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Effects of Low-Temperature Catalytic Pretreatments on Coal Structure and Reactivity in Liquefaction

Technical Progress Report
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DISCLAIMER

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ABSTRACT

In this quarter, progress has been made in the following two aspects: the influences of temperature, dispersed Mo catalyst, and solvent on the liquefaction conversion and composition of products from low-rank coals; and the hydrous pyrolysis of a lignite and spectroscopic characterization of its structural transformation during the hydrous pyrolysis. The analytical work described in this quarter also represents molecular-level characterization of products.

The purpose of the first part of the work described in this quarter is to study the influences of temperature, solvent and dispersed Mo catalyst on the liquefaction conversion and chemical composition of the products. Recently there has been intense interest in aromatic specialty chemicals and monomers for advanced engineering polymers, which represent a rapidly growing market. Many specialty chemicals, including one- to four-ring aromatics, could potentially be produced by liquefying coal. To achieve this goal, not only a high coal conversion but also a desirable product distribution is necessary. Therefore, it is of great importance to understand the structural changes of the coal during reaction and to investigate the conditions under which the aliphatics or aromatics can be removed from the macromolecular structure of coal. In this work, three low-rank coals, two subbituminous and one lignite, were selected. Reactions are carried out at temperatures between 250°C and 450°C with the presence of hydrogen. Tetralin and 1-methylnaphthalene are used as the hydrogen-donor and non-donor solvents. Ammonium tetrathiomolybdate is chosen as the catalyst precursor. The results of one of the subbituminous coals show that over 95% conversion can be achieved at 400°C with the catalyst or the donor solvent; that the removal of aliphatic carbons from the coal strongly depends on temperature; but that the removal of aromatic carbons depends on not only temperature but also the nature of the solvent and the catalyst.

This quarterly report also describes the hydrous pyrolysis of Potapsco lignite and spectroscopic characterization of its structural transformation during the hydrous pyrolysis. This work has some implications both on the structural changes of low-rank coals during pretreatment and on the geochemical reactions during coalification stage. Vitrinite, a major component of most coals, is derived from degraded wood in ancient peat swamps. Organic geochemical studies conducted on a series of coalified wood samples derived mostly from gymnosperms have

allowed the development of a chemical reaction series to characterize the major coalification reactions which lignin, the major coal-producing component of wood, undergoes. These involve mostly hydrolysis of aryl ethers, reduction of alkoxyl side chains, alkylation of reactive aromatic sites, and finally condensation reactions of phenolic moieties. Thus, lignin is transformed to catechol-like structures and these are converted to phenol-like structures. The former reactions are well understood to occur during peatification by the action of microorganisms, but the latter have not been shown to be possible in other than model systems. To demonstrate that the catechol-like structures can be made to evolve to phenol-like structures under natural conditions, we attempted to simulate natural burial processes by artificially coalifying a sample containing mostly catechol-like structures under conditions of hydrous pyrolysis. These conditions did indeed induce transformations of catechol-like structures to phenol-like structures, but the reactions do not reproduce well the coalification reactions with regard to aliphatic structures in coal.

PROJECT OBJECTIVES

This work is a fundamental study of catalytic pretreatments as a potential preconversion step to low-severity liquefaction. The ultimate goal of this work is to provide the basis for the design of an improved liquefaction process and to facilitate our understanding of those processes that occur when coals are initially dissolved. The main objectives of this project are to study the effects of low-temperature pretreatments on coal structure and their impacts on the subsequent liquefaction. The effects of pretreatment temperatures, catalyst type, coal rank and influence of solvent will be examined.

The specific objectives are to identify the basic changes in coal structure induced by catalytic and thermal pretreatments by using spectroscopic, thermochemical and chemical techniques; and to determine the reactivity of the catalytically and thermally treated coals for coal liquefaction. Combining the two lines of information will allow us to identify the pretreatment-induced desirable or undesirable basic changes in coal structure; to clarify the impacts of pretreatments on coal liquefaction; to identify the structures responsible for retrograde reactions; to evaluate the structural differences resulting from different catalytic actions in relation to the overall catalytic effects in liquefaction; and ultimately, to develop a structure-reactivity relationship for liquefaction associated with catalyst type, coal rank and solvent. Furthermore, this research will contribute greatly to the development of effective pretreatment procedures which will allow coals to be liquefied more efficiently than the current practice. Finally, much of the knowledge to be generated from this research is not only critical for developing advanced hydroliquefaction processes, but also very useful to development of coal/petroleum resid co-processing, pyrolysis and hydropyrolysis processes.

TECHNICAL PROGRESS

TASKS 5 AND 6: EFFECTS OF PRETREATMENT ON COAL LIQUEFACTION AND PRODUCT QUALITY

1. LIQUEFACTION OF LOW-RANK COALS AND MOLECULAR-LEVEL CHARACTERIZATION OF REACTION PRODUCTS

INTRODUCTION

Recently there has been significant progress in the development and application of aromatic engineering plastics, thermoplastic materials, liquid crystalline polymers, and membrane materials [1, 2]. Some of the monomers for making these advanced materials can be prepared from one- to four-ring aromatics, which can potentially be produced by liquefying coals [1-3]. It is generally accepted that in low-rank coals (lignite and subbituminous), the majority of aromatic structural units contains one or two rings, such as phenol, alkylphenols, alkylbenzenes and small amounts of alkylnaphthalenes [4, 5]; while in high-rank coals (bituminous), two- to four-ring structural units seem to be more prevalent [5, 6].

In this study, three low-rank coals, including two subbituminous and one lignite, were liquefied in an attempt to produce one- or two-ring aromatic chemicals. Reaction conditions (temperature, catalyst and reaction solvent) were carefully studied in order to find the optimum conditions under which progressive reactions are maximized while retrogressive reactions are minimized, and thus high conversions can be achieved. The liquefaction products were characterized by solid state ^{13}C NMR, gas chromatography and gas chromatography/mass spectrometry, and correlated to the reaction conditions.

EXPERIMENTAL

The coal samples were a Big Brown subbituminous (DECS-1), a Montana subbituminous (DECS-9), and a North Dakota lignite (DECS-11). Their compositional data are summarized in Table 1. The reaction solvents were tetralin (Aldrich, 99%) and 1-methylnaphalene (1-MN, Aldrich, 98%). The catalyst precursor was ammonium tetrathiomolybdate (ATTM, Aldrich, 99.97%). All the chemicals were used without further purification.

The catalyst loading was 1 wt% of Mo based on the dmmf coal. A THF/H_2O (1:1) mixture was used to make the solution of the catalyst precursor, because this binary mixture was superior to H_2O in terms of providing higher conversion and oil yield [7]. The catalyst precursor was first added to water, of just enough volume to dissolve the desired amount of the precursor. An equal volume of THF was then added to the H_2O solution. After being stirred to achieve a homogeneous mixture, the THF/H_2O/ATTM mixture was added to the dried coal to make a slurry. After 20 minutes of stirring at room temperature under N_2 atmosphere, the excess water and THF was removed by rotary evaporator. The "wet" sample (still containing some residual H_2O and THF) was then dried in a vacuum oven at room temperature for 20 hours, at 45°C for 5 hours and at 95°C for 4 hours, sequentially.

Liquefaction experiments were conducted in 25 mL microautoclaves in a fluidized sandbath. For each reaction, 4 grams of a coal sample and 4 grams of a solvent, if a solvent was applied, were loaded into a microautoclave. The reactor was purged three times with H_2 and the final pressure was 1000 psi (7 MPa) at room temperature. For every reaction, the sandbath was preheated and kept at a desired temperature, ranging from 250°C to 450°C. The microautoclave was then plunged into the sandbath and agitated at a rate of 200 cycles per minutes. The total time in which a microautoclave was kept in the sandbath was 33 minutes, with 3 minutes being the time for rapid heat up and 30 minutes for reaction at the desired temperature. Finally, after reaction, the microautoclave was taken out of the sandbath, and rapidly quenched by dipping into cold water.

After the microautoclave was cooled to room temperature, the reactor was vented, the volume of the gas was measured using the water displacement method, and a sample was collected for further analysis. The liquids and the solids in the microautoclave were washed into a tared ceramic thimble using hexane. Then the products were separated under a nitrogen atmosphere by Soxhlet extraction using hexane, toluene and tetrahydrofuran (THF) sequentially. The soluble products are classified as oil, asphaltene and preasphaltene, respectively. The THF-insoluble product is called residue.

The gaseous products were analyzed using a Perkin-Elmer Autosystem gas chromatograph (GC). Details are described elsewhere [7]. The components in the hexane solubles (oils) were identified by a Hewlett-Packard 5890 Series II GC coupled with 5971A mass selective detector (MSD) and quantified by a Hewlett-Packard 5890 GC. The reaction residues, asphaltenes and preasphaltenes were analyzed by ^{13}C solid state NMR using cross polarization magic angle spinning (CPMAS) technique. All CPMAS spectra were obtained on a Chemagnetics NMR Model M100s. The ^{13}C frequency was 25.15 MHz. The pulse delay was 1 second and the contact time was 1 ms.

RESULTS AND DISCUSSION

Conversions of Liquefaction

The structures of low-rank coals are characterized by smaller aromatic ring clusters joined by a higher proportion of weak crosslinks than coals of higher rank. This kind of structural feature results in their thermally sensitive natures. The bond cleavages of those weak crosslinks may occur at low temperatures to yield free radicals. If the radicals are not stabilized, retrogressive reactions producing materials difficult to liquefy will take place. Therefore, it is important to determine the optimum temperatures for each coal at which thermal cleavages readily occur while retrogressive reactions are unlikely to occur. Liquefaction experiments were carried out at 250°C, 300°C, 350°C, 400°C and 450°C with the presence of H_2 and the absence of a catalyst and a solvent. The conversion data are shown in Figure 1. At 350°C and below, reactions of all three coals are very limited, with conversions below 20%. As temperature increases to 400°C and 450°C, conversions significantly and continuously increase. However, our earlier study [8] has shown that although a temperature of 450°C seems to be more beneficial in obtaining high conversions, it causes severe retrogressive reactions which are indicated by very high aromaticities of the reaction residues. Therefore 400°C is considered to be the best temperature for liquefaction of these coals.

However, even at the optimum temperature, 400°C, no more than 50% of the coals can be converted to THF solubles when neither a catalyst nor a solvent is involved. In an effort to enhance the conversions, ATTM was added as a catalyst precursor; tetralin and 1-methylnaphthalene were used as a hydrogen donor and a non-donor solvent respectively. The effects of the catalyst and solvents are presented in Figure 2. By using the catalyst, the conversions were increased from 45% to 95.5% for the DECS-1 coal, from 24.2% to 78.5% for the DECS-9 coal, and from 30.6% to 63.5% for the DECS-11 coal. These increases are contributed by significant gains in oils and asphaltenes. The gas yields in the catalytic and non-catalytic reactions are very similar for each coal, which is in an agreement with our earlier observation that the gas yield is a function of temperature, and the use of the catalyst or the donor solvent has no significant effect on it [8]. To maximize the conversion, tetralin and 1-MN were applied in addition to the catalyst. As a donor solvent, tetralin further causes more coal converted to THF solubles for DECS-9 and DECS-11. For DECS-1, there is no increase in conversion, although that is because even with only the catalyst, the conversion reaches 95%. It is reasonable to say that this may already be the practical maximum conversion limit. As a non-donor solvent, 1-MN has a very insignificant effect on the conversions of all the three coals. Comparing conversions at different reaction conditions, it is found that adding the catalyst is sufficient to achieve the highest conversion for the DECS-1 coal; while it is necessary to add both the catalyst and the donor solvent for the DECS-9 and the DECS-11 coals. Among these coals, the DECS-11 is relatively unreactive, its conversion can reach only about 80% at the best reaction condition applied in this study.

Product Characterization

To produce materials from a coal for making the special chemicals, a high conversion has to be achieved and, more importantly, those desirable structural units in the coal macromolecular network have to be converted to individual molecules. In this work, one- to four-ring aromatic or alkylaromatic compounds were desired. In other words, more aromatic carbons have to be converted to THF solubles. To determine the amounts of aromatic carbons converted, the reaction residues as well as the vacuum-dried coal samples were analyzed by CPMAS ^{13}C NMR. The spectra were curve-fitted and integrated, and the aromaticities (f_a) were calculated based on the areas covered by the spectra in aromatic and aliphatic regions. Since the weights of both coals and residues are known, and data of overall conversions from coals to THF solubles are available, the percentages of the reacted aliphatic and aromatic carbons can be determined, as shown in Figure 3 and 4. In these figures, it is apparent that converting aliphatic carbons from the coal networks to THF solubles is much easier than converting aromatic carbons. At 400°C, even without catalyst or solvent, over 50% of aliphatic carbons are converted for all three coals. Adding the catalyst can increase the aliphatic conversions to greater extents. Furthermore, if tetralin is used in addition to the catalyst, slight increases in the aliphatic carbon conversions of DECS-9 and DECS-11 are observed, while that of DECS-1 shows almost no change, which is expected because even only with the catalyst, the conversion approaches 100%. Comparing these three coals, the aliphatic carbons in DECS-1 are the easiest to be converted; those in DECS-11 are the least. In Figure 4, the aromatic carbons appear to be more difficult to be removed from the coal networks, and they are affected more strongly by the catalyst or the donor solvent than the aliphatic carbons. Without the presence of the catalyst or the donor solvent, less than 20% can be converted. For the DECS-9 coal, the conversion is negative, meaning that there are more aromatic carbons than we start with. This indicates the occurrence of retrogressive reactions. Therefore, to convert the aromatic carbons, it is crucial to use the catalyst, the donor solvent or both. For the DECS-1 coal, the catalyst is sufficient to achieve over 95% aromatic conversion; for the DECS-9 coal, with both the catalyst and the donor solvent, 98% can be obtained; while for the DECS-11 coal, the least convertible coal in terms of conversion, even with both the catalyst and the donor solvent, only about 70% aromatic conversion can be achieved.

The asphaltenes and the preasphaltenes were also studied by CPMAS ^{13}C NMR. Unfortunately, their spectra look so much like the vacuum-dried coals that they can not be characterized without other analytical techniques. The hexane solubles, defined as oils, were analyzed by gas chromatography, identified by gas chromatography/mass spectrometry. Figure 5 represents the oils from the DECS-9 coal without the catalyst or the donor solvent, *a*; with the catalyst but not the donor solvent, *b*; and with both the catalyst and the donor solvent, *c*. In Figure 5-*a*, the oil contains a high proportion of long-chain alkanes, i. e. from n-C_{12} to n-C_{33}. At retention time of about 6.0 minutes, there is a very strong peak identified as toluene. In low-rank coals such as DECS-9, small aromatic clusters dominate [4, 5], and they are connected by aliphatic crosslinks. Once the crosslinks break, these small aromatic clusters will be released. In the DECS-9, as shown in our recent work [4], one-ring structural units are abundant and thus when liquefying the coal, toluene (instead of benzene) will be a major product, because the benzylic C-C bond has a much lower dissociation energy than the phenyl C-C bond [9]. Relative to those of aliphatics, the amounts of aromatic compounds in the oil (with relation times from 15 minutes to 30 minutes) are much smaller (Figure 5*a*), indicating that this reaction condition suppresses the production of aromatic compounds in the oil. Comparing with the case without the catalyst or the donor solvent, adding ATTM into the reaction system appears to favor the yields of aromatic compounds. As shown in Figure 5*b*, the alkylbenzenes, phenol and alkylphenols are the major components in the oil. This observation agrees with our earlier finding that the catalyst is particularly beneficial in converting the aromatic carbons from the coal to THF solubles rather than converting the aliphatic carbons [8]. Furthermore, when we use tetralin in addition to the catalyst, the yields of phenolic compounds remain very high, Figure 5*c*; the one-ring aromatics seem to be in a lower proportion; and the yields of two-ring aromatics, such as indane, alkylindanes and alkylnaphthalenes have increased. The large peaks at retention times about 24.5 minutes and 27.0 minutes are due to tetralin and naphthalene, the solvent and the dehydrogenated solvent. It is likely that the increased yields of alkylindanes and alkylnaphthalenes are due, at least in part, to the use of tetralin. In the GC study, three- or four-ring compounds appear to be in small amounts and not affected by either the catalyst nor the solvent. This may be because they are less abundant than the one- or two-rings in the coal, or because their solubilities in hexane are smaller and therefore it is hard to detect the differences at different cases.

CONCLUSIONS

In liquefaction of the three low-rank coals, temperature is found to be optimum at 400°C. Reactions without the catalyst or the donor solvent provide very low conversion, i. e. less than 50%, for all three coals. As for the DECS-1 coal, the ATTM-derived catalyst is sufficient in terms of a high conversion. As for the DECS-9 coal, only when both the catalyst and the donor solvent are used can conversion as high as 98% be achieved. For the DECS-11 coal, even under the best reaction condition, which is at 400°C with the catalyst and the solvent, the conversion only reaches 78%. Therefore, the DECS-11 coal is the least convertible coal among the three.

The investigation on reaction residues by solid-state NMR shows that it is relatively easier to convert aliphatic carbons from coals to THF solubles, and that the catalyst and the donor solvent can both be beneficial but the effects are moderate. The amounts of aromatic carbons being converted from the coals appear to be small when the catalyst or the donor solvent is not present, and they can even be negative, indicating that retrogressive reactions have occurred. Adding the catalyst and the solvent significantly enhances the reactions of aromatic carbons.

The study of the oils agrees with what has been observed on the residues. Without the presence of the catalyst or the solvent, the oils contain large amounts of long-chain alkanes; while with the catalyst and the donor solvent, more aromatic materials, such as phenolic compounds, alkylbenzenes and some two-ring compounds, can be produced. With further extraction and purification, these compounds might be used as for making specialty chemicals for some advanced materials.

Studies on the other two coals are in progress to test the general applicability of the above-mentioned findings.

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2. HYDROUS PYROLYSIS OF POTAPSCO LIGNITE AND SPECTROSCOPIC CHARACTERIZATION OF ITS STRUCTURAL TRANSFORMATION

Introduction

It is well recognized that coal is a complex assemblage of macromolecularly discreet components of varied origin. Accordingly one would expect the chemistry of each type of discreet component to be different, though some may exhibit certain similarities. Defining the chemical structural compositions of all these discreet components is a formidable task, even by today's standards of rapid sophisticated analyses. Perhaps the one aspect of coal structure which has prevented more thorough investigations of the components is the fact that many components, macerals in the vernacular, exist as minute entities finely comminuted within a matrix composed of other macerals. The inability to cleanly separate macerals for detailed chemical analysis has placed some severe constraints on our knowledge of their chemical structural compositions. Separation methods based on density have allowed some progress in this area (*1,2*), but these methods cannot provide reliable separations for all macerals. The recent introduction of a new technique of laser pyrolysis (*3,4*) which has the capability of focusing on the pyrolytic chemistry of macerals within a laser beam's path of 25 μm, holds some promise for future work. Thus at present, we are forced to rely on hand-picking methods to reliably isolate macerals for chemical analysis. The major drawback here is the inability to hand-pick all but the macerals existing in large physical domains. Even in such cases, we can never be certain of maceral purity. Our only hope of defining coal's chemical structural composition is by a systematic isolation and characterization of the major maceral types, as a start, and then the development of new techniques of microanalysis. In cases where macerals cannot be cleanly isolated at the macroscopic scale, we must resign ourselves to separation by density gradient centrifugation of finely ground coal. However, in cases where macerals can be isolated on a macroscopic scale, it is best to resort to hand-picking techniques for isolation. Accordingly, the major maceral type which can be easily recognized and physically isolated is vitrinite derived from coalified wood specimens.

The structural evolution of vitrinite has been previously studied in our group through detailed characterization of coalified wood which spans the entire coalification range (*5-7*). The use of coalified logs was demonstrated to be especially useful as it removes the superposed problem of maceral scale heterogenieties from the problem of identifying fundamental transformations which delineate the coal's chemical structural evolution. The net result of these detailed studies using ^{13}C NMR and pyrolysis/gas chromatography/ mass spectrometric (py/gc/ms) methods is the identification of several key chemical structural transformations which typify the coalification of woody material into high volatile bituminous coal.

Although, the coalification series represents a continuum of parallel and serial processes; several principle stages of coalification are clearly evident. The initial, biochemical, stage of coalification is characterized by a complete loss in hemicellulose, a significant reduction in cellulose, and selective preservation ,with minimal alteration, of lignin derived material (*8,9*). Early diagenetic changes accompanying the transformation from brown coal into lignite result in a near complete removal of cellulose and some modification of the lignin, a macromolecular material composed of methoxyphenols with a polyhydroxypropanol side-chain as basic building blocks. These modifications are, dominantly, rearrangement of alkyl-aryl ether bond that links the methoxyphenols together to yield methoxyphenols linked by an aryl-alkyl bond between the structural units, as well as some demethylation of methoxy groups yielding catechol-like structures (*7*). The transformation of coalified wood from lignite through the subbituminous rank range to high volatile C rank bituminous coal is characterized by transformations which result in complete demethylation of methoxyphenols to catechols and a subsequent reduction of the catechol-like structures, presumably through reaction, to form phenol-like structures. The focus of this paper is to review our current understanding of the evidence for these aforementioned chemical transformations and to present some new data relating to the specific reactions responsible for the major part of oxygen loss during coalification.

Recently, Siskin and Katritzky (*10*) have demonstrated that many of the reactions which typify coalification are facilitated, if not completely initiated, by the presence of water. They recognized that, since coalification occurs in a water saturated system, water may play an integral role in the chemistry 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 are clear. The demethylation of methoxybenzene, for example, has been shown to be acid catalyzed yielding phenol as the predominant product (*11*). The mechanism by which the alkyl-aryl ether linkage (known as the ß-0-4 linkage) of the modified lignin is rearranged to the ß-C-5 linkage as proposed by Hatcher (7) to explain coalification of lignin in wood to brown coal and lignite may reasonably be expected to parallel the mechanism that Siskin et al.(*12*) demonstrated for their model compound study of the hydrous pyrolysis of benzylphenylether. They observed a significant yield of 2 benzyl phenol; this product is a perfect analog for the rearrangement necessary to yield the ß-C-5 linkage found to be important in brown coal wood.

Currently, there is no mechanism proposed for the conversion of catechol-like structures to phenol-like structures during coalification. However, this transformation appears to be a principal means by which the oxygen content of coal is reduced during the transformation from brown coal and lignitic wood through wood coalified to the subbituminous range (7) and is, therefore, of considerable interest. Although Siskin and Katritzky (*10*) have not investigated the chemistry of catechols specifically, they did study 4-phenoxyphenol. It appears reasonable to assume that the reactions involving condensed catechols, as might be found in coal, may follow a similar reaction chemistry. The present paper sets out to investigate this possibility as well as to investigate the role of hydrous pyrolysis on coalification in a broader sense by initiating artificial coalification studies on a lignitic coalified log. By comparing the chemical structural evolution of the lignitic log, which has been subjected to hydrous pyrolysis, to the results from previous studies of natural coalification, it should be possible to derive the most probable mechanism for the catechol reduction pathway. In addition to this specific transformation, the success of artificial coalification in general is considered through the comparison between the residues of treated lignitic log with essentially equivalent rank, naturally coalified, logs.

Review of the coalification of wood

The advent of some new techniques in the 1980's has provided the methodology for establishing a better understanding of the chemistry of coal and its maceral components. The application of these techniques, principally ^{13}C nuclear magnetic resonance (NMR) and flash pyrolysis/gas chromatography/mass spectrometry (py/gc/ms), to studies of series of coalified wood samples has provided a new glimpse of the processes responsible for coalification. By comparisons of the chemical compositions of wood at various stages of coalification, one can infer specific reactions responsible for coalification.

Peatification. It was made especially clear from studies of fresh wood and peatified wood (*8,9,13-15*) that cellulosic components of wood, the ones contributing more than 60% of the structure, essentially are mineralized or degraded and lost within a short span of time geologically. Thus, the cellulosic components do not play a significant role in the structural make-up of coalified wood. The lignin, however, is selectively preserved in a relatively unaltered state during peatification and is the substance which eventually forms the coalified wood's vitrinitic component.

Perhaps the most astounding aspect of this degradative process is the selectivity and structural precision with which it occurs. Essentially all of the major mass component of wood, the cellulose, is lost. One might infer that tremendous physical destruction ensues; however, peatified wood remarkably retains its morphology. This can clearly be seen in Figure 6 which shows an SEM photomicrograph of degraded wood in peat. Delicate wood structures such as bordered pits and cell wall tracheids appear physically intact even though all the cellulose has been degraded. Apparently, the wood has been degraded by bacteria which use extracellular enzymes to enable destruction of the cellulosic materials. This process apparently does not involve physical maceration.

Coalification to brown coal and lignite. The lignin which survives this initial degradative process relatively unscathed, is eventually altered over the course of geological time as wood in peat is buried in sedimentary systems. We know this from studies of coalified wood in brown coals and lignites (*5-7,13-17*). By comparing the chemistries of peatified wood, mainly lignin, with brown coal or lignitic woods of the same family (e.g., gymnosperms, angiosperms), we can decipher reactions which might be responsible for observed changes. We certainly can identify the nature of chemical changes which occurred. These are depicted in Figure 7.

Perhaps the most chemically and microbiologically labile bond in lignin is the bond linking the methoxyphenolic aromatic monomers together, the β-O-4 bond. Evidence that this bond is cleaved during coalification was provided by Hatcher (*7*), from an examination of the NMR spectra of brown coal woods. If we consider that all such bonds in lignin are broken and the fact that approximately 60% of the bonds in lignin are of this type, then we might expect the lignin, or the peatified wood, to be completely macerated because rupture of this bond would release molecular fragments which are likely to be soluble in water. Examination of SEM photomicrographs of brown coal wood in which such bond ruptures have occurred shows that physical disruption of the wood anatomy does not occur to any great extent (Figure 8). Delicate structures such as bordered pits would not physically survive a maceration. Also, the SEM photos do not provide any evidence for dissolution or even partial dissolution of cell walls. This must imply that another reaction maintains the macromolecular integrity of the lignin.

The reaction most likely responsible for maintaining structural integrity must be one which allows connectivity between methoxyphenolic structures in lignin. Thus, we must maintain some bond between the aromatic units. Alkylation following β-O-4 bond rupture is the likely reaction. Botto (*18*) has shown that such an alkylation is possible when lignin labeled at the β carbon is subjected to artificial coalification in the presence of clays. In essence, the rupture of the β-O-4 bond releases a carbocation, the β carbon on the sidechain, which is a good electrophile and will attack positions on the aromatic ring of adjacent phenolic structures which are susceptible to electrophilic substitution (e.g., the C-5 predominantly). The most likely aromatic ring to be alkylated is the one from which the β-O-4 bond rupture occurred. The rupture of the β-O-4 bond would produce a phenol which would likely activate the C-5 site to alkylation. Evidence that such a reaction occurs in brown coal wood comes from the NMR data which show increased aromatic ring substitution (*6,7*). Dipolar dephasing NMR studies indicate that brown coal wood samples have fewer protons per ring than their respective counterparts in peat, indicating that, on the average, one of the ring sites has become covalently bound to an atom other than hydrogen. The NMR data also indicate that the additional substituent atom is not an oxygen but a carbon atom. It is clear that the data all point to the fact that cleavage of the β-O-4 bond during coalification of the lignin in peatified wood leads to a alkylation of an adjacent ring by the resulting carbocation, and this overall process leads to a maintenance of the physical integrity of the wood.

To maintain this integrity observed unambiguously from SEM data (Figure 8) it is necessary that the above reaction occur without much structural rearrangement of the lignin. In other words, the reaction must proceed rapidly and must occur at a relatively proximal site to the β-O-4 cleavage. If one considers a lignin model as one which is random in the connectivity between methoxyphenolic units (*19,20*), then the likelyhood that structural order will be maintained with the above-mentioned transformation is minimal. In a random model, distances between aromatic reaction centers are variable and some significant physical disruptions will ensue if the carbocations formed from β-O-4 bond rupture have to link up with aromatic centers which are more than just local.

Faulon and Hatcher (*21*) have recently proposed a new model for lignin which would overcome this problem. The model is one which is ordered rather than random. The order is believed to derive from the fact that the methoxyphenolic units linked by the β-O-4 bonds in lignin exist in an helical conformation. With such a configuration, cleavage of this bond releases a carbocation which is in relatively close proximity to the C-5 site on the aromatic ring. The alkylation of this site causes minimum disruption of the helical order as a β-C-5 bond is formed (J.-L. Faulon, personnal communication). Thus, we might also expect minimum disruption of the physical integrity of the sample, consistent with what is observed in brown coal wood.

Another important coalification reaction which is observed to occur through the lignite stage of coalification is the cleavage of other aryl-O bonds in lignin. The specific bonds are those of methoxyl groups attached to the aromatic ring. Both NMR and py/gc/ms data show that this is happening (*15,16*). The chemical degradative data of Ohta and Venkatesan (*17*) also show this reaction. All these studies indicate that the loss of methoxyl is through a demethylation process whereby the bond between the methyl carbons and the oxygen attached to the ring is cleaved. The molecular modeling studies show that the helical configuration is not affected by such a reaction (*22*). The resulting structure of the coal contains a phenol where there once was a methoxyl group, and the structure is now said to have one similar to that of catechols, if one considers that the cleavage of the β-O-4 bond has already occurred.

Additional changes in lignin structure are more subtle, but somewhat evident from NMR data. In lignin and peatified wood, the sidechains are hydroxylated at both the α and γ sites. Loss of hydroxyl groups from the sidechains is another reaction resulting from coalification of the lignin. NMR resonances attributable to these hydroxyls diminish substantially during coalification through to the rank of subbituminous coal. Simple loss of the sidechain units by a pyrolytic process would explain the loss of these resonances, but this would lead to a significant increase in aromaticity. Because aromaticities of coalified wood samples do not increase over the course of the observed loss of hydroxyls, it is likely that simple reduction of the hydroxyls to alkyl groups is the preferred pathway. This would shift the NMR resonances into the alkyl region of the spectra and preserve carbon aromaticities. Such a reaction would also be consistent with the physical structural data, because reduction of hydroxyls would maintain the presumed helical conformation and would cause minimum disruption of the macromolecular structure. Pyrolytic loss of the sidechain carbons would likely macerate the structures beyond recognition. Clearly, to preserve physical integrity to the rank of brown coal or even lignite, the side chains must not be lost.

Coalification to subbituminous and bituminous coal. The transformations of brown coal and lignitic woods to higher rank involve some significant changes in chemical structure. This is perhaps the primary cause for the change in physical morphology often observed as coal becomes more lustrous and the virtrinite becomes more homogeneous.This transfromation has often been referred to as gelification (*23*). Figure 9 shows the SEM of a sample of wood coalified to the rank of subbituminous coal. The wood cells have become deformed significantly, presumable due to increased burial pressure, and some cells have actually been annealed to a homogeneous mass.

While structures in brown coal and lignite are dominated by the catechol-like rings arranged in an helical conformation perhaps, the major components of subbituminous and bituminous woods are phenol-like structures. Evidence for the transformation of catechol-like structures to phenol-like structures as shown in Figure 10 comes from both NMR and py/gc/ms data (*7,24*). The NMR data clearly indicate a loss of aryl-O carbon. In lignite, aryl-O carbons account for approximately 2 of the six aromatic carbons on the ring, whereas in subbituminous and bituminous coal, only 1 of six aromatic carbons is an aryl-O carbon. Pyrolysis data demonstrate the same observation, with lignitic wood samples being rich in catechols and subbituminous wood samples being rich only in phenols and alkylated phenols. Elemental data show that a significant diminution of oxygen content can explain these tranformations.

Coalification to the rank of high-volatile bituminous coal leads to further reductions in oxygen contents for coalified wood. Considering the fact that the amounts of aryl-O do not change significantly, it is likely that the changes imply a further condensation of phenols to aryl ethers or dibenzofuran-like structures as shown in Figure 11 (*24*). The py/gc/ms data confirm this as more alkylbenzenes and dibenzofurans are observed. The alkylbenzenes in pyrolyzates could arise from thermal cracking of dibenzofuran or diaryl ethers during flash pyrolysis. Also, the increased quantities of condensed aromatic rings, naphthalenes and fluorenes, in pyrolyzates suggests that aromatic ring condensation is occurring. It is likely that this condensation will disrupt the helical structure proposed. At this time we have little to offer in the way of a mechanism for this condensation. Aromaticity of coalified wood appears to increase at this rank

(*16*), suggesting that one possible route for the formation of condensed rings is ring closure and aromatization of the alkyl sidechains. Further studies are needed to verify such a pathway.

Perhaps the next most apparent difference between woods coalified to the rank of subbituminous / bituminous coal and those at the rank of lignite or lower rank is the lack of oxygenated alkyl structures (i.e., hydroxyls or alkyl ethers). The NMR data for subbituminous and bituminous coalified woods show essentially baseline in this region of the spectra, evidence that such functional groups are not significant. Thus what were originally hydroxylated lignin sidechains have been altered. As discussed above, it is most likely that the lignin-derived hydroxyl groups have been reduced rather than lost by pyrolysis of the sidechain. The reduction of hydroxyls is essentially complete at the rank of subbituminous coal.

Consequently, the structural composition of subbituminous coal is that of a lignin structure which has lost its methoxyl groups (via demethylation and dehydroxylation) and all its hydroxyls and alkyl ethers. Presumably, all these reactions can occur with minimal disruption of the three dimensional network inherited from lignin. Indeed, some semblance of cellular morphology still remains at the rank of subbituminous coal (Figure 9). Pressure and temperature begin to combine at these and higher ranks to have a significant effect on physical morphology of wood. Thus, it becomes less clear whether loss of morphology is purely a physical or chemical phenomenon or both. With such a disruption in the macromolecular structure of wood brought on by the formation of condensed ring systems, it seems reasonable that cellular morphology which persists well up to the rank of bituminous coal begins to degrade into a homogeneous glassy appearance with little semblance of cell wall boundaries at ranks of bituminous coal or higher.

To acertain the effect of chemistry on physical morphology, it is imperative that we understand better the nature of the reactions which transform the catechol-like structures of lignitic woods to the phenol- and diarylether-like structures of subbituminous and bituminous woods. Herein lies the focus of this paper.

Experimental

A crushed sample of a coalified gymnospermous wood described previously as the Patapsco lignite (*16*) was heated under hydrous conditions in a 22 ml autoclave reactor described in a previous report (*26*). The reactor was charged under nitrogen with approximately 1 gram of coal and 7 milliliters of deionized, deoxygenated water following a procedure similar to that of

Siskin et al. (*12*). 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 at various temperatures. Experiments were run for 10 days at 100° C, 30 minutes to 48 hours at 300° C, and 3 hours, 6 hours and 3 days at 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 gases, the liquids and the solids were collected and analyzed. Only trace amounts of gases were detected. An entire series of hydrous pyrolysis experiments were repeated at 300°C with more water added to the reactor than many of the previous experiments. This was done to ensure that water would remain in the liquid state throughout the experiment and would not be in the supercritical state.

The bombs were opened and the liquid content pipetted off. The organic matter dissolved in the water was separated by extraction with diethylether, and the data will be reported at a later date. The residual lignite was extracted in a 50:50 mixture of benzene and methanol. The residue was then treated first with acetone and then with pentane to remove any benzene:methanol from the altered coal. The coal was then dried in a vacuum oven at 45° C for twenty four hours, and weighed.

Both the original lignite and the solid residues from the reactors were analyzed by flash pyrolysis and by solid state ^{13}C NMR. The flash pyrolysis technique used was that published by Hatcher et al. (*25*). Using a Chemical Data System Pyroprobe 1000, approximately one milligram of sample was loaded into a quartz capillary tube.and this tube was placed inside the coils of the pyroprobe. The probe and sample were then inserted into the injection port (temperature maintained at 280°C) of a Varian 2700 gas chromatograph and the sample pyrolyzed. The residue was first thermally desorbed at 300°C for thirty seconds. The samples were then pyrolyzed. Flash pyrolysis conditions were as follows: temperature, 610°C for 10 s with a heating rate 5°C/msec. The pyrolyzate was cryotrapped with liquid nitrogen prior to being chromatographed on a 25 m x 0.25mm i.d. J & W DB-17 capillary column. The GC was temperature programmed from 30° to 280°C at 4°C/min. The effluent was swept into the source of a DuPont 490B mass spectrometer fitted with a Technivent Vector 1 data system for detection and compound identification. Compounds were identified by a combination of methods which included comparison of mass spectra to the NBS/Wiley library, to published mass spectra, and to authentic standards whenever possible.

Solid-state ^{13}C NMR spectra were obtained by the method of cross polarization and magic angle spinning (CPMAS) using the conditions previously given (*16*). The spectrometer was a Chemagnetics Inc. M-100 spectrometer operating at 25.2 MHz carbon frequency. Cycle times of 1sec and contact times of 1msec were chosen as the optimal conditions for quantitative spectroscopy.

Results

Elemental analyses and product yields. The hydrous pyrolysis of the Patapsco lignitic wood induced pronounced alteration of the sample as depicted by the elemental compositions and product yields for some of the experiments shown in Tables I and II, respectively. Elemental compositions are only available for the original unaltered sample and three of the hydrous pyrolysis residues. The data indicate a general loss of hydrogen, increase in carbon and loss of oxygen as a function of increasing thermal severity that are all consistent in only a general way with trends during increased coalification. Product yields measured as the loss of sample weight during hydrous pyrolysis vary from a low of 8.4% to a high of 40%, with the products being mostly water soluble phenols and catechols (Wenzel and Hatcher, unpublished data).

^{13}C NMR. The NMR spectra of Patapsco lignite and its hydrous pyrolysis residues at different temperatures and heating times are shown in Figure 12. The unaltered Patapsco lignitic wood has an NMR spectrum dominated by aromatic carbons with a major peak at 145 ppm that is assigned to aryl-O carbons in catechol-like structures. The aliphatic region (0-85 ppm) shows peaks assigned to alkyl-C carbons(0-50 ppm), methoxyl carbons (56 ppm), and alkyl-O carbons (60-80 ppm). A small and broad peak at 170- 200 ppm is assigned to carboxyl and carbonyl carbons. The most obvious change due to severity of hydrous pyrolysis is the diminution of the catechol peak at 145 ppm. The most severely altered residue shown in Figure 12, 300°C for 48 hrs, shows a nearly complete loss of this peak; the peak of significance that emerges is the one at 155 ppm, that of phenolic carbon.

The other major change occurring with increasing hydrous pyrolysis severity is the loss of aliphatic carbons relative to the aromatic carbons. Accordingly, the carbon aromaticity, f_a, in Table 4 shows this trend as f_a increases from 0.68 to 0.88. The diminution of aliphatic carbons (Figure 12) involves loss of methoxyl, alkyl-O, and alkyl-C carbons. The methoxyl carbons decrease rapidly but appear to persist at 300°C. The alkyl-O carbons are lost at low thermal severity. It is clear that a temperature of at least 350°C is required to reduce the methoxyl carbons to below detection. The alkyl-C carbons show resonances distributed over a large chemical shift range with an apparent shift in the intensity maximum from about 30 ppm to about 20 ppm. This is consistent with the conclusion that methyl carbons, which resonate at lower chemical shifts, are dominant in the thermally stressed lignitic wood. Perhaps the residual aliphatic carbons are simply methyl carbons.

The NMR data for samples subjected to hydrous pyrolysis at 300°C for intervals varying from 0.5 to 48 hrs and with additional water in the reactor are shown in Table 4. The overall trends in this data are similar to those described above. Carbon aromaticity is observed to increase steadily over the course of 48 hrs of heating. Inverse trends are observed for aryl-O carbons (140-160 ppm), aryl-O/ aryl (aryl-O carbons normalized to total aromatic carbons), and aliphatic carbons (0-50 ppm). These trends are consistent with what was noted above-that hydrous pyrolysis induces loss of catechols and aliphatic structures. The precipitous loss of aryl-O carbons at the long heating time indicates additional loss of oxygenated functional groups, perhaps representing the condensation of phenols as is observed at higher coal rank (*24*).

Dipolar dephasing of the unaltered Patapsco lignite (16) indicates that approximately 3.5 substituents are attached to the aromatic ring ($f_a^{a,H}$, or the fraction of protonated aromatic carbons, is 0.41). The value of $f_a^{a,H}$ for the residue stressed at 350°C for 3 hours is 0.27, significantly less than that of the original sample. This decrease in $f_a^{a,H}$ is indicative of increased aromatic substitution resulting from thermal stress.

PY/GC/MS

Flash pyrolysis GC/MS was preformed on the Patapsco lignite and the residues generated from the hydrous pyrolysis experiments in an effort to characterize the chemical changes that occured during alteration of the coalified wood. The changes in the lignite are best represented by comparing the pyrograms of the raw lignite (Figure 13) and of the series of altered residues from hydrous pyrolysis (Figure 14). The pyrograms are normalized to the highest peak. Major peaks are identified by number. See Table 5 for the complete list of identified compounds for all the pyrograms. The pyrolyzate of the Patapsco coalified wood is dominated by peaks attributable to residual lignin structures as indicated by the presence of guaiacol, methylguaiacol, ethylguaiacol, and other methoxyphenols. The intense signals for catechol and alkylcatechols confirms the existence of a predominantly catechol-like structure for this sample. Phenol and alkylated phenols are present but in lesser amounts. Some of the phenols derive from thermal decomposition of catechol-like structures and lignin-like structures.

Pyrograms for the samples subjected to hydrous pyrolysis are distinctly different from those of the unaltered lignitic wood. With increasing hydrous pyrolysis severity, a significant diminution of catechols and lignin phenols (guaiacols) is observed. The pyrograms become dominated by phenol and its alkylated homologs, in much the same way which occurs naturally during coalification of wood. However, the major difference compared to naturally coalified wood is the general lack of significant quantities of the alkylated phenolic homologs. The pyrolysis of the residues yields mostly phenol and cresol isomers. Other alkylated phenols, the C_2 and C_3 phenols, are not as abundant relative to phenol and cresols as are the C_2 and C_3 phenols in the pyrolysis of the original Patapsco lignite or in coalified wood from a natural coalification series (*24*). The relative depletion of C_2 and C_3 alkylphenols in the artificial series is probably related to the fact that alkyl substitutents are not abundant in the residue and the alkyl substituents are probably mostly methyl substituents as was deduced from NMR data.

Figure 15 shows the trends in the compound yields from the flash pyrolysis products of hydrous pyrolysis residues heated at 300°C for varying periods of time. Compounds are grouped according to five major groups. The groups of compounds are benzene, phenol, guaiacol, catechol and naphthalene and their alkylated derivatives. The loss of catechol-like structures is documented with a significant loss of catechols in the pyrolyzate of the altered residues. With the loss of catechols, phenols and alkyl phenols become the dominant products in the pyrolyzate, as noted above.

Discussion

Hydrous pyrolysis of the Patapsco lignite was conceived as a means to induce artificial coalification. Accordingly, our goal was to examine the residues before and after thermal treatment and to infer coalification pathways from this treatment. It is important to note that there appeared to be a loss of mass during thermolysis. 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 (Hatcher and Wenzel, unpublished results) 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 quantified because the amount of gas evolved was negligible.

The van Krevelen diagram (Figure 16) best represents the elemental changes that occur in the naturally coalified wood samples versus the elemental changes that occur in the artificially altered coalified wood samples. With increasing maturation, the H/C ratio for vitrinite remains relatively flat while the O/C value decreases steadily until HvA bituminous at 0.02 O/C, (appox. 88 % carbon). In the artificial series there is an immediate loss of both hydrogen and oxygen. The hydrogen content for the Patapsco coalified wood is initially 4.8 percent and this value decreases to a low in the most altered residue of 3.4 percent. It is quite evident that the artificial thermal pathway does not follow the natural coalification pathway of vitrinites on the van Krevelen diagram (*26*). Not enough oxygen is lost with respect to hydrogen. The trend appears to follow one of dehydration which involves loss of 2 hydrogens for each oxygen.

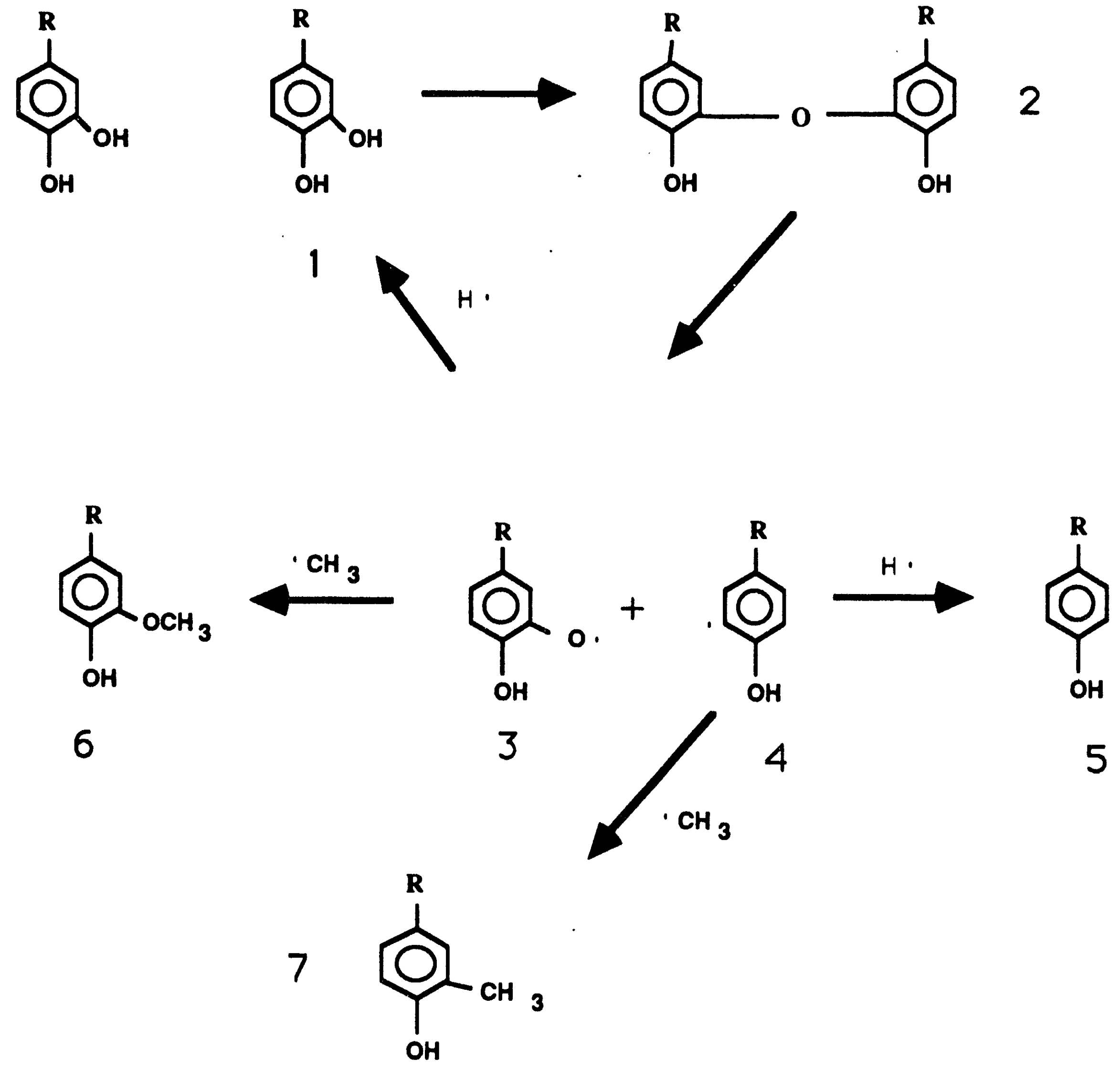
The NMR data of the thermolysis residues indicates clearly the evolutionary path during thermolysis . Comparing the NMR data for the residues (Figure 12, Table 4) with the original lignite and with gymnospermous wood coalified to higher rank (*16*) there appear to be several changes which describe the 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 (*16*) 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. The NMR spectrum of the hydrous pyrolysis residue has clearly lost most of the intensity at 145 ppm but now shows a peak at 155 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 (*24*). It is obvious that the catechol-like structures of the lignitic wood have been tranformed to phenol-like structures somewhat similar to those in higher rank coal. Thus, the hydrous pyrolysis has reproduced, to some degree, the coalification reactions acting on aromatic centers.

The second most apparent change to occur during hydrous pyrolysis 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 hydrous pyrolysis 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 hydrous pyrolysis 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 hydrous pyrolysis residues become dominated by methyl carbons with increasing thermal stress.

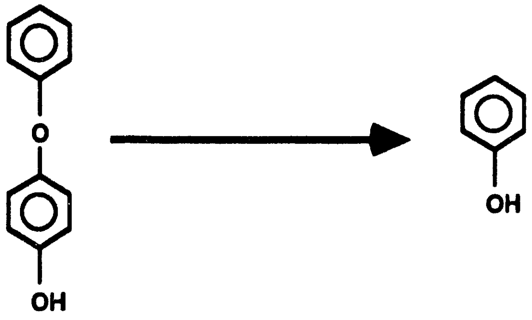
The pyrolysis data provide confirmation for the average changes in structure observed by NMR. The loss of catechol-like structures is documented with the significant diminution of catechols in the pyrolyzate of the hydrous pyrolysis residue compared to that of the original lignitic wood. This loss of catechols is the singular most significant change in pyrolysis products. The pyrolyzate of the residue mimics somewhat the pyrolysis data for subbituminous coalified wood (*24*), being dominated by phenol and alkylphenols. Another difference between hydrous pyrolysis residues and the original lignitic wood is in the abundance of methoxyphenols derived from lignin-like structures. The hydrous pyrolysis 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 residues yield mostly phenol and the cresol isomers; other alkylated phenols, the C_2 and C_3 phenols, are not as abundant relative to phenol and cresols as the C_2 and C_3 phenols are in the pyrolysis of original lignite or coalified woods of higher rank (*24*). 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 C_2 and C_3 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. (*12*).

By noting the changes in the NMR and pyrolysis data when lignitic wood is subjected to hydrous pyrolysis and by comparing the residue thus formed with coalified wood of subbituminous rank, a generalized schematic of the transformation pathway may be deduced. It is clear that the catechol-like structures are being transformed to phenolic structures. From previous studies on the lignitic wood, catechol-like structures are thought to be the dominant structural element, similar to the one depicted in structure **1**. Thermolysis can easily induce dehydration or condensation (*10*) to form an ether link between two catechols as shown in structure **2**. Hydrolysis of the ether can reverse the reaction to regenerate the catechols, but thermolysis can also induce homolytic cleavage of the ether to generate a phenoxy radical (**3**) and a catechol radical (**4**). If we assume that sufficient hydrogen transfer occurs under the high temperature regime to cap the radicals, then the products **3** and **4** would be tranformed to a phenol (**5**) and a catechol (**1**). It is also possible that radicals are capped by methyl or alkyl radicals formed from other thermolytic reactions elsewhere in the coal structure (e.g., the side chain sites). In such cases methoxy or alkoxyphenols (**6**) could be formed. Such reactions could explain why methoxyphenols persist in pyrolyzates of the residues during hydrous pyrolysis. It is also possible that the alkyl radicals could attack the aromatic ring sites and induce alkylation (**7**). This would lead to increased substitution of the rings, consistent with the dipolar dephasing NMR data which show an increase in the average number of aromatic substituents with increased hydrous pyrolysis.


R
OH
1
2
O
H ·
· CH 3
OCH 3
O ·
+
3
4
5
6
7
CH 3

Recently, Siskin et al.(*12*) demonstrated that hydrous pyrolysis at 343°C will induce cleavage of 4-phenoxyphenol (**8**) to form phenol; the detailed pathway being presumably unknown. This compound has some similarity to structure **2** found in the lignitic wood.



8

Thus we can expect the above mechanism proposed for catechol to be analogous to that shown for 4-phenoxyphenol. In fact, we might expect the reaction to proceed at a much faster rate due to the fact that additional phenol substituents at *orto* or *para* positions to the ether linkage can activate the reaction.

Summary

Vitrinite, a major component of most coals, is derived from degraded wood in ancient peat swamps. Organic geochemical studies conducted on a series of coalified wood samples derived mostly from gymnosperms have allowed the developtment of a chemical reaction series to characterize the major coalification reactions which lignin, the major coal-producing component of wood, undergoes. These involve mostly hydrolysis of aryl ethers, reduction of alkoxyl side chains, alkylation of reactive aromatic sites, and finally condensation reactions of phenolic moieties. Thus, lignin is transformed to catechol-like structures and these are converted to phenol-like structures. The former reactions are well understood to occur during peatification by the action of microorganisms, but the latter have not been shown to be possible in other than model systems. To demonstrate that the catechol-like structures can be made to evolve to phenol-like structures under natural conditions, we attempted to simulate natural burial processes by artificially coalifying a sample containing mostly catechol-like structures under conditions of hydrous pyrolysis. These conditions did indeed induce transformations of catechol-like structures to phenol-like structures, but the reactions do not reproduce well the coalification reactions with regard to aliphatic structures in coal.

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Table 1 Analysis of the coal samples

	DECS-1	DECS-11	DECS-9
Sources & Rank			
state	Texas	North Dakota	Montana
county	Freestone	Mercer	Bighorn
city	Fairfield		Decker
seam	Bottom	Beulan	Dietz
ASTM rank	subbit C	lignite	subbit B
sampling date	12/11/89	6/15/93	6/12/90
Proximate (wt%, ar)			
moisture	30	33.38	24.68
ash	11.07	6.37	4.8
volatile	33.18	37.36	33.46
fixed carbon	25.75	22.89	37.06
Elemental (wt%, dmmf)			
carbon	76.13	74.2	76.11
hydrogen	5.54	4.39	5.14
nitrogen	1.5	1.01	0.91
organic sulfur	1.05	0.44	0.33
oxygen	15.78	19.96	17.5

Table 2. Elemental data and vitrinite reflectance for the Patapsco log and its residues obtained from hydrous pyrolysis.

sample	rank	R_0	%C	%H	%N	%O	H/C	O/C
Patapsco lignite	lignite	0.269	65.5	4.8	.34	28.4	0.873	0.326
residue 10 days 100° C	lignite*	0.296	69.2	4.4	.33	26.0	0.758	0.282
residue 0.5 hr 300° C	subbit.*	0.496	73.2	4.3	.22	22.3	0.700	0.229
residue 2 hr 300° C	HvC bit.*	na	76.9	3.4	.01	19.7	0.527	0.192
residue 3 hr 350° C	Mv. bit.*	1.37	na	na	na	na	na	na

*= rank obtained due to thermal alteration
na = data not available
R_0 = vitrinite reflectance, mean maximum

Table 3. Hydrous pyrolysis yields at various temperatures.

time, hrs	temperature, °C	$^{+}$conversion %
240	100	29.3
.5	300	29.8(8.4)*
2	300	30.6(22.9)
3	300	(22.9)
5	300	(22.4)
8	300	(29.9)
3	350	39.7

*values in parenthesis are for samples to which more water was added to ensure hydrous pyrolysis
$^{+}$refers to the yield of non-residue

Table 4. NMR parameters for the Patapsco lignitic wood and hydrous pyrolysis residues measured by integration of the spectra.

Sample	f_a	Aryl-O/Aryl	#C=O	#COOH	$f_a^{a,H}$
Patapsco lignitic wood	0.68	0.40	2.6	3.2	0.41
residues/exp. 1:					
300°C/0.5hr	0.75	0.35	2.0	2.5	
300°C/2hr	0.75	0.25	1.7	1.7	
300°C/ 3hr	0.80	0.12	2.7	2.9	NA
350°C/3hr	0.83	0.16	<0.5	2.4	0.27
350°C/72hr	0.88	0.12	<0.5	<0.5	NA
°residues/ exp. 2:					
300°C/5hr	0.74	0.30	3.1	2.1	
300°C/8hr	0.77	0.26	1.8	2.0	
300°C/12hr	0.75	0.28	1.4	1.8	
300°C/36hr	0.80	0.27	1.8	1.8	
300°C/48hr	0.81	0.13	1.3	3.0	

°in these experiments more water was added to reactor and temperature was kept constant at 300°C

\# values are % of total carbon

f_a carbon aromaticity

$f_a^{a,H}$ fraction of aromatic carbons which are protonated

Table 5. Peak assignments for the pyrograms in Figures 8 and 9.

Peak #	assignment
1	toluene
2	xylene
3	xylene
4	phenol
5	*ortho*-cresol
6	*meta and para*-cresol
7	guaiacol
8	2,4-dimethylphenol
9	4-ethylphenol
10	4-methylguaiacol
11	catechol
12	C_2-guaiacol
13	3-methylcatechol
14	4-methylcatechol
15	C_4-guaiacol
16	C_2-catechol
17	ethylcatechol
18	C_2-naphthalene
19	C_5-naphthalene

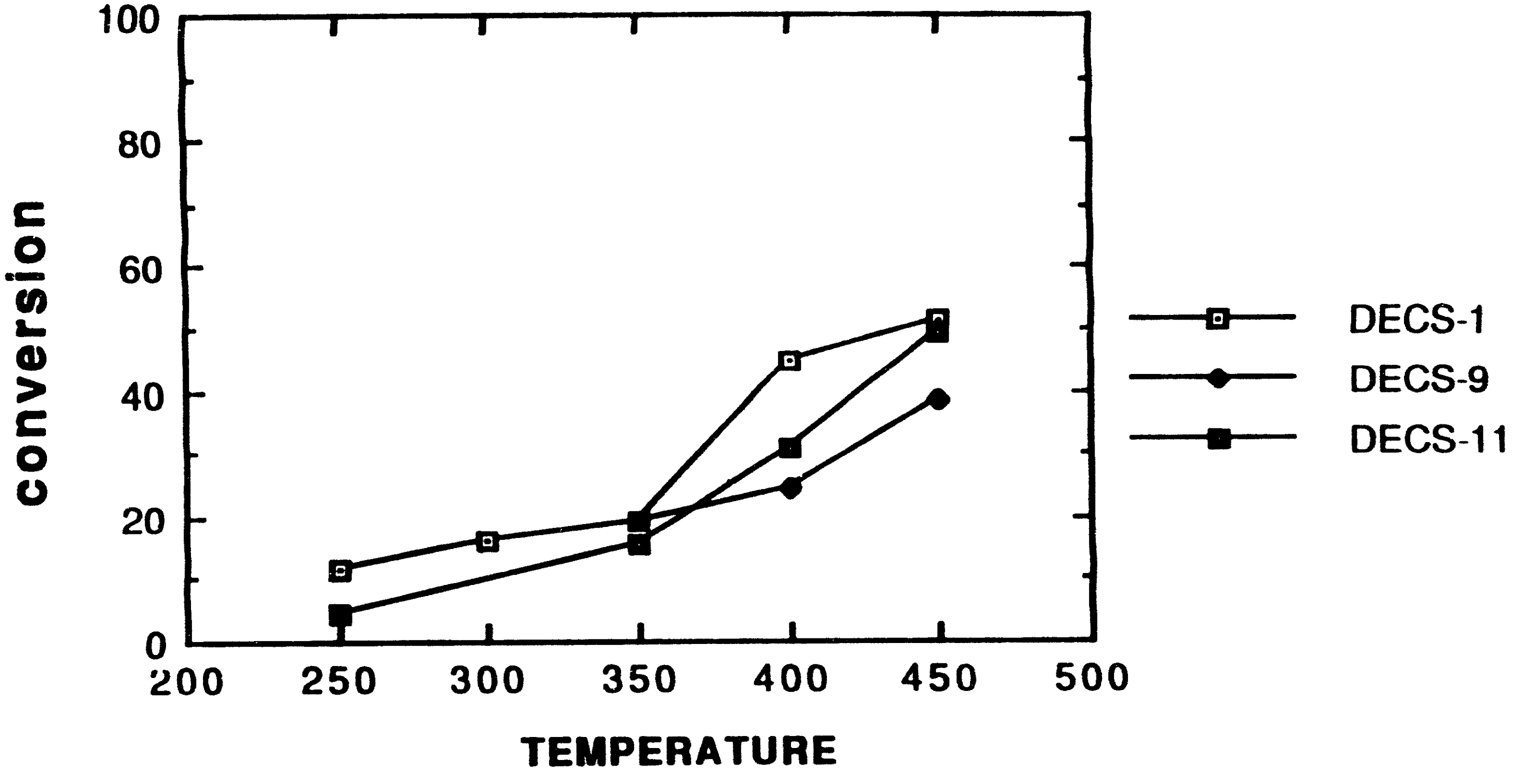
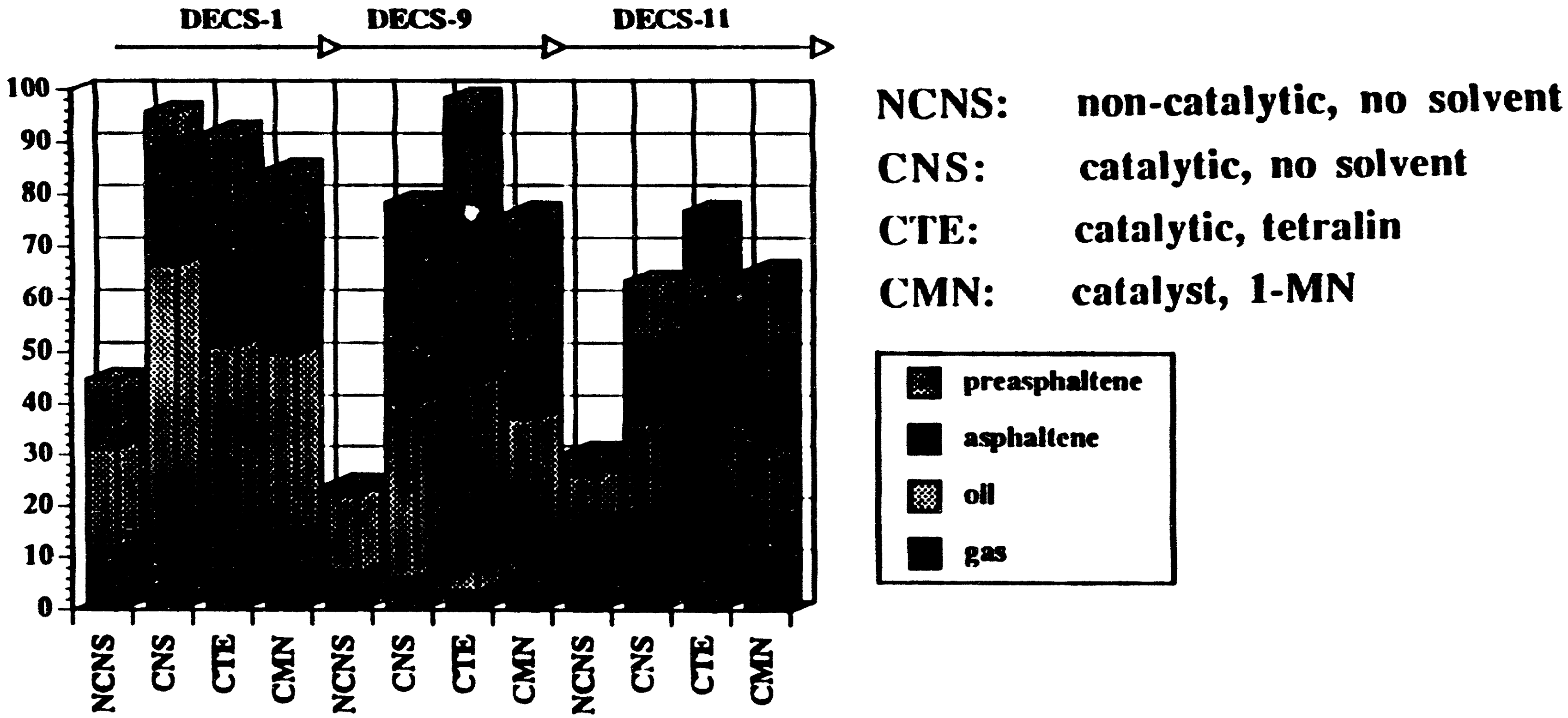


Figure 1. Conversions of the three coals at temperatures from 250°C to 450°C without a catalyst or a solvent



NCNS: non-catalytic, no solvent
CNS: catalytic, no solvent
CTE: catalytic, tetralin
CMN: catalyst, 1-MN

Figure 2. Liquefaction conversions of the three coals at 400°C under four different reaction conditions

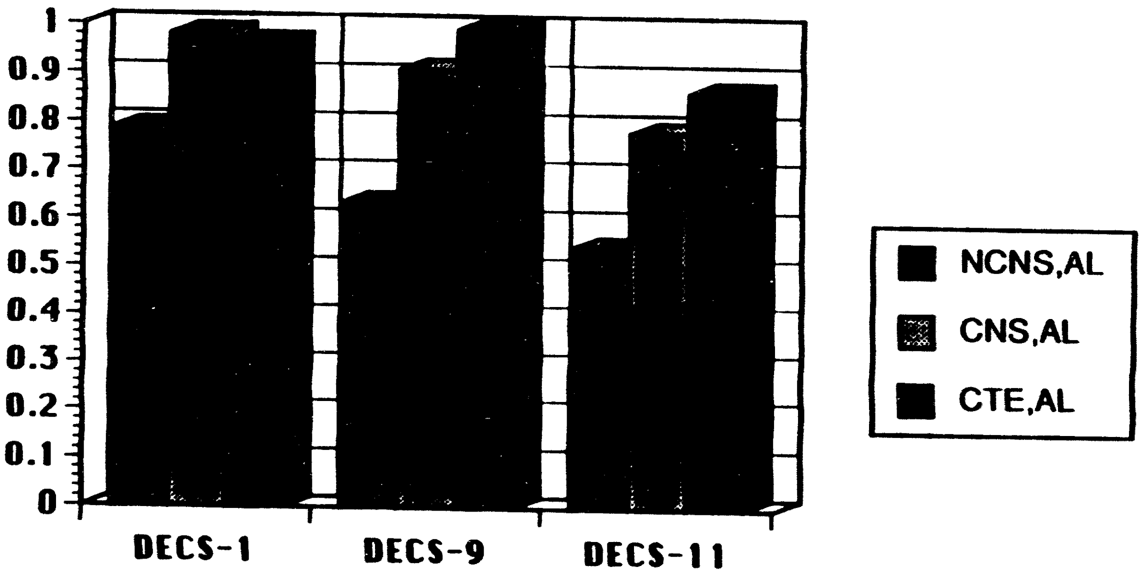


Figure 3. The amounts of aliphatic carbons being converted from the three coals to THF solubles at 400°C under three different conditions

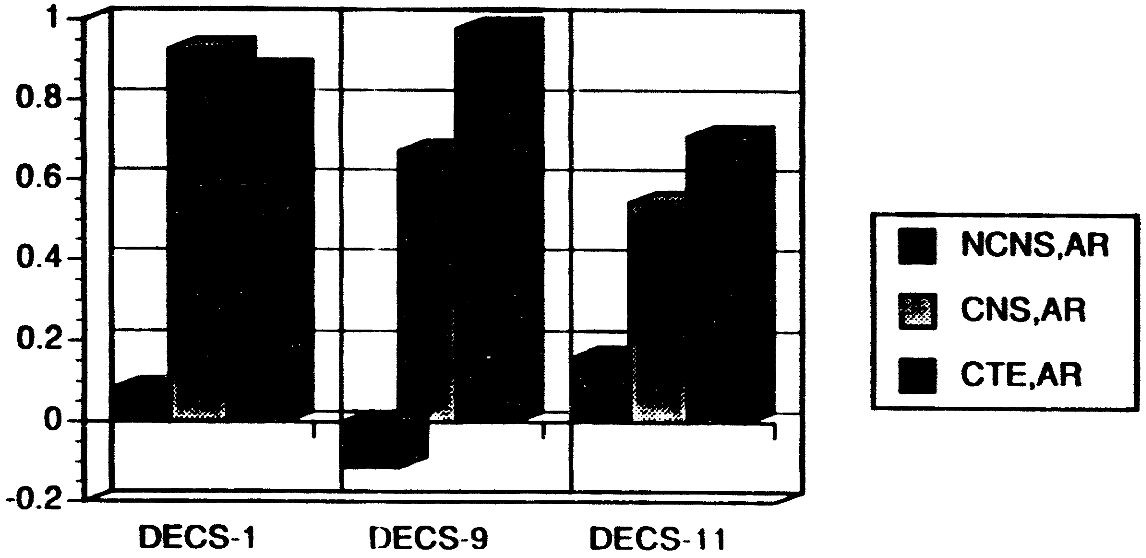


Figure 4. The amounts of aromatic carbons being converted from the three coals to THF solubles at 400°C under three different conditions

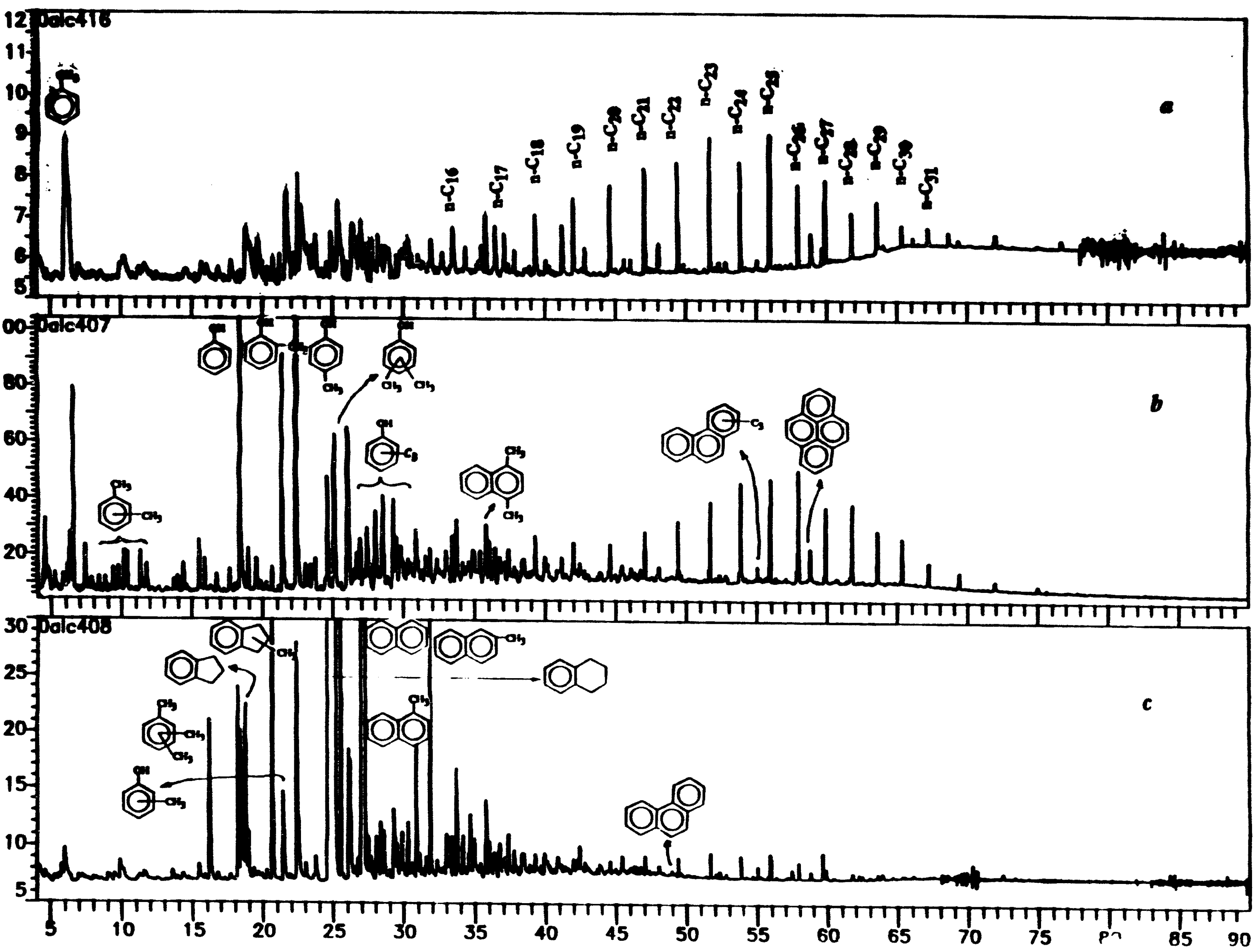


Figure 5. Analysis of the oil samples from the DECS-9 coal using gas chromatograph. a) the sample from the reaction without a catalyst or a solvent; b) the sample from the reaction with the ATTM-derived catalyst but without a solvent; c) the sample from the reaction with both the catalyst and tetralin.

Figure 6. SEM photmicrograph of peatified white cedar wood from the Dismal Swamp, VA. Bordered pits and cell walls appear well preserved even though nearly all the cellulose has been degraded and lost from the wood.

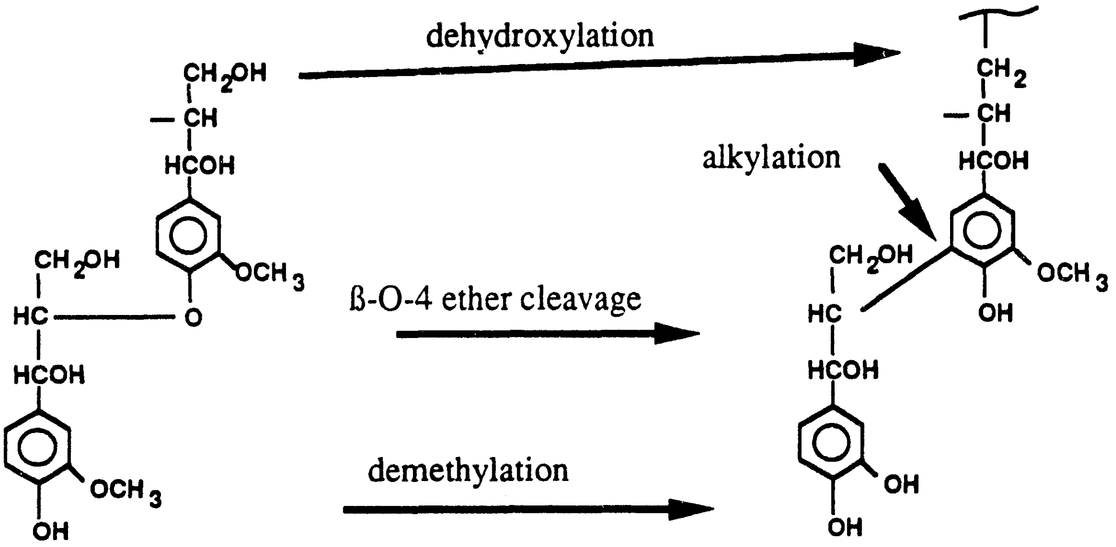


Figure 7. Chemical reactions proposed for the transformation of gymnospermous lignin in peatified wood to brown coal and lignitic gymnospermous wood.

Fig 2

Figure 8. SEM photomicrograph of coalified wood in brown coal. Note the excellent physical preservation of cell walls and other elements characteristic of wood cells.

Figure 9. SEM photomicrograph of coalified subbituminous wood showing compressed and deformed cells, some of which appear to be annealed (upper center).

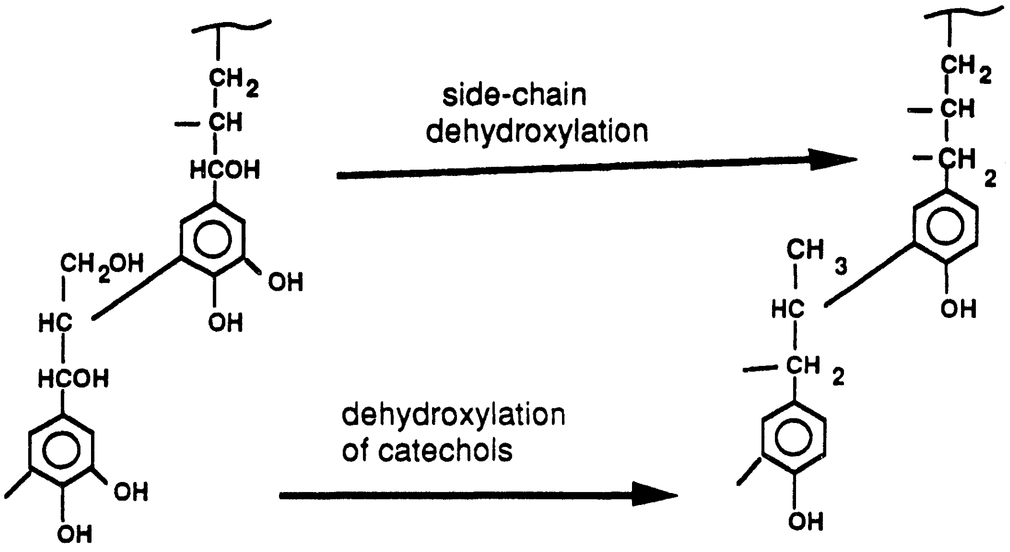


Figure 10. Proposed reactions responsible for the transformation of lignitic gymnospermous wood to subbituminous wood.

Fig 5

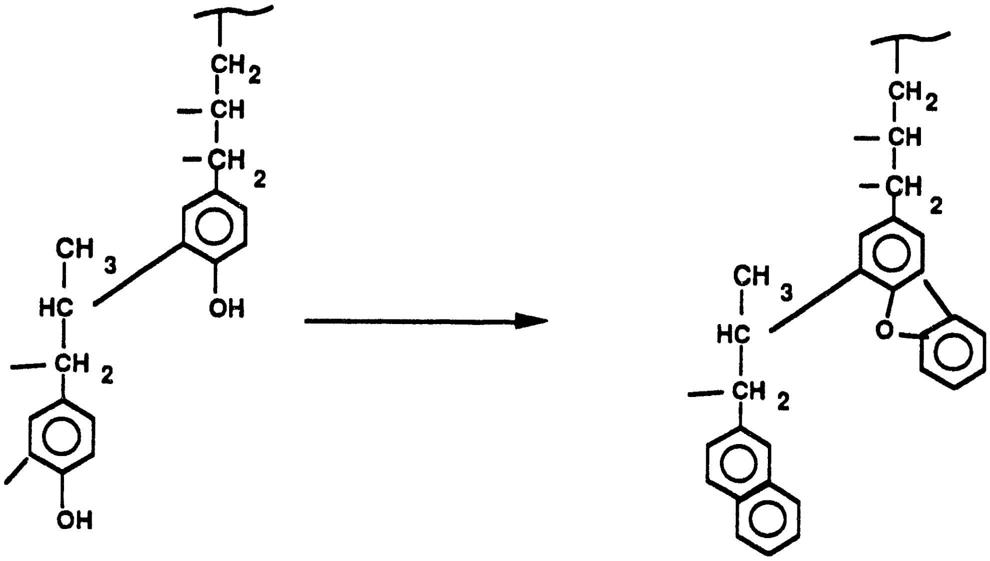


Figure 11. Proposed reactions responsible for the transformation of phenolic structures in subbituminous wood to dibenzofurans and naphthalenes.

Fig. 6

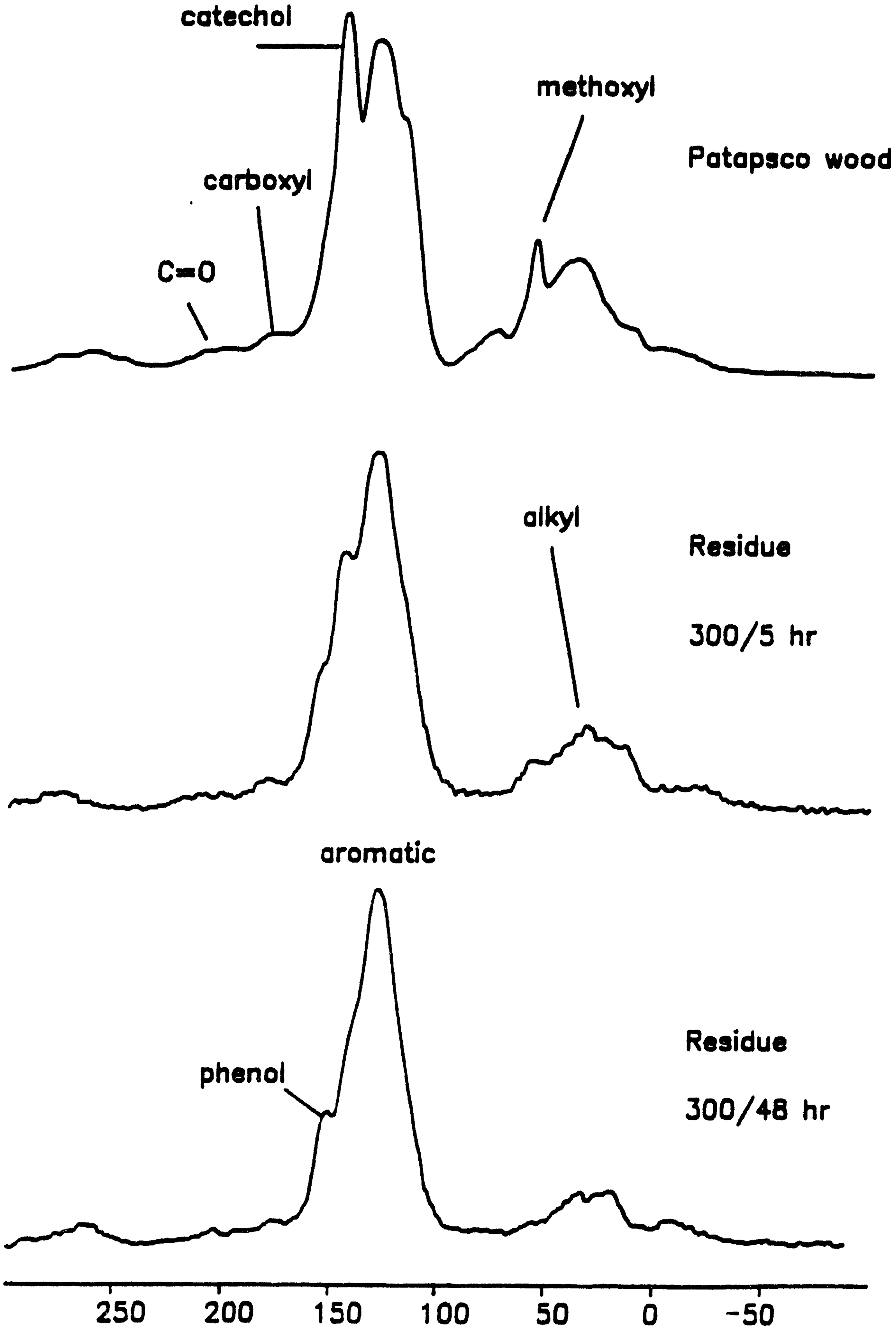


Figure 12. Solid-state ^{13}C NMR spectra of unaltered Patapsco lignitic wood and its hydrous pyrolysis residues heated at the various temperatures and times indicated.

Fig. 7

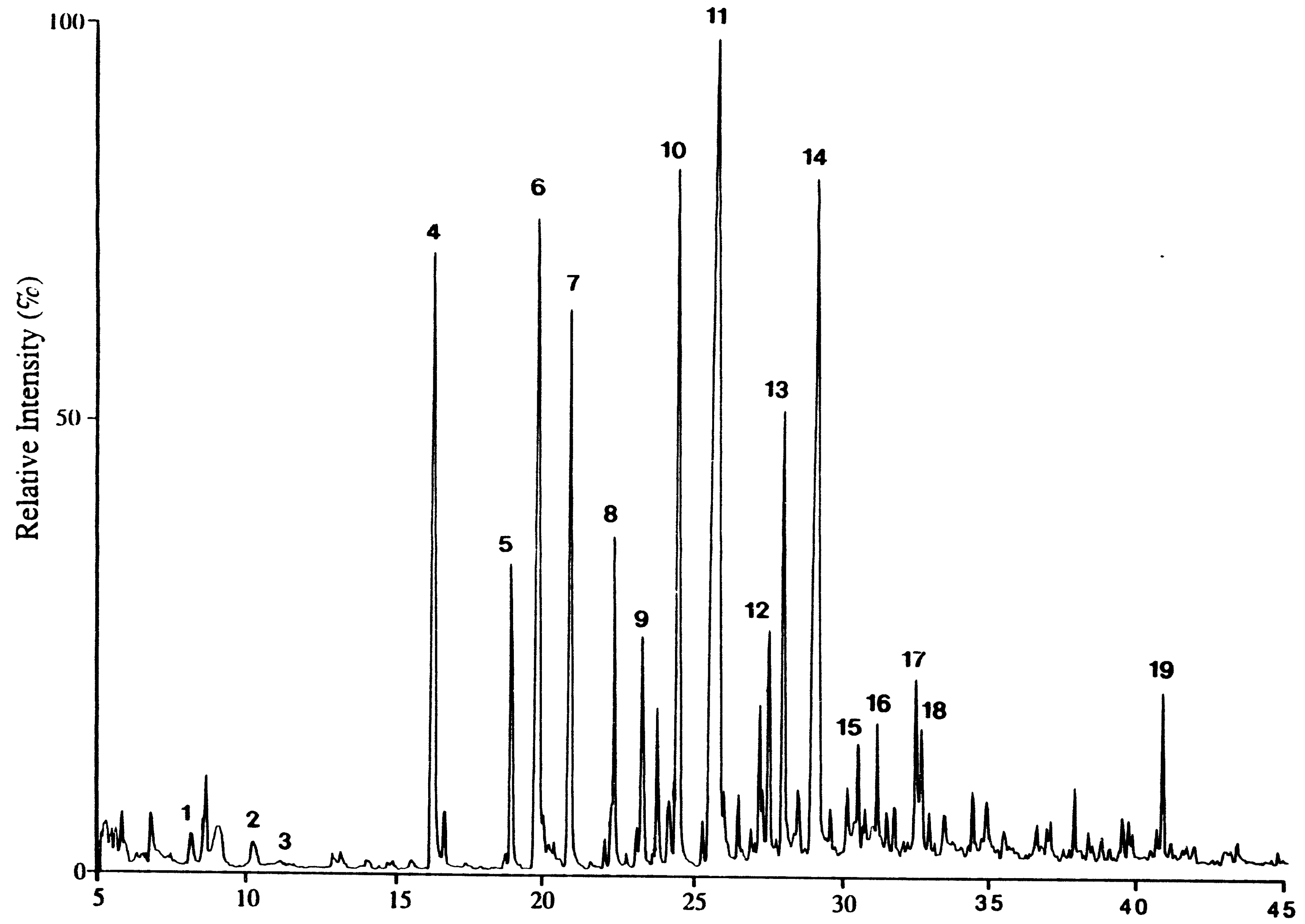


Figure 13. Flash pyrolysis/gc/ms trace of the unaltered Patapsco lignitic wood sample with identifications for major numbered peaks listed in Table 5.

Fig 8

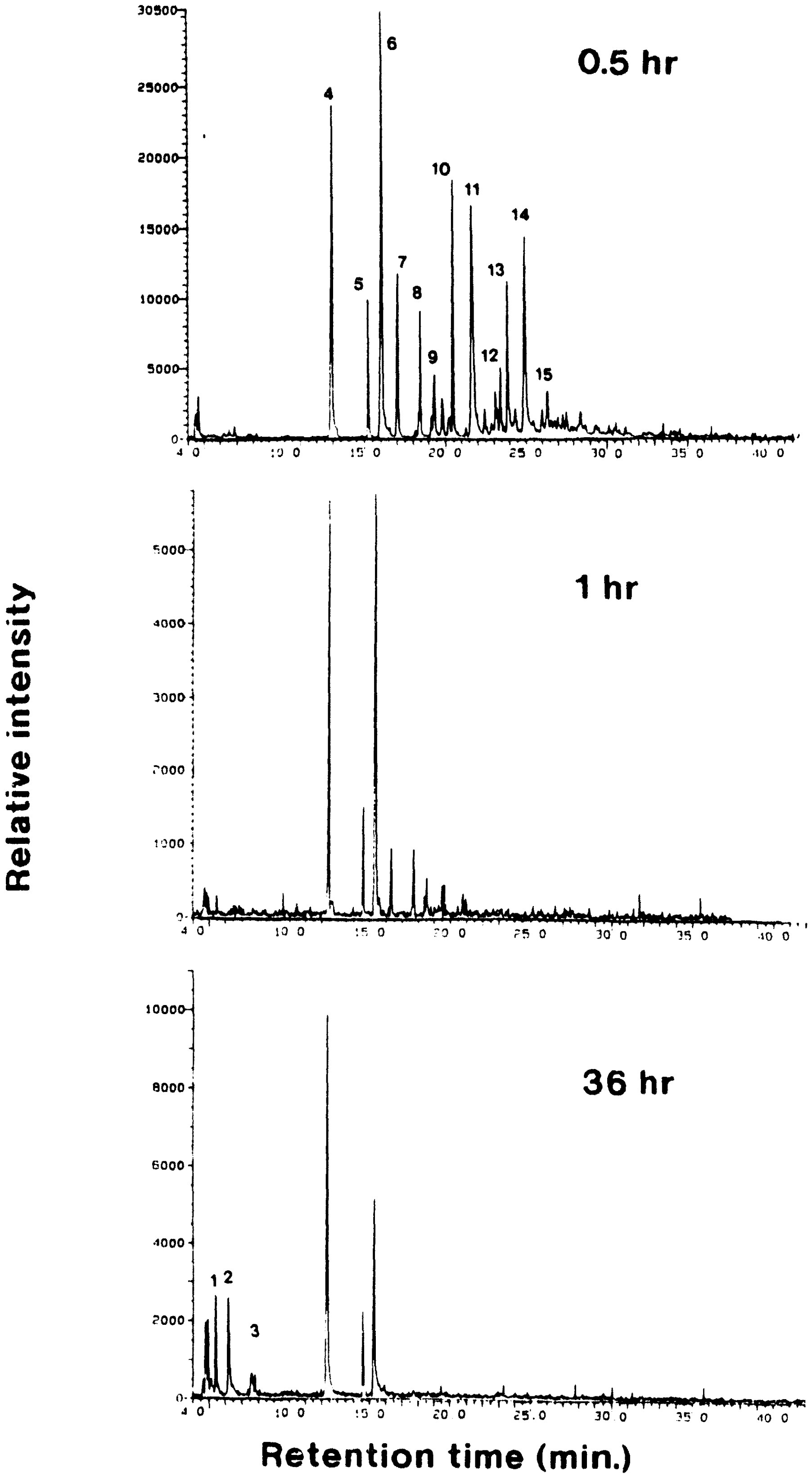


Figure 14. Flash pyrolysis/gc/ms trace of hydrous pyrolysis residues of the Patapsco lignitic wood heated for the various times indicated at 300°C. The numbered peaks are identified in Table 5.

✓

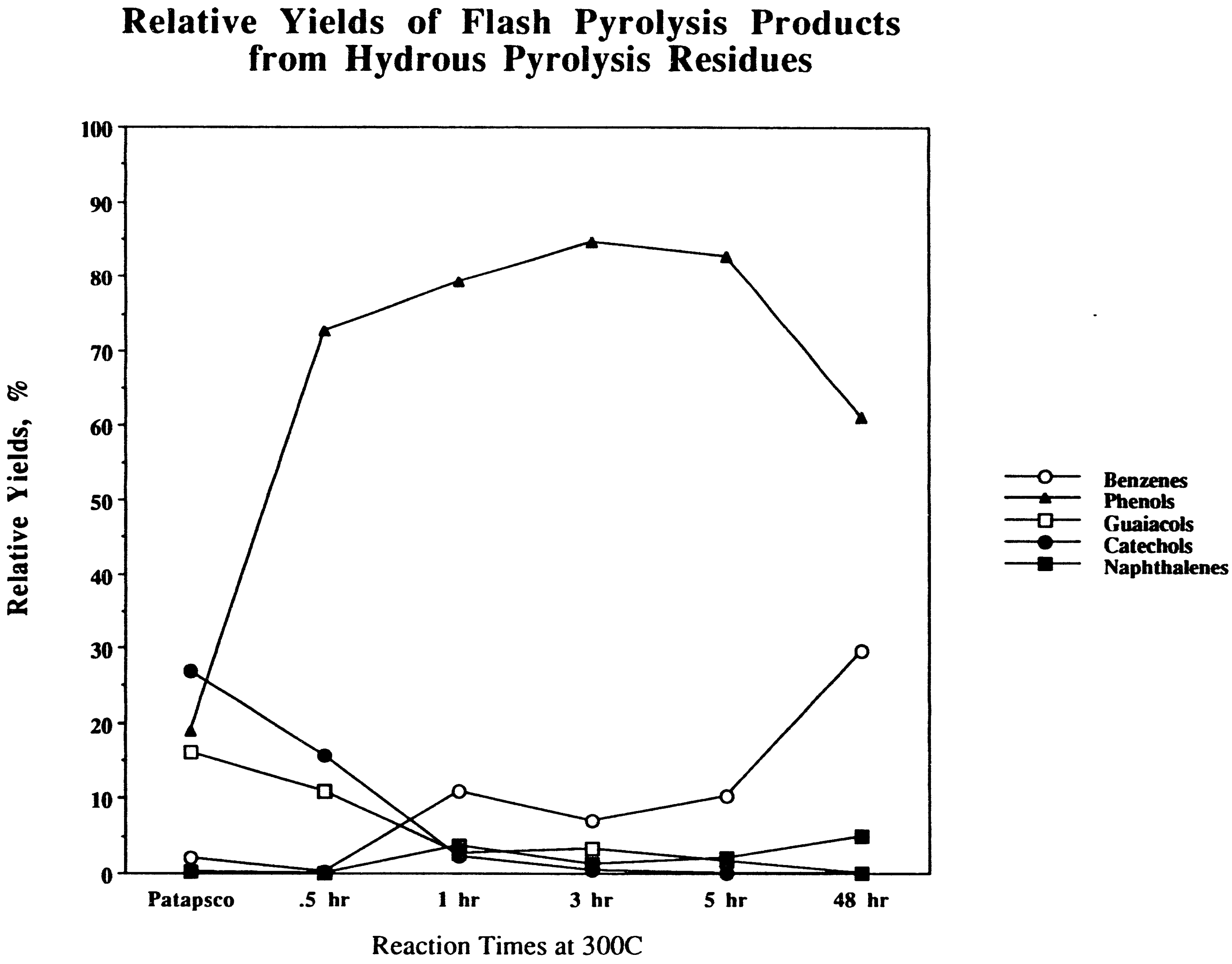


Fig. 10

Figure 15. Relative yields of individual compounds from flash pyrolysis/gc/ms of hydrous pyrolysis residues obtained at 300°C plotted as a function of heating time (hrs). The compounds are grouped into compound classes and include all the various alkylated isomers of each class.

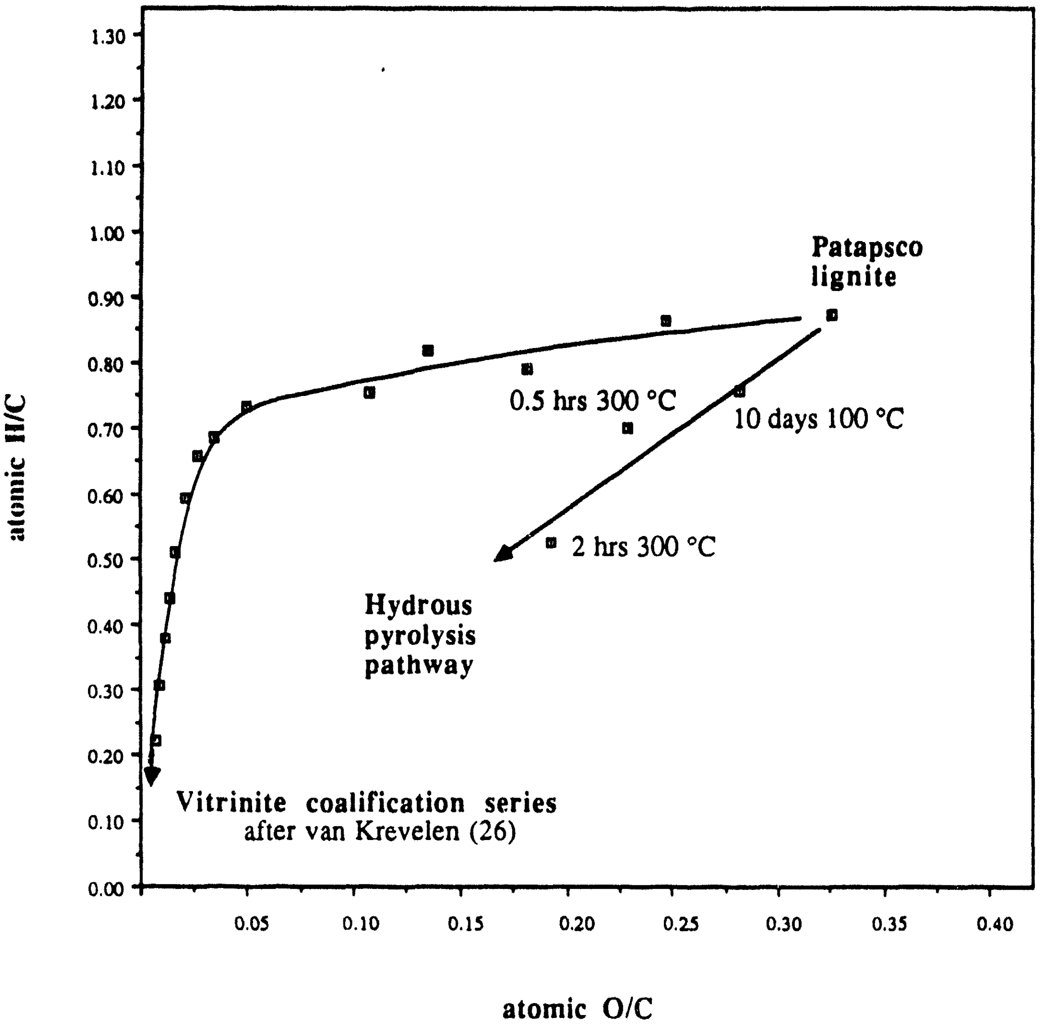


Figure 16. van Krevelen diagram showing trends in the nature of hydrous pyrolysis residues and a natural coalification series.

Fig. 11.

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