

## A THREE DIMENSIONAL STRUCTURAL MODEL FOR VITRINITE FROM HIGH VOLATILE BITUMINOUS COAL

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### **Introduction**

In recent years, several models have been proposed for the chemical structure of coal (1-4). Some of these models have been visualized in three dimensions by use of computer graphics (5). The models have been constructed by considering elemental, spectroscopic, and pyrolysis/gas chromatography/mass spectrometry data. While the models have provided a visual framework for evaluating the kinds of structural elements that are contained in coal macromolecules, they fail to depict the chemical heterogeneity that exists in coal due to the many varied macerals. Developing structural models for individual macerals such as vitrinite would limit some of the heterogeneity, but vitrinite, a petrographically defined component, can also have a heterogeneous composition. There are numerous petrographic forms of vitrinite.

The approach towards defining a more homogeneous maceral component of coal used in our laboratory is one which has focused on coalified wood as a representative for vitrinite derived from xylem in ancient trees (6-9). Structural models were developed from a lignin template, because lignin has been determined to be the major source of chemical structures in coalified wood. By examining the chemistry of series of woods from peat to coalified woods from ancient rocks and seams, we have been able to discern changes in the lignin framework induced by coalification to the rank of subbituminous coal. The models were then developed by applying the observed changes to the lignin template. The model for lignin was that proposed by Adler (10).

Detailed examination of coalified wood samples of higher rank, high-volatile bituminous coal, have allowed us to extend the model to this rank range. This paper presents the data and the model for vitrinite from coalified wood of high volatile C bituminous coal rank. The model is constructed from elemental, solid-state  $^{13}\text{C}$  NMR, and flash pyrolysis/gas chromatography/mass spectrometric data.

### **Methodology**

The sample is a fossil stem which was recovered from a lacustrine shale from the Midland Formation (Triassic) near Culpeper, Virginia. Elemental and  $^{13}\text{C}$  NMR data for this sample have been previously published, but are here reevaluated for purposes of developing a structural model. Flash pyrolysis/gas chromatography/mass spectrometry was employed in a manner analogous to that described previously (6). Pyrolysis products were quantified by integrating the total ion chromatogram (TIC), assuming equivalent response factors for individual components, and normalizing the concentrations to the total peak area for all peaks in the pyrogram.

The solid-state  $^{13}\text{C}$  NMR data were obtained by both the method of cross polarization with magic angle spinning (CPMAS) and by a Bloch decay. The CPMAS conditions were similar to those described previously (7). The cycle time for the Bloch decay was 45 sec. Both NMR data

sets were transferred to a PC computer format and the peaks were deconvoluted by Lab Calc software available from Galactica Industries, Inc.

## Results

The elemental and NMR data for the coalified wood sample are shown in Table 1. The carbon content of 85.5% and a vitrinite reflectance value of 0.6 (N. Bostick, personal communication) indicate that the rank of this sample is equivalent to high volatile C bituminous coal. The oxygen content of 5.9%, measured by direct analysis (7), is significantly lower than oxygen contents (13.9%) of coalified logs of subbituminous rank (7). A significant amount of nitrogen, 2.2%, is also observed.

Comparison of the NMR data obtained by CPMAS and by Bloch decay indicates that the two methods yield virtually identical spectra (Figure 1). The Bloch decay does show greater aromaticity and possibly a higher yield of phenolic carbon (Table 1). In both spectra the broad peaks for aromatic (100 - 160 ppm) and aliphatic (0-60 ppm) carbons dominate. Discernible shoulders at 140 and 153 ppm are observed in the aromatic carbon region, and these can be assigned to aromatic bridgehead or nonprotonated aromatic carbons and phenolic carbons, respectively. With a ratio of aryl-O to total aromatic carbon of about 0.12, it appears that nearly all aromatic rings have at least one phenolic OH or aryl ether carbon. The aliphatic carbon region also exhibits fine structure with a distinct peak at 17 ppm which can be assigned to methyl carbons. Dipolar dephasing studies confirm that this peak is that of methyl carbons (7). Deconvolution of the aliphatic region shows that approximately one third of the aliphatic carbons are methyl carbons. Due to insufficient spinning speeds of the sample rotor, spinning sidebands are observed at 260 and 0 ppm.

Flash pyrolysis data for the coalified wood sample are shown in Figure 2 and the peaks are identified and quantified in Table 2. Phenol and alkylphenols are the most readily visible pyrolysis products. Of these, the three cresol isomers, 4-ethylphenol, and 2,4 dimethylphenol predominate. Other isomers of C<sub>2</sub>-phenols are apparently minor or trace components. Only 4 isomers of C<sub>3</sub>-phenols predominate, trimethyl phenol, 2 isomers of ethyl, methyl phenols, and propylphenol. The specific substitution sites have yet to be discerned. As a whole, the phenols account for approximately 60% of the aromatic pyrolysis products and 40% of the total pyrolyzates. Benzene and alkylbenzenes are the second most prominent components, accounting for about 11% of the pyrolyzates. C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub> benzenes with undetermined substitution patterns comprise the prominent components eluting in the 0-10 min retention time window.

Other pyrolysis products which account for numerous other peaks in the pyrogram are naphthalenes, alkylidibenzofurans, and n-alkane/n-alkene pairs. C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub> alkyl naphthalenes are present as various, as yet undetermined isomers. The n-alkane/n-alkene pairs show a range of carbon numbers ranging from C<sub>6</sub> to C<sub>22</sub>. The lower molecular weight homologs predominate and the distribution tapers off with increasing carbon number. Quantitatively, the n-alkanes/n-alkenes contribute to 33% of the pyrolyzate, a rather large percentage as a whole. At higher retention times in the pyrogram, peaks for alkylidibenzofurans are found. These contribute to only 3.5% of the pyrolyzate and 5.2% of the aromatic products.

## Discussion

The quantitative information on carbon types afforded by the NMR data and the molecular-level information supplied by the flash pyrolysis data provide sufficient detail to allow construction of a molecular model from a lignin template. It is clear that the original lignin structures have been modified by coalification because the coalified wood does not show any characteristics of the lignin-derived methoxy phenol structures. Previous studies (8,9) have suggested that lignin undergoes a series of coalification reactions that include 1) B-O-4 aryl-ether cleavage, 2) demethylation to form catechol-like structures, 3) dehydroxylation of the 3-carbon side chain, and 4) dehydroxylation of catechols to form phenols. In this previous study, a structural model was developed for ranks of brown coal, lignite, and subbituminous coal, using the lignin template published by Adler (10), and modifying the aromatic structures according to the coalification reactions observed for each rank level.

It is a logical progression to take the model developed in this prior study for subbituminous coal and to alter it in a way which would reflect the changes in chemistry observed between the high volatile C coal in the present study and the subbituminous coal in the previous study whose elemental and NMR data are shown in Table 1. The major changes between the two coalified woods in going towards higher rank include 1) a decrease in oxygen content from 13.9% to 5.9% with a corresponding increase in carbon content and 2) a significant increase in benzene and alkylbenzenes in pyrolyzates. Interestingly, the carbon aromaticity does not change greatly, but the fraction of aryl-O carbon to total aromatic carbon decreases by about half. This and the significant loss of oxygen from the elemental data would imply that the primary transformation of the catechol and alkylphenolic structures in subbituminous coal is a loss of aryl-O-containing structures and a condensation of the phenols to diaryl ethers.

While tracing a template through coalification is certainly a valid approach, we have begun to investigate other approaches to molecular modeling, using primarily computer methods that have recently been described (11, 12). Using a molecular modeling software similar to the one developed by Faulon et al. (12), we have generated two models, one which will be described in this paper and the other to be described by Faulon et al. (13). The model generated here provides a three dimensional graphical display of a structure constructed from a lignin framework. Briefly, the input to the model is the quantitative NMR information and the elemental data. The pyrolysis data is not used in a quantitative sense but rather a qualitative sense to input structures found that relate to lignin structural units. The lignin skeletons and inferred bonding sites are deduced from the pyrolysis data and from the previous studies on the coalification of wood showing the reactions of the various functional groups associated with lignin. For example, it is clear that the presence of 2,4 dimethylphenol in pyrolyzates indicates a lignin-derived phenol where the attachments to other structural entities are at the 2 and 4 positions. Indeed, the three-carbon side chain of lignin is in the C-4 position and a significant number of lignin units are also linked at C-2. From previous studies of coalified woods of low rank, we have deduced that the methoxy group is lost and that the three-carbon side chain is reduced to a propenyl group.

From a practical point of view, to verify the correlation between the lignin and our structure, three molecular fragments were introduced in the computerized model: propylbenzene, 4-propylphenol, and dipropylphenol. These fragments were built and stored in a library using the molecular modeling software PCMODEL (Serena software). Then, our program was asked to generate a structure containing these fragments by taking account of all analytical data. This operation was realized in two steps. First, the program computed the correct amount of fragments and connections between fragments to obtain a structure consistent with  $^{13}\text{C}$  NMR and elemental analysis. The model of lignin used as template in our previous publication (9) contains 115 carbon atoms, therefore we asked the program to find all the solutions between 95 and 135 carbon atoms. The best solution found is  $\text{C}_{113}\text{H}_{105}\text{O}_5$  and is composed of 3 propylbenzenes, 2 propylphenols, and 2 dipropylphenols. The connections between these fragments are the following: 4 biphenyl bonds, 5 benzylphenyl ether bonds, 8 bibenzyl bonds, 3 biphenylpropane bonds, and one biphenylethane bond. In a second step, from the previous list of fragments and bonds, the program was run to generate automatically a 3D structure. The program estimated first the number of structures which can be generated. The number found was too big to build all of them, therefore one structure was chosen randomly and constructed in 3D space.

Figure 3 shows a two-dimensional projection of the 3D model built by the program. There are some important features of this model that need explanation. It is important to highlight the fact that this displayed model is only one of numerous possible models that the program has calculated, and as such should be viewed as only an example whose chemistry is consistent with the chemical information provided to the program. Note that all aryl-O carbons are phenolic ethers and that the structure is composed of principally one- and two-ring aromatic systems. Also, the presence of dibenzofurans is a characteristic feature that is consistent with the pyrolysis data. In fact, the entire structure can be visualized as providing pyrolysis fragments which match rather well with the distribution of aromatic pyrolysis products. What is conspicuously absent is the presence of long-chain aliphatic structures which could give rise to the n-alkane/n-alkene pairs observed in

pyrolysis. We feel that these components are minor components of the coalified wood and are not derived from lignin structural units. It is likely that they were incorporated into the coal from either external materials migrating into the sample or from microbial remains present within the wood as it decomposed and was later coalified. It is also likely that the flash pyrolysis accentuates these substances because they are more readily pyrolysed in comparison with the lignin-derived materials. Also absent are the nitrogen-containing structures. Elemental data for this sample shows about 2% nitrogen (8). We do not have any data concerning the types of nitrogen-containing structures that might be present in this sample. Thus, we choose to omit these structures until which time we might have enough information to include them.

The three dimensional display is not readily visualized in two dimensions, but examination of the structure in Figure 3 shows the connecting points which imply that the structure is three-dimensional. The visualization of the structure in three dimensions is important from the standpoint that we must visualize coal reactivity as a three dimensional phenomenon. The ability to utilize sophisticated computer graphics displays adds to our ability to eventually utilize such structures for the prediction of coal reactivity.

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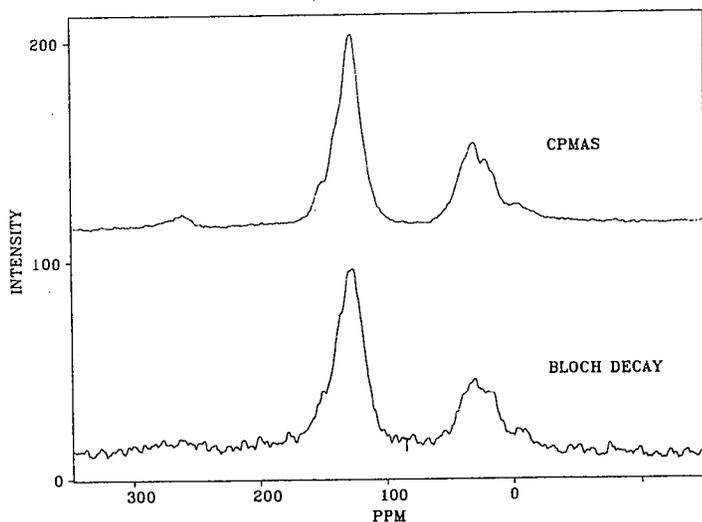


Figure 1. Solid state C NMR data for the high volatile C bituminous coalified wood obtained by the CPMAS and Bloch decay methods.

Table I. Solid-state  $^{13}\text{C}$  NMR data for coalified wood samples.

Parameter	Hv Bituminous coal	Subbituminous coal
% carbon*	85.8	77.5
% hydrogen*	6.5	5.28
% oxygen*	5.9	13.9
% nitrogen	2.2	1.0
carbon aromaticity	0.64 (0.61)	0.59
aryl-O/aryl	0.11 (0.13)	0.22
methyl/total aliphatic	0.33 (0.28)	
aryl-H/aryl	0.44	0.40

\*- moisture and ash-free values in ( ) are for Bloch decay data

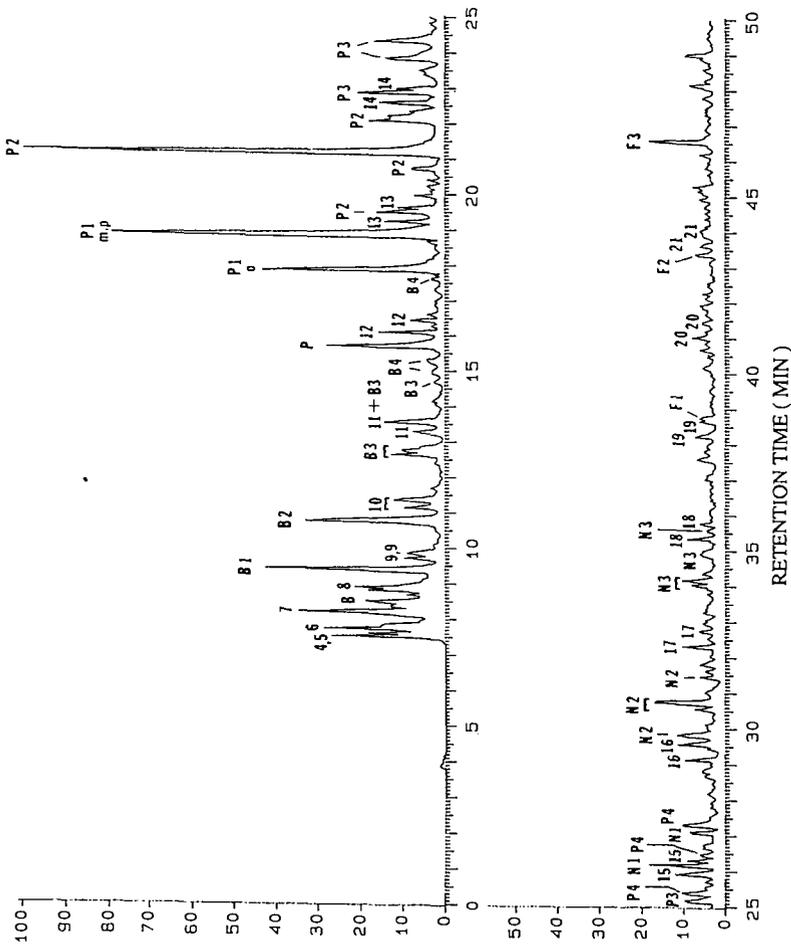


Figure 2. The pyrolysis/gc/ms trace of total ion current for the sample of Hv Bituminous coalified wood. Peak identifications are given in Table 2.

Table 2. Flash pyrolysis data for Hv C bituminous coalified wood

compound	peak designation in Figure 2	weight %	weight % normalized to aromatics
benzene	B	2.2	3.3
toluene	B1	3.2	4.8
C-2 benzenes	B2	3.4	5.2
C-3 benzenes	B3	2.6	3.9
Total benzenes		11	17
phenol	P	2.3	3.6
<i>o</i> -cresol	P1	3.7	5.7
<i>m</i> + <i>p</i> -cresol	P1	8.9	13
2,4 dimethylphenol	P2	8.2	12
other C-2 phenols	P2	6.8	11
C-3 phenols	P3	7.2	11
C-4 phenols	P4	3.2	4.8
Total phenols		40	61
alkylnaphthalenes	N1, N2, N3	11	17
alkyldibenzofurans	F1, F2, F3	3.4	5.2
C <sub>4</sub> - C <sub>22</sub>			
n-alkane/alkenes	4- 22	33	

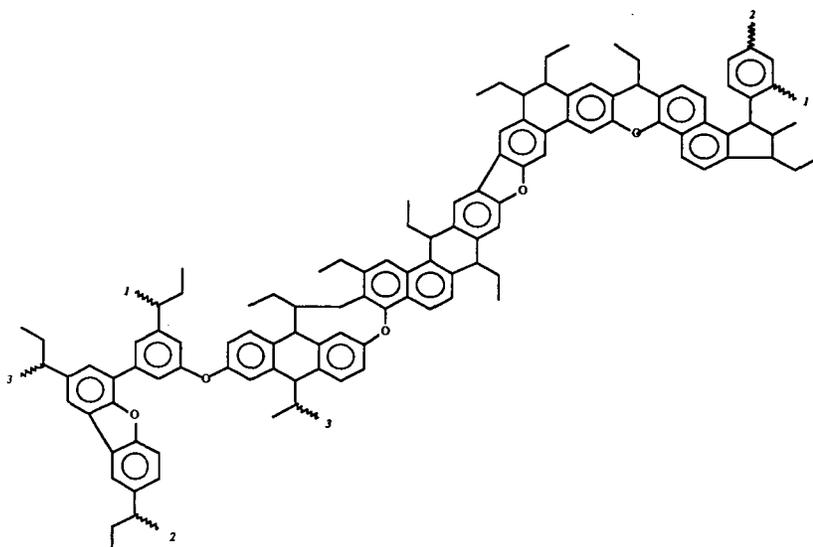


Figure 3. The two-dimensional display of the three-dimensional structural model for high volatile bituminous coalified wood.