

THE STRUCTURAL ALTERATION OF HUMINITE BY LOW SEVERITY LIQUEFACTION

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Introduction

Hydrous pyrolysis experiments were performed on low-rank coalified wood to investigate the chemical transformations that occur in huminite (vitrinite) during low severity liquefaction. The coal chosen for the experiments was of lignite rank. It consists of a single maceral huminite which consists predominantly of guaiacol- and catechol-like structures. These structures are believed to be responsible for many of the retrogressive reactions during liquefaction (1). Tubing bomb reactions were varied with reaction times ranging from 30 minutes to 240 hours and temperatures ranging from 100°C to 350°C. Structural characterization of the reacted residues were quantified by solid state ¹³C NMR and flash pyrolysis/gas chromatography/mass spectrometry. The combined analytical techniques show there is a progressive loss of oxygen which corresponds with the loss of catechols and guaiacols with increasing thermal stress. Further, dehydration of these catechol structures involves the transformation to phenol, and alkyl phenol structures that make up the macromolecular structure of the altered coalified wood. Dealkylation is also a dominant reaction pathway, as revealed by a decrease in alkyl substituents in the residue.

Detailed studies using NMR spectroscopic and pyrolysis GCMS techniques indicate that the natural evolution of humic coals proceeds through several fundamental stages (2-6). The transformation of huminite to vitrinite is characterized by reactions which result in complete demethylation of methoxy phenols to catechols and a concomitant reduction in catechols (and alkylated catechols), presumably through reaction, to form phenols and cresols; the details of the catechol reaction are so far unknown. Low severity hydrous pyrolysis of lignite parallels many of the natural coalification reactions.

Recently, Siskin et al. (7) have demonstrated that many of the reactions which typify coalification are facilitated, if not initiated, in the presence of water. They recognized that since coalification occurs in a water saturated system, water may play an integral role in the geochemistry of coalification. From their study of an enormous number of reactions with model compounds, several mechanisms with direct bearing on the chemical structural evolution of coal during liquefaction under hydrous conditions are clear. The demethylation reaction, for example, has been shown to be acid catalyzed yielding phenol as the predominant product (8). The mechanism by which the alkyl-aryl ether linkage (beta-0-4) of the modified lignin is rearranged to the beta-C-5 linkage may reasonably be expected to parallel the mechanism that Siskin et al. (7) demonstrated for their model compound study of the aquathermolysis of benzyl phenyl ether in which they observed significant yield of 2 benzyl phenol; this product is a perfect analog for the rearrangement necessary to yield the beta-C-5 linkage.

To date there is no mechanism proposed for the reduction of catechols and their alkylated analogs, through conversion, to phenol and cresols. This reaction appears to be a principal means by which the oxygen content of coal is reduced during the transformation through the subbituminous range (2-6). Although Siskin et al. (7) have not investigated the chemistry of catechols specifically, it appears reasonable to assume that the reactions of catechols may be ionic as well as thermolytic.

Experimental

A crushed sample of a coalified log described previously as the Patapsco lignite (2) was heated under hydrous conditions in a 22 ml autoclave reactor. The reactor was charged with approximately 1 gram of coal and 7 milliliters of deionized, deoxygenated water following a procedure similar to that of Siskin et al. (7). The tubing bomb reactor was consecutively pressurized to 1000 psi and depressurized with nitrogen three times to ensure all the oxygen was removed from the reactor. Finally it was depressurized to atmospheric pressure before heating. The bomb was inserted into a heated fluidized sand bath for different reaction periods, ranging from 30 min. to 10 days, and at various temperatures, ranging from 100°C to 350°C. After the elapsed heating times the reactor was removed and immediately quenched in water and then allowed to cool to room temperature. The liquids and solids were collected and analyzed. Only trace amounts of gases were detected. The bombs were opened and the liquid content pipetted off. The organic matter dissolved in the water was separated by extraction with diethyl ether. The residual lignite was removed, extracted in a 50:50 mixture of benzene:methanol, dried in a vacuum oven at 45° C for 24 hours, and then weighed.

The original lignite and solid residue from the reactors were analyzed by flash pyrolysis and by solid state NMR. The flash pyrolysis technique used was that published by Hatcher et al. (4). Solid-state ¹³C NMR spectra were obtained by the method of cross polarization and magic angle spinning (CPMAS) using the conditions previously given (2). The spectrometer was a Chemagnetics Inc. M-100 spectrometer operating at 25.2 MHz carbon frequency. Cycle times of 1 sec and contact times of 1 msec were chosen as the optimal conditions for quantitative spectroscopy.

Results and Discussion

Aquathermolysis of the Patapsco lignite was conceived as a means to trace the chemical changes that occur to the dominant maceral in low rank coals during liquefaction. Accordingly, our goal was to examine the coal before and after thermal treatment and to infer liquefaction pathways. Conversions ranged from 29 to 40 percent for the different experiments (Table I). This mass loss probably reflects low molecular weight products formed, water, and partial solubilization of lignitic structures originally of low molecular weight. The GC/MS analysis of the water soluble materials indicates the presence of lignin phenols and catechols, all of which are components of the lignite prior to thermolysis. Cleavage of a few bonds on the macromolecule could conceivably produce a catechol or methoxyphenol which would be soluble in water. Another water soluble product identified was acetic acid. This product is most likely derived from thermolysis of the side-chain carbons associated with the original lignin and coalified lignin in the sample. The content of evolved gases was not measured, because the amount of gas evolved was negligible.

The NMR data of the thermolysis residues (Figure 1) indicates clearly the evolutionary path during thermolysis. Comparing the NMR data for the residues with the original lignite and with gymnospermous wood coalified to higher rank (2) there appear to be several changes which describe the average chemical alteration. First, the most obvious change is the loss of aryl-O carbons having a chemical shift at 145 ppm. From previous studies (2) this peak has been assigned to aryl-O carbons in catechol-like structures in the coalified wood, based on chemical shift assignments and pyrolysis data. These are thought

to be originally derived from demethylation of lignin during coalification (2-6). The NMR spectrum of the aquathermolysis residue has clearly lost most of the intensity at 145 ppm but now shows a peak at 153 ppm which is related to aryl-O carbons in monohydric phenols. These are the primary constituents of subbituminous and high volatile bituminous coalified wood as depicted in the NMR spectra for such woods. It is obvious that the catechol-like structures of the lignitic wood have been transformed to phenol-like structures somewhat similar to those in higher rank coal. Thus, the aquathermolysis has reproduced, to some degree, the coalification reactions acting on aromatic centers.

The second most apparent change to occur during aquathermolysis is the loss of aliphatic structures. The methoxyl groups at 56 ppm are lost from the lignitic wood as are the other alkyl-O carbons at 74 ppm, consistent with demethylation reactions and dehydroxylation of the three carbon side chains of lignin which occur naturally during coalification of woods. However, the loss of alkyl-C carbons (those aliphatic carbons not substituted by oxygen) is the most significant change in the aliphatic region in the aquathermolysis residue. Loss of substantial amounts of aliphatic carbon is not observed during coalification of wood from lignite to high volatile bituminous coal. In fact, in most coalified wood samples, loss of alkyl-C carbon occurs only at higher ranks, above that of medium volatile bituminous coal. The lack of retention of aliphatic carbon during aquathermolysis is an indication that this treatment probably does not reproduce well the low-rank coalification reactions associated with aliphatic structures. It is important to note that the alkyl-C carbons in the aquathermolysis residues become dominated by methyl carbons with increasing thermal stress.

The pyrolysis data (Figure 2) provide confirmation for the average changes in structure observed by NMR. The loss of catechol-like structures is documented with the significant diminution of catechols in the pyrolyzate of the aquathermolysis residue compared to that of the original lignite. This loss of catechols is the singular most significant change in pyrolysis products. The pyrolyzate of the residue mimics somewhat the pyrolysis data for subbituminous coalified wood (3), being dominated by phenol and alkylphenols. Another difference between aquathermolysis residues and the original lignitic wood is in the abundance of methoxyphenols derived from lignin-like structures. The aquathermolysis has apparently reduced the relative yields significantly, consistent with the NMR data showing loss of methoxyl carbons. Some of the methoxyphenols may have been transformed to water soluble phenols and washed out of the residue in the aqueous phase; others may have undergone demethylation reactions, converted to catechols and then transformed to phenols.

The pyrolysis of the residue yields mostly phenol and the cresol isomers; other alkylated phenols, the C₂ and C₃ phenols, are not as abundant relative to phenol and cresols as the C₂ and C₃ phenols are in the pyrolysis of original lignite or the subbituminous log. This is probably related to the fact that alkyl substituents are not as abundant in the residue and the alkyl substituents are probably mostly methyl substituents as was deduced from the NMR data. Thus, the lack of significant relative amounts of C₂ and C₃ phenols in the thermolysis residue's pyrolyzate further supports the conclusion that thermolysis does not reproduce coalification reactions with regard to the aliphatic structures in the residue. The relatively high temperatures used in this study may force proportionally more thermolytic pathways over ionic pathways. The potential for such a situation has been recognized by Siskin et al. (7).

Acknowledgments

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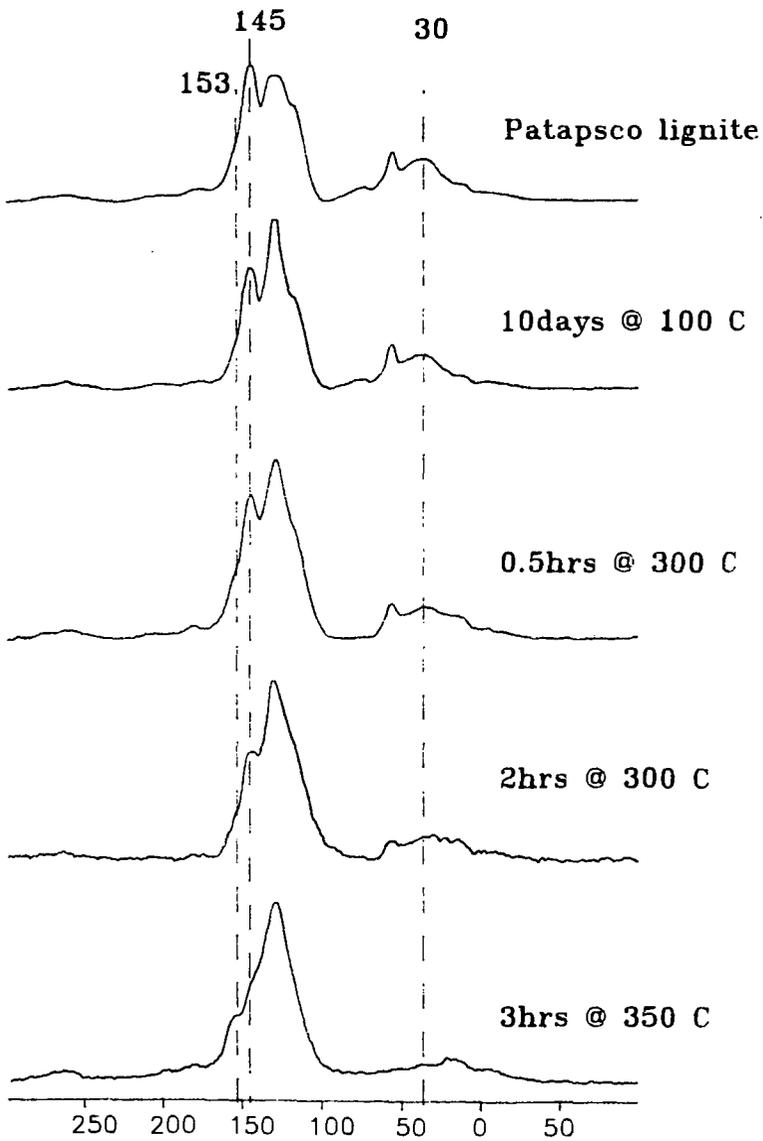


Figure 1. CPMAS ^{13}C NMR of the Patapsco lignite and the thermally altered residues.

Table I. Conversion data for hydrous pyrolysis experiments.

#	time	temperature	conversion, %
1	240 hrs	100°C	29.3
2	.5 hrs	300°C	29.8
3	2 hrs	300°C	30.6
4	3 hrs	350°C	39.7

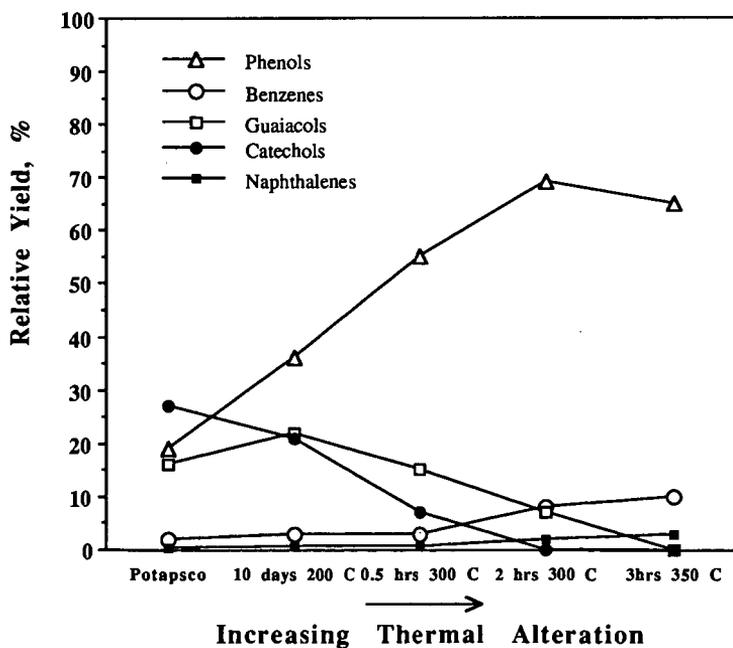


Figure 2. Relative Yields of Flash Pyrolysis Products from Aquathermolysis Residues