoluble matrix of a coal structure. The amount of extractable material that is truly soluble, so that it can be analyzed by modern techniques, is usually rather small (5-15%). Inference of an overall coal structure from the 5% of its composition that can be analyzed is always fraught with difficulties. The yield of extract can be raised significantly by a variety of thermal and chemical means; however, these extracts may be criticized as being too substantially transformed to be meaningful for coal structural studies. How would a reviewing organic chemist react if the identification of an organic solid was accomplished by analyzing the sample as a THF extract after heating to 300°C with 10% water and 15% added mineral matter?

Bulk spectroscopic analyses of coal that are capable of yielding direct structural information on the solid are infrared (IR) and nuclear magnetic resonance (NMR). Infrared spectroscopy is always capable of yielding qualitative information, but quantitation has proven elusive. The solid-state CP¹³C NMR spectra of coal can provide very useful structural information; however the question of what fraction of the total carbon is being observed is still being debated (4). If the ¹³C aromaticity is determined on a nonrepresentative fraction of the total carbon, our picture of the average structure of a coal may be seriously in error.

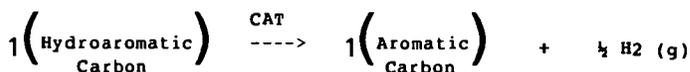
Investigation of chemical reactions involving coal is rendered very uncertain by our problems in analyzing the coal itself. It is difficult to describe the chemistry of an organic reaction when the nature of the starting material is uncertain. An improved understanding of the fundamental chemistry of direct liquefaction is an ongoing area of interest at PETC. This goal requires development of analytical techniques appropriate to the coal liquefaction system. One approach has been application of CP-MAS-¹³C NMR techniques for measurement of net hydrogenation. By combining this measurement with material balance information, it is possible in principle to determine the relative amounts of hydrogen consumed in hydrogenation, bond cleavage, and heteroatom removal.

The analysis of a variety of liquefaction systems using this hydrogen utilization approach has led to several conclusions: (1) under conventional liquefaction conditions, the net hydrogen consumed in hydrogenation of aromatic components is often small, (2) significant changes in "conversion" measured by solvent solubility can be accomplished with virtually no net hydrogen chemistry, and (3) analytical methods for analysis of slurries of coal and vehicle oil are a major limitation to the improvement of our understanding of coal conversion chemistry. A typical hydrogen utilization profile for a coal conversion experiment conducted at 380°C is shown in Table 1.

The conversion of coal to THF solubles was in excess of 80% in this experiment. Although the experiment indicates an >80% "conversion", all of the numbers in Table 1 may be nonsignificant because of experimental error. A major potential contributor to the experimental error in both heteroatom removal and total hydrogen consumption is the inability to accurately determine water in coal. If 1 wt % molecular water exists in the "dry coal"

the analytical method conventionally used for direct oxygen and hydrogen determinations translates this water content into an error of -2 H/ 100C in the coal and would also result in a significant overestimation of the amount of organic oxygen in the slurry. This sensitivity of organic hydrogen and organic oxygen to the accuracy of the water determination indicated to us a need for improved confidence in the coal moisture analysis. A recently completed study of the water content of a variety of coal samples, both from the Argonne sample bank and from coals typically used for liquefaction research, indicates that the problem may be significant, especially for air-dried (or mildly air oxidized) samples (5). This study used an isotope exchange procedure that is capable of determining water that is not volatile under conditions of the ASTM procedure. The method does not require removal of the water from the coal to obtain an analysis. It is hoped that this method will provide a more accurate evaluation of the water content of a coal, which in turn will improve the accuracy of organic oxygen and hydrogen determinations.

Another significant uncertainty in discussions of coal chemistry is the measurement of the hydrogen within the slurry that is available in hydroaromatic structures. Such structures as the hydropyrenes have repeatedly been shown to be very effective in enhancing coal conversion. However, the content of such materials in complex heavy recycle vehicles, not to mention coal, is not easily determined. The content of multi-ring hydroaromatics in a coal structure is very important in establishing the amount of internal hydrogen readily available for participation in thermolytic reactions. Catalytic dehydrogenation of coal and vehicle has been used as a measure of this available hydrogen. We have attempted to use this technique coupled with NMR measurement of the aromaticity change on dehydrogenation to better understand the source of the hydrogen in such experiments. Conversion of a hydroaromatic to an aromatic with H₂ generation should conform to the following stoichiometry:



Thus it should be possible to plot change in moles of aromatic carbon versus moles of hydrogen gas produced and obtain a slope of 2 (moles of carbon aromatized per mole H₂ produced). An example of such a system, the Pd catalyzed dehydrogenation of the bitumen gilsonite, is shown in Figure 1. Gilsonite was chosen because of its apparent high hydroaromatic content and its complex composition. The slope indicated in Figure 1 is near enough to the theoretical value for classical hydroaromatic dehydrogenation to conclude that the approach may be workable. This very simple analysis is applicable to complex systems and has potential for providing quantitative information relevant to coal conversion chemistry. If condensation of aromatics is the dominant source of the hydrogen gas generated, then a slope near zero might be expected because condensation should not affect the carbon aromaticity, f_a. If the hydrogen produced from hydroaromatic dehydrogenation is subsequently consumed by some unspecified bond cleavage chemistry within the liquefaction system, a slope greater than two would be expected. This technique has some promise for investigating internal redistribution of hydrogen in coal- vehicle slurries at mild temperatures.

Another example of a well-accepted concept in coal chemistry that is difficult to study directly is the role of free radicals in the thermal chemistry of coal. The existence of a huge reservoir ($\sim 10^{19}$ spins/g) of stable radicals in coal itself complicates the direct observation of the effects of the incremental transient of thermolytically produced radicals via ESR(6). An alternative method for observing the radical involvement in complex systems is to introduce into the system a nonintrusive chemical probe molecule sensitive to the presence of radicals. This approach attempts to circumvent our inability to directly monitor the formation and destruction of reactive free-radical species in coal with any reliability. The hope is that the appropriate probe will be selectively sensitive to the population of coal radicals that are directly involved in conversion. Recent work at PETC has used the equilibration of cis- and trans-decalin as a probe of the time-averaged steady-state concentration of radicals in complex coal liquefaction systems. A greater steady-state concentration of radicals results in a more rapid conversion of pure cis-decalin to the equilibrium mixture of cis and trans isomers. In this chemical-probe approach, only a small amount of a pure compound is added to the liquefaction feedstock. Because the chemistry of complex liquefaction systems is not likely to be perturbed by a small amount of additive, the chemical probe method has the potential to yield more relevant information than that from investigation of reactions in which a model compound is the sole or the predominant reactant. The decalin isomerization probe has been used to determine the steady-state concentration of free radicals in coal liquefaction using heavy petroleum resid as vehicle.

Conclusions

Studies of the net chemistry of direct liquefaction have focused attention on a number of analytical deficiencies that limit our confidence in describing coal chemistry and/or coal structure. The most obvious analytical limitations are the accuracy of the ^{13}C f_a value, which allows us to quantitatively assess the hydrogenation of aromatics, and the accuracy of the water determination in coal, which determines the accuracy of subsequent measurement of organic oxygen and hydrogen. These concerns are, of course, not new, but it is important that they be kept firmly in mind so that research aimed at resolving our analytical deficiencies can go on simultaneously with our investigations of the relevant chemistry of liquefaction and the structure of coal.

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Table 1.

	Hydrogens per 100 Carbons of Slurry
Hydrogenation	1
Heteroatom Removal	1
Gas Production	0
<u>Matrix Bond Cleavage</u>	2
Total Hydrogen Consumption	4

Conditions: Feed = Illinois No. 6 coal (4g) + SRC II HD (7g)
 Temperature = 380°C
 Reaction Time = 20 minutes
 Catalyst = Molybdenum (as ammonium heptamolybdate), 0.006g
 Gas = H₂, 2000 psi

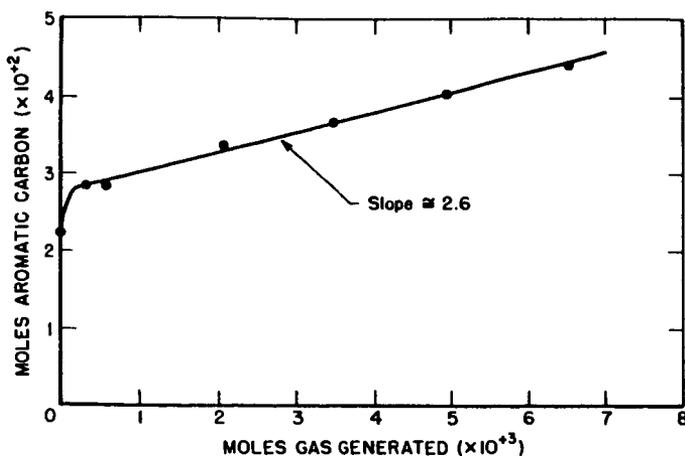


Figure 1. Relationship between change in aromaticity and gas generation on catalytic "Dehydrogenation" of gilsonite.

THE MACROMOLECULAR STRUCTURE OF BITUMINOUS COALS: MACROMOLECULAR ANISOTROPY, AROMATIC-AROMATIC INTERACTIONS, AND OTHER COMPLEXITIES

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INTRODUCTION

A homogeneous piece of vitrinite containing no mineral matter has two organic phases. One of these consists of a crosslinked macromolecular network and the other is a soluble family of macromolecules having a very broad molecular weight distribution. The network is held together by covalent bonds as well as by non-covalent interactions. There is abundant evidence for an important role of hydrogen bonds in the macromolecular structure and growing evidence for an important role for dipole-based interactions between the aromatic groups.¹⁻⁴ These same non-covalent forces are important in binding the extractable phase to the insoluble network. This paper deals with the way the macromolecules pack together in the solid and especially the role that the aromatic-aromatic interactions play in the packing of the macromolecular segments.

Evidence for the Existence of Non-covalent Interactions and their Geometry

Hydrogen bonds in coals can be observed directly in the IR spectra of coals. The disruption of coal-coal hydrogen bonds by organic bases has also been directly observed spectroscopically.² Coals swell much more in solvents which are strong hydrogen bond acceptors than they do in very similar material without hydrogen bonding capabilities.¹ There can be no doubt but that hydrogen bonds between different parts of the coal network exist and can be broken by external reagents and presumably can re-arrange within the coal provided the conditions are right. There is an enormous literature on the geometry of hydrogen bonding. For our purposes, it is simple enough to state that the hydrogen will lie on a line collecting the two nuclei which serve as the terminus for the non-covalent interaction.

Attractive interactions exist between aromatic units due to London dispersion forces.⁵ There have been a number of calculations on various systems, but since they are very time consuming, they emphasize small molecules, particularly benzene-benzene interactions.⁶ In addition, there are experimental studies of gas phase complexes, complexes in biological systems and also crystal structures of PNA systems.⁷ In small rings, the most favorable interaction occurs when the rings are at right angles to each other in a T-shaped configuration. Face-to-face parallel stacking is repulsive at all distances. This is not surprising since one is bringing two electron clouds into increasingly close proximity. As the ring size grows larger, there is a tendency to move off of the perpendicular somewhat, but the parallel stack remains repulsive.⁶ In crystal structures where there is the necessity for filling space, a "herringbone" pattern is adopted which preserves both the "T" interactions and provides a packing geometry which is space filling.

In an amorphous polymer network like coals, we anticipate a compromise between the thermodynamic driving force for "T" configuration interactions between aromatics and a packing which efficiently fills space. It is not easy to predict what the outcome will be. Hirsch's X-ray data are quite explicit in identifying some parallel stacking in coals but it is impossible to compare the frequency of this geometry with that of a perpendicular orientation of aromatics.

Orientation of Aromatics with Respect to the Bedding Plane

It is often assumed by coal scientists that the aromatic systems in coals both have a strong tendency towards parallel alignment and tend to align parallel to the bedding plane. While there is clear X-ray evidence for some tendency towards parallel stacking, the evidence for alignment of aromatic rings parallel to the bedding plane is much more tenuous. In Hirsch's classical papers, he provides evidence for the alignment of aromatic systems parallel to the bedding plane in an anthracite coal but states that "the degree of preferred orientation is small in the low rank coals and increases with rank, particularly in the anthracite region".⁸

The other factor which comes into play is the striking anisotropy in coal mechanical properties. Coals are much stronger perpendicular to the bedding plane than parallel to the bedding plane. This is a significant factor in mine design but it has not heretofore been determined whether the mechanical anisotropy was an inherent property of the material or was due to the cleats and cracks which form whenever a piece of coal is hacked from a seam.

The alignment of aromatic structures in coals with reference to the bedding plane was investigated using Fourier transform IR dichroism with photoacoustic detection. A solid disk of coal was cut and the bedding plane accurately determined. This was placed in the photoacoustic detector of an IBM FTIR and spectra obtained using plane polarized light indexed to the bedding plane. Spectra were obtained at 45° intervals moving in a 360° circle. To verify that the instrument was operating properly, a crystal of acrylamide was oriented in the IR instrument and the dichroic spectra obtained. From these spectra, we could accurately back-calculate the known bond angles in the oriented single crystal. Based on these calculations, we estimate that our error is $\pm 3^\circ$. Dichroic spectra of Ill. No. 6 coal and acrylamide are shown in Fig. 1. In none of the coals was any alignment of the organic structures parallel to the bedding plane detected.

We have applied ^{13}C NMR using oriented samples in a single crystal probe as well as optical birefringence to some of these coals. Both of these techniques indicate a net orientation of the aromatic rings of about 1.5° , within the experimental error of the IR measurements. Our conclusion is that the organic groups in coals are essentially randomly arranged.

To probe the mechanical anisotropy, a series of coal thin sections were swollen under a microscope and the swelling measured on photographs of the thin sections. Features on the thin section were identified, these features being connected by lines which would run either parallel to or perpendicular to the bedding plane. The coal is wet with a solvent and as it expands it was photographed and the movement of these features measured on the photographs, directly giving linear expansions. These data were obtained for six coals and are shown in Fig. 2. For all coals and solvents, the swelling is highly anisotropic. The coals expand much greater perpendicular to the bedding plane than they do parallel to the bedding plane. The mechanical anisotropy of coals must be a direct consequence of their macromolecular structure.

We are faced with an apparent contradiction in that coals have randomly oriented groups on a molecular level but are mechanically anisotropic on a larger scale. There are two possibilities. There may be a random coil network with a non-random distribution of branch points, the branch points occurring more frequently parallel to the bedding plane than perpendicular to it. Another possibility is a coal structure which features an array of sheets dividing and twisting and eventually achieving an individual group random orientation while maintaining a bulk structure anisotropy under stress.

Such structures have been proposed for amorphous carbons and recently for a low-rank coal based on X-ray data.

Reversible Association of the Coal in the Macromolecule

As if this was not sufficient structural complexity, the coal is not at an equilibrium configuration when removed from the mine to atmospheric pressure and is capable of undergoing a number of internal re-arrangements. A plot of linear expansion during solvent swelling parallel to and perpendicular to the bedding plane for several coals vs. time is shown in Fig. 3. Both of these coals show excess expansion both parallel and perpendicular to the bedding plane, that excess occurring at different times. The existence of the swelling excess was first noted by Peppas and ascribed to a metastable state¹¹ caused by the slow motion of the coal macromolecular segments. We agree with his interpretation.

When the solvent is removed from the coal, the solid which remains has a somewhat different shape than the starting coal did: it is higher perpendicular to the bedding plane and not quite as wide. Subsequent swellings of this material are totally reversible, always returning to the same shape and size. Wetting the coal with the solvent, allowing it to expand, and then contracting it by removing the solvent lets the coal macromolecular segments find the equilibrium positions to which they will return again and again as the process is repeated. The configuration of coals in the seam is not at equilibrium at 1 at. Coals do not re-arrange to their equilibrium form without some treatment because they are glassy. If made rubbery, then re-arrangement will occur.

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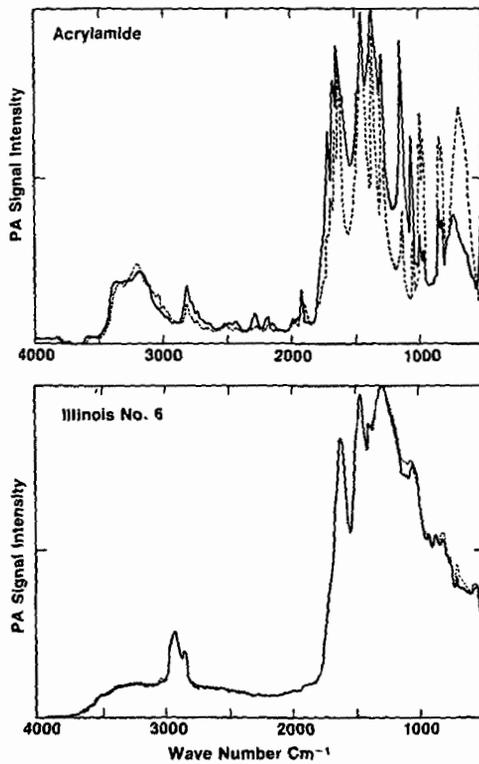


Figure 1. Photoacoustic FTIR Spectra Obtained with Polarized Light
 a) Single Crystal Acrylamide; — Light Polarized Parallel to C Axis, ---- Polarized Parallel to B Axis
 b) Ill. No. 6 Coal; — Light Polarized Parallel to Bedding Plane, ---- Polarized Perpendicular to Bedding Plane

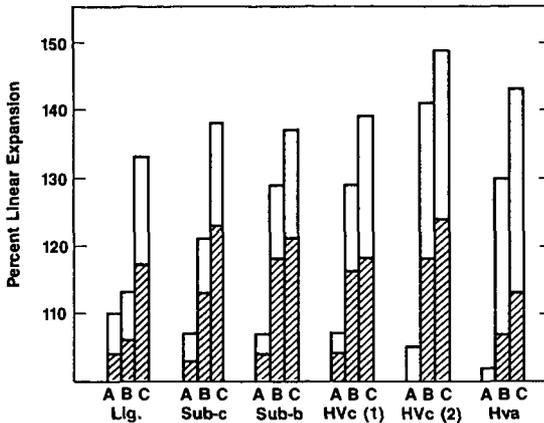


Figure 2. Linear Expansion of Coals in Chlorobenzene (A), THF (B), and Pyridine (C) Measured Parallel (crosshatched) to and Perpendicular to the Bedding Plane. Lig. = Big Brown (Texas); Sub-c = Smith Seam; Sub-b = Wandoan; HVC(1) = Correjon (Columbia); HVC(2) = Ill. No. 6; HVa = Pittsburgh No. 8.

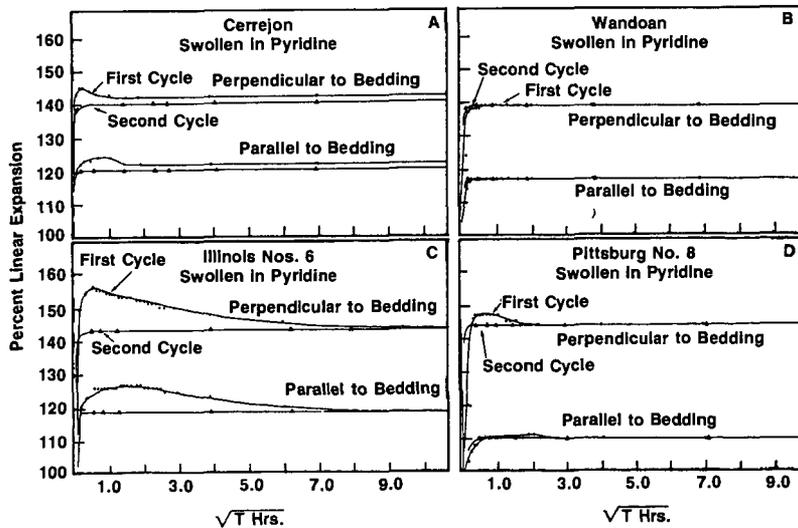


Figure 3. Time Dependence of Linear Expansion of Coals Swollen in Pyridine Parallel to and Perpendicular to the Bedding Plane

AROMATIC STRUCTURES IN WHOLE COALS AND COAL MACERALS

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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.

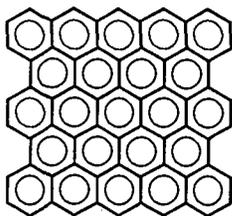


Figure 1. Early thoughts on the aromatic structure of coals.

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 NaHSO₃ and the solution filtered. The derivatized coal was washed free of pyridine, dried and analyzed. In a typical oxidation, fresh Ag₂O prepared from 9.5 g of AgNO₃ 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 ⁺ /100°C	Ag ₂ O Oxidation Yields*	
						Organic Soluble, %	Humic Acid, %
APCS #1	Upper Freeport	mv Bituminous	85.5	C ₁₀₀ H ₆₆ ^N _{1.5} S _{0.3} O _{6.6}	2.8	27	5
APCS #2	Wyodak-Anderson	Subbituminous	75.0	C ₁₀₀ H ₈₆ ^N _{1.3} S _{0.2} O _{18.0}	4.1	40	26
APCS #3	Illinois Herrin	hvc Bituminous	77.7	C ₁₀₀ H ₇₇ ^N _{1.5} S _{1.1} O _{13.0}	3.7	25	34
APCS #4	Pittsburgh	hva Bituminous	83.2	C ₁₀₀ H ₇₇ ^N _{1.7} S _{0.4} O _{8.0}	3.3	30	30
APCS #8	Beulah-Zap	Lignite	72.9	C ₁₀₀ H ₈₀ ^N _{1.3} S _{0.4} O _{20.9}	3.6	39	21
SRC	Wilsonville (Pittsburgh coal)		86.9	C ₁₀₀ H ₇₆ ^N _{1.8} S _{0.5} O _{3.8}	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 Et₂O-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.

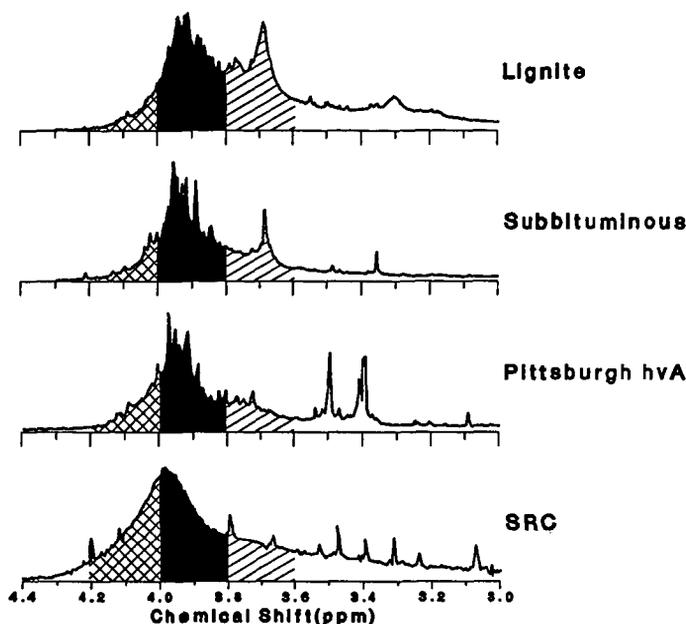


Figure 2. Methyl ester region of the ^1H NMR spectra of the methylated solvent-soluble fractions from the Ag_2O oxidation recorded on a Nicolet 200 MHz instrument with CDCl_3 as the solvent. (/ / / -aliphatic, ■ -single ring aromatic, ⊗ -polycyclic aromatic.)

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

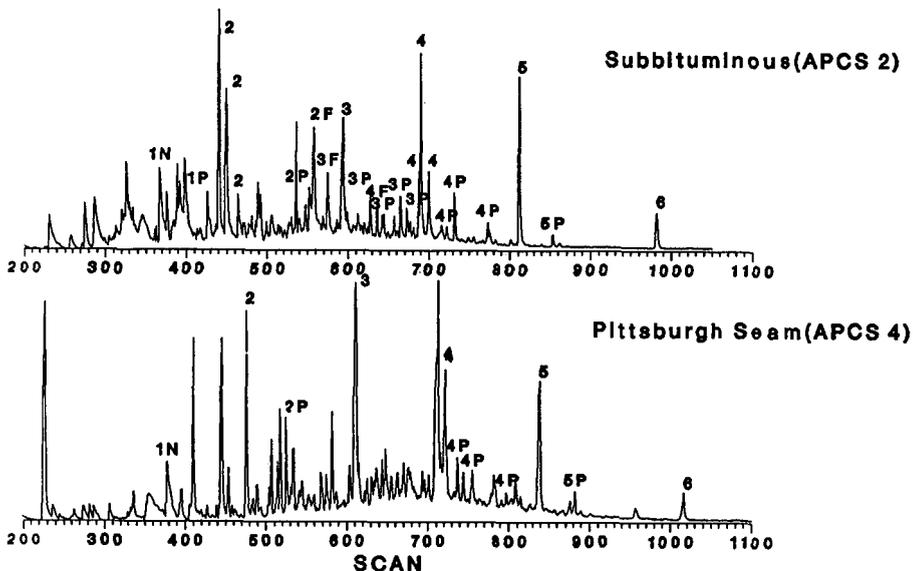


Figure 3. Total ion chromatograms of solvent soluble fractions from the Ag₂O oxidation of two premium coals. Major peaks: 2-6 number of methyl carboxylates on benzene; 1P-5P, on phenol; 1N, on pyridine; 2F-4F, on furan.

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.

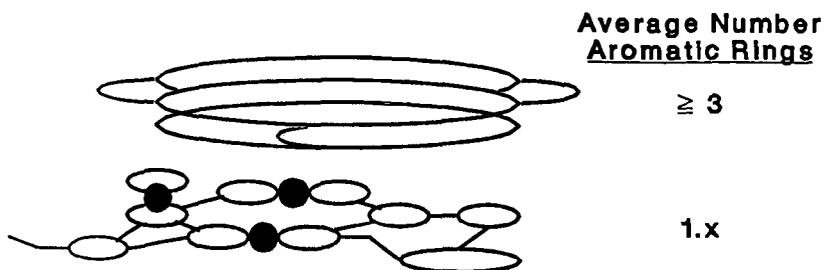


Figure 4. Possible coal structural arrangements. Top-stacked polycyclic aromatics, bottom-single ring aromatics with hydrogen bonding.

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