

## ORGANIC STRUCTURE COMPONENTS WITHIN THE ARGONNE PREMIUM COAL SAMPLES\*

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### INTRODUCTION

The nature of the major organic molecular types that make up the structures in the Argonne Premium Coals will be discussed. Data derived using a number of approaches from the literature and from our laboratory will be included to assemble statistical models for these coals. The nature and distribution of the heteroatoms will be emphasized. In addition, deficiencies in our information such as quantitation of linkages between stable clusters will be examined.

Elucidation of the important structural features in coals has been facilitated by the availability of the Argonne Premium Coal Samples. For the first time, differences between techniques and labs using the same techniques cannot be attributed to differences in the coal sample. Also, the method of storage of the samples, sealed in glass, ensures that studies started today can be compared to studies done on these samples a number of years ago. These samples are with one exception, vitrinite rich, and the discussion in this paper will focus on the organic structures in vitrinites. It is fairly clear that a majority of vitrinite is derived from lignin.<sup>1,2</sup> While the nature of the starting material is important in studying the "structure" of coal, there are ambiguities in our understanding of the structure of lignins.<sup>3</sup> The nature of the monomers is fairly well known, but it is not totally clear how they combine to make the biopolymer. Given the complexity of the starting materials, the severe reaction conditions, and the insolubility of the finished product, one can only hope to develop a statistical picture of coal structure. However, such a picture can be very useful in the development of new technology for coal utilization.

One objective of this paper is to examine what we now know about the structural features of the Argonne coals using information derived from a number of complementary approaches. The second objective is to determine what other information would be useful to better define a statistical picture of coal structure. It should be noted that the literature cited in this paper is not complete but is only representative. The broad topic of physical structure will not be discussed in this study.

Of all the direct techniques used to examine the Argonne Coals, solid <sup>13</sup>C NMR is the most popular.<sup>4,5</sup> A round-robin study focusing on the determination of aromaticity, involving thirteen groups, resulted in a book with a summary of all the results presented in the final chapter.<sup>4</sup> In addition, EPR studies are presented in this compilation. Both XPS<sup>6</sup> and XANES<sup>5,7</sup> have been used to speciate the main sulfur groups. This work has recently been reviewed.<sup>8</sup> Also recently, nitrogen compounds have been investigated by XPS.<sup>9</sup>

Most indirect methods use thermolysis to release smaller molecules, which can then be individually detected. These results are rich in information but are thought to be quantitatively less reliable than direct techniques. Various mass spectrometric methods are the most popular and those applied to the Argonne coals are listed in Table 1. Also, TG-FTIR has been used to quantify thermally released gases and tars.<sup>17</sup>

**Table 1**

Mass Spectrometric Techniques used to analyze the Argonne Premium Coals.

Ionization	Instrument	Resolution	Reference
Low voltage EI	Quadrupole	Low	10
Field Ionization	Sector	Low	11, 12
Fast Atom Bombardment	Sector	Low	13
Desorption Chemical Ionization	Sector	High	14
Desorption EI	Sector	High	15
TGA - LVEI	Quadrupole	Low	10
Laser Desorption	Time-of-flight	Low	16

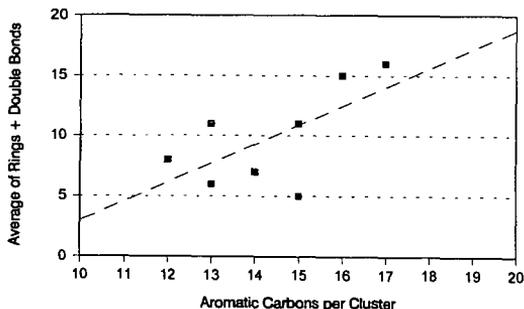
The use of coal extracts simplify some of the problems in coal structure studies and are being used by a number of researchers.<sup>5,14,15,16</sup> Some exotic solvent mixtures result in very high yields for some of the coals. In addition, chemical modification such as alkylation has been used in studies of these coals.

#### EXPERIMENTAL

The preparation and properties of the samples have been described.<sup>18</sup> The Desorption Electron Impact High Resolution Mass Spectrometry (DEIHRMS) experiments were performed using an HRMS EI source modified to take a desorption chemical ionization probe.<sup>15</sup> With this probe the sample is desorbed and pyrolysed directly in the source of the mass spectrometer which reduces the likelihood of secondary reactions such as recombinations and aromatizations. The pyridine extractions have been described elsewhere.<sup>14</sup>

#### RESULTS AND DISCUSSIONS

**Aromatic Structures.** The fraction of aromatic carbons in the Argonne Premium coals have been determined by NMR and it is apparent that the single pulse excitation is the best approach.<sup>4</sup> Molecular weight determinations are not nearly so well defined. Mass spectrometry of volatile extracts or pyrolysis products should provide fairly good numbers. However, the results are very technique dependent. If one examines all of the methods in Table 1 being applied to the same sample, the following trend for average molecular weight results are: lveI/Quad < DEI < DCI = LD < FAB < FI. The differences can be contributed to a combination of fragmentation, ionization technique sensitivity, mass analysis sensitivity, and secondary reactions. Even with these problems several trends are normally observed. Average molecular weight normally increases with rank specifically for aromatic molecules. With aliphatic molecules the trends depend on the biomarker content and types in the coal. The average molecular weights are relatively low, normally between 300 and 500. However, these methods will observe larger molecules if they exist.



HRMS results can be compared to NMR results for the extracts which are shown in Figure 1. Considering the assumptions and

**Figure 1.** Correlation of aromatic carbons from NMR<sup>5</sup> with hydrogen deficiencies from HRMS<sup>15</sup> data derived from extracts of the Argonne Premium Coals.

errors from both techniques, the correlation is quite good. The lignite is the most obvious outlier, but the yields from extraction were much different. A demineralized lignite which gave a greater yield was used in the MS experiment. The MS data shows a smooth increasing average size, while the NMR shows similar trends with a few discontinuities. The important result of all these studies is that the structures are not dominated by large polycyclic aromatic compounds.

**Heteroatoms.** Because of their large abundance, heteroatoms must dominate the chemistry of most coals. Figure 2 shows the average number of heteroatoms per aromatic carbon. Even for the high rank coals, the heteroatom content is significant, but they are likely to be involved as links. This is especially true for oxygen, as can be seen in Figure 3 which shows the amount of ethers or furans present, estimated from three different techniques. The methylation data is incomplete, but the available numbers agree very well with the HRMS estimates. A similar trend is seen for NMR results, but the numbers are much lower which is attributed to difficulties in separating overlapping resonances. All three approaches agree for the Pocahontas coal. The nature of this coal has been thoroughly discussed in a recent paper<sup>19</sup>. The most inconsistent results are for the lignite which has also been observed in the NMR study of extracts.<sup>5</sup> In summary, phenols derived from lignin dominate in the lower rank coals, while furans and ethers may be major links in the higher rank coals.

From XANES, XPS, DEIHMS, and TG-FTIR it is apparent that coals contain a significant amount of aliphatic sulfur. Data from all four techniques have been averaged and the result is shown in Figure 4. Although not shown here, a significant finding is that the indirect, thermal techniques agree very well with the direct methods. Also, there is a very distinct rank dependence with aliphatic sulfur becoming a very minor fraction in the high rank coals.

Nitrogen is found as pyrolic, pyridinic and quaternary by XPS with no evidence for free amines. Pyrolic content varies between

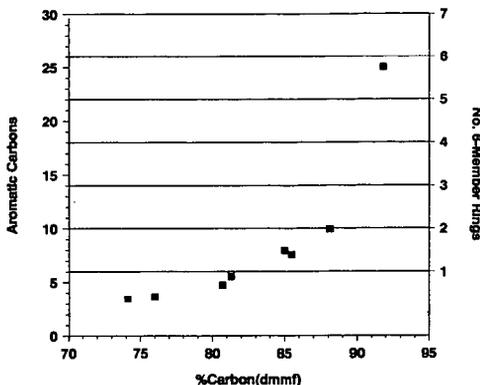


Figure 2. Number of aromatic carbons per heteroatom for the Argonne Premium Coals.

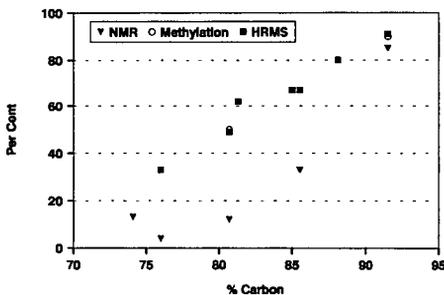


Figure 3. Estimates of the amounts of oxygen species as ethers or furans in the Argonne Premium Coals.

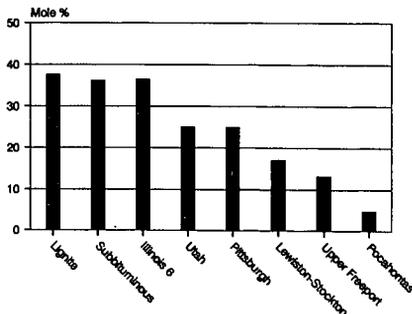
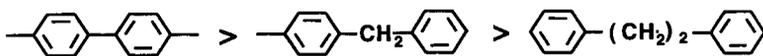


Figure 4. Averages of all available aliphatic sulfur data.

55% and 65% with little rank dependence while quaternary decreases with increasing rank. This species is probably protonated pyridinic nitrogen. DEIHMS indicates that a significant amount of the nitrogen compounds contain an additional heteroatom. This is not surprising if one considers the data in Figure 2.

**Linkages.** Generally, it is thought that aliphatics such as ethylene make up the links between aromatic clusters in coals. However, the evidence for this is not compelling. Biaryl links are thought to be important in the Pocahontas coal and could be significant contributors in many of the >85% carbon bituminous coals. Biaryl and methylene links also tend to be more thermodynamically stable as is shown in the series below.



Oxygen functionalities likely play an important role in linkages, especially in higher rank coals. The decreasing oxygen content is compensated for by an increasing percentage of ethers and furans and an increase in aromatic cluster size. More information is needed to quantitate the distribution of linkages which is critical to an understanding of coal reactivity.

#### SUMMARY

Several key features are evident from examining the data from the Argonne coals. First, the aromatic clusters are not very large. Second, heteroatoms are associated with a majority of the clusters. Finally, we need more quantitative information on the links between clusters.

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