

PYROLYSIS/GAS CHROMATOGRAPHY/MASS SPECTROMETRY OF A SERIES OF BURIED WOODS
AND COALIFIED LOGS THAT INCREASE IN RANK FROM PEAT TO SUBBITUMINOUS COAL.

by

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INTRODUCTION

To better understand the coalification process, we have conducted numerous studies (1-4) of the chemical structural composition of xylem tissue from gymnosperm wood and related woods that has been coalified to varying degrees. These previous studies have relied primarily on use of solid-state ^{13}C nuclear magnetic resonance methods to obtain average chemical structural information as wood is buried in peat and then transformed to coal. The samples included xylem tissue from modern wood buried in peat, xylite brown coal, lignitic wood, subbituminous coalified logs, and from several logs of high volatile bituminous coal rank.

The studies presented here, a continuation of the above studies, examine the chemical nature of buried and coalified xylem tissue at the molecular level. To achieve this, we employed pyrolysis/gas chromatography (py/gc) and pyrolysis/gas chromatography/mass spectrometry (py/gc/ms). Pyrolysis techniques have been used to examine peat, coal, coalified wood, and related substances (5-7). However, the technique has not been previously applied to a systematic and histologically-related series of coalified woods. It is particularly useful to compare the results from pyrolytic studies with the data obtained from solid-state ^{13}C NMR (1-4,8).

METHODS

Approximately 0.2 mg of dry, powdered sample of modern buried wood and coalified xylem tissue, whose nature and rank were described in earlier reports (2-4), were weighed into a quartz capillary tube and placed in the coil of a Chemical Data Systems Model 120 Pyroprobe.* The probe, with sample, was inserted into the injection port of either a Perkin-Elmer Sigma 3B or a Varian 2700 gas chromatograph. The injection port temperature was maintained at 280°C. The Perkin-Elmer gas chromatograph, fitted with a 25 m x 0.25 mm i.d fused silica column (HP-17) coated with a crosslinked 50 percent phenylmethyl-silicone liquid phase, was used strictly for py/gc using a flame ionization detector (FID) whose output was recorded with a Perkin-Elmer Sigma 15 recording

* Any use of trade names is for descriptive purposes and does not imply endorsement by the U.S. Geological Survey.

integrator. The Varian gas chromatograph was fitted with the same column but the effluent stream was split. One part of the effluent was swept by means of a helium make-up gas into a jet separator and into the source of a DuPont 490B mass spectrometer. The other part of the effluent was routed to an FID interfaced to a Perkin-Elmer Sigma 10 recording integrator.

Following insertion of the pyroprobe into the injection port, the gas chromatograph was heated at 8°C/min to 300°C to sweep out compounds volatile at injection-port temperatures. After cooling to room temperature and applying liquid nitrogen to the front end of a portion of the fused-silica column, the sample was pyrolyzed at 610°C for 10 sec. The column was immediately temperature-programmed from 40°C to 300°C at 4°C/min.

Further py/gc/ms analyses were performed on a Hewlett-Packard 5970B/5890 gc/ms system equipped with an identical Chemical Data Systems pyroprobe and similar column as above (25m x 0.25mm SGE, BP-5). Samples were flash pyrolyzed at a filament temperature of 710°C for 20 sec. Prior to temperature-programming (20°-80°C at 8°C/min) the column was held at 20°C for 5 min. After reaching 80°, the column was programmed to 310°C at 4°C/min. Compounds were identified by comparing relative retention times with pyrolysis data in the literature (9) and by comparison to mass spectra from the EPA/NIH library as well as from published data (10). Gas chromatographic peak areas for identified compounds were measured as a percentage of the total peak area calculated by summing areas for all peaks. No corrections were made for FID response factors.

RESULTS

Peat and Brown Coal

Representative py/gc chromatograms for gymnosperm xylem tissue buried in peat and brown coal xylite are shown in Figure 1. The solid-state ¹³C NMR spectra for these samples are shown in Figure 2. The buried gymnosperm xylem tissue was shown to be essentially lignin-like in composition (3) as indicated by the NMR peaks at 56, 120, 135, and 148 ppm. The peaks at 72 and 106 ppm, minor contributors to the total peak area, indicate that much of the cellulosic material originally present in the unaltered wood has been degraded and lost during burial, as shown by Hedges *et al.* (9), Hatcher *et al.* (11), and Spiker and Hatcher (12). The py/gc data confirm this as the peaks identified are essentially those characteristic of softwood lignin (13). Guaiacol, 4-methyl guaiacol, 4-ethylguaiacol, 4-vinyl guaiacol, *trans*-isoeugenol, acetoguaiacone, and *trans*-coniferyl alcohol are the major py/gc components. The low amounts of phenol, cresol, and catechol as well as the relatively large amounts of coniferyl alcohol attest to the fact that the lignin is relatively undegraded (13). Peaks directly related to lignin-derived products (e.g. methoxyphenols) account for about 95% of the total peak areas in buried wood. The broad peak tentatively identified as that of levoglucosan indicates that some carbohydrate-like material is present, consistent with the NMR data.

Brown coal xylite, a log belonging to the Podocarpaceae family collected from the Yellourn seam, Morwell, Victoria, Australia, shows an NMR spectrum that is only slightly different from that of modern buried wood (Figure 2). The principal differences are for the intensity of methoxyl carbons at 56 ppm and the peak at 115 ppm for protonated aromatic carbons *ortho* and *para* to aryl-O carbons. The smaller amount of methoxyl carbons relative to total aromatic carbons (100-160 ppm) for the brown coal xylite, compared to the modern buried wood, is an indication that methoxyl groups have been lost from lignin structures. This assumes that the lignin of coniferous wood originally had approximately the same amounts of methoxyl groups per aromatic ring as

lignin from modern buried wood. The peak at 72 ppm, mostly that of carbohydrate carbon, is significantly reduced in relative intensity compared to that in the spectrum of buried wood.

The py/gc data for the xylite brown coal (Figure 1) confirm that methoxylated phenols are still major components. Guaiacol, 4-methylguaiacol, 4-vinylguaiacol, and trans-isoeugenol are the four largest components like in the pyrogram for modern buried wood. Other lignin-derived methoxyphenols found in buried wood are also present; however, the yield of these lignin phenols normalized to total phenols is 88 percent, slightly less than that of buried wood. Phenol and the cresols are relatively larger peaks in pyrograms of brown coal xylite compared to buried wood (Figure 1). This is evident from the ratio of lignin phenols to simple phenols. In the modern buried wood this ratio is high but in the brown coal xylite sample it drops to approximately half of the value for the modern buried wood. The methoxyl content determined by NMR and normalized to total aromatic carbon intensity also decreases by half. This indicates that either aromatic rings in lignin are losing methoxyl groups or that methoxylated phenols are being selectively lost during coalification. Either way, the end result is that lignin phenols are becoming smaller contributors to total phenol yields on pyrolysis.

Lignites

Gymnosperm wood coalified to a rank of lignite displays an NMR spectrum that shows a progressive loss of methoxyl carbon when compared to spectra of lignin or brown coal xylite. The samples examined are lignitic logs collected from various locales along the eastern United States (2,4), and a representative NMR spectrum is shown in Figure 3 for a sample collected from the Patapsco Formation (Cretaceous) near Landsdowne, Maryland. The aryl-O carbons at 150 ppm are major contributors, and the area for the peak at 56 ppm for methoxyl carbon is small compared to the area for aryl-O carbons at 146 ppm. This indicates that methoxylated phenols are minor compared to other phenols.

Intensity of the peak at 146 ppm, compared to total aromatic intensity, is nearly the same for lignite logs as it is in the modern buried wood. A ratio of the area for the peak of 146 ppm to the total aromatic carbon area (100-160ppm) shows that approximately 2 aryl-O carbons are present per aromatic ring. This indicates that the proportion of aromatic carbons having an attached oxygen (1/3 of aromatic carbons) does not change from buried wood to lignite even though a precipitous decline in methoxyl groups is observed. This loss of methoxyl groups and retention of aryl-O most likely involves a demethylation reaction rather than demethoxylation and the resultant chemical structures would resemble catechol-like structures.

The pyrolysis data for lignitic gymnosperm woods is consistent with the NMR data showing loss of lignin-like components (Figure 4). Peaks for guaiacol, 4-methylguaiacol, 4-vinylguaiacol, and trans-isoeugenol are significant peaks but phenol, the cresols, and dimethylphenols are much more significant components than they are in buried wood or brown coal xylite. The presence of eugenol and isoeugenols in lignitic logs is evidence that lignin exists in nearly unaltered form with the propyl side chain preserved.

Though methoxyphenols account for about half of total phenols, the presence of simple phenols such as phenol, the cresols, and dimethylphenols indicates that coalification leads to the production of phenolic structures and these most likely originate from methoxyphenols. As discussed above, the NMR data suggest the formation of catechol-like structures from the guaiacyl units in gymnosperm lignin via demethylation. The pyrolysis data show evidence for the presence of catechol, as has been reported in other lignitic logs (14).

The presence of significant amounts of catechol only in lignitic logs indicates it might be diagnostic of specific structural intermediates in the conversion of lignin phenols to the aromatic structures that are dominant in most coals.

Subbituminous Coal

Gymnosperm xylem tissue of subbituminous coal rank from several samples shows a characteristic ^{13}C NMR spectrum, and Figure 3 depicts a representative NMR spectrum for a sample collected from the Doswell Formation (Triassic) near Taylorsville, Virginia. The primary peak is for aromatic carbons at 130 ppm, but aryl-O carbons appear as a small peak at about 150 ppm. The intensity of this aryl-O peak is significantly less than in lignite samples described above. The calculated intensities suggest that approximately one in six aromatic carbons have an attached oxygen, a strong indication that simple phenols are primary chemical structural elements. The exact chemical shift of this aryl-O carbon is also characteristic of specific structural arrangements. In lignitic logs the peak is at 146 ppm, a chemical shift characteristic of two aryl-O carbons adjacent to each other as in methoxyphenols and catechols. For logs of subbituminous coal rank this peak shifts to 153 ppm which is characteristic of aryl-O carbons having no adjacent aryl-O carbons such as simple phenols. The lack of significant intensity in the NMR region of 50 to 100 ppm suggests that few oxygen-substituted aliphatic carbons are present and that methoxyl groups are gone. This suggests that the propyl side chain of lignin has been modified and that methoxyphenols are no longer present.

The py/gc data (Figure 4) confirm the above NMR observations as the primary pyrolysis products (greater than 50 percent of total pyrolysis products) are phenol, the cresols, dimethyl phenols, C_3 -phenols, and C_4 -phenols. Using py/gc/ms we were unable to detect the presence of methoxyphenols characteristic of lignin or the catechols as observed in lignite. It is likely that the phenols originate from lignin structural units, but these have been modified by loss of methoxyl groups. The lack of catechol in pyrolysis products of subbituminous logs suggests that the catechol-like structures thought to be in lignite have been converted to phenol-like structures via loss of one hydroxyl group per aromatic ring. This is entirely consistent with the NMR data which show an average of 1 aryl-O carbon per aromatic ring.

The major pyrolysis products are phenol and the cresols, but an intense peak in the pyrogram of subbituminous logs is identified as an unresolved mixture of 2,4-dimethylphenol and 2,5-dimethylphenol. The py/gc/ms data suggest that the major contributor to this peak is 2,4-dimethylphenol. The overwhelming amount of 2,4-dimethylphenol, compared with other dimethylphenol isomers, indicates that a specific structural arrangement is retained during alteration of catechol-like structures to phenol-like structures.

DISCUSSION

Py/gc and py/gc/ms have proven to be valuable techniques for characterizing the chemical composition of coal and coal macerals (5,6,9,14-16). Applying this technique to a series of histologically-related coalified logs that increase progressively in rank has allowed us to chart the evolution of lignin from modern buried wood to subbituminous coal. Because the xylem tissue from each of the samples is from gymnosperm wood, we can be reasonably certain that each sample has organic matter derived from a common component, namely lignin composed primarily of guaiacyl structural units. Accordingly, we can make comparisons among the samples and speculate on the chemical transformations that must have occurred during coalification of this gymnosperm lignin. Of course, we must assume that extraneous substances derived from non-lignin sources have not been incorporated to any significant extent.

Both the pyrolysis data and the NMR data shown here and recent studies (10,11) convincingly show that wood buried in peat and in sediments has selectively lost most of its cellulosic components and has retained lignin in a relatively intact form. Consequently, we feel that cellulose does not play a major role in coalification, in contrast to recent suggestions that it does (17). Xylem tissue coalified to a rank of brown coal contains relatively large amounts of lignin, whereas cellulose is not present to any great extent. A gradual change in the lignin can be discerned. This change primarily involves alteration of lignin structural units such that the average number of methoxyl groups per aromatic ring decreases by half, and peaks for lignin pyrolysis products diminish relative to total pyrolysis products. Examination of xylem tissue coalified to a higher rank of lignite reveals that the most likely mechanism for removing methoxyl groups is by demethylation. The lignin is eventually transformed to catechol-like structures. Such a transformation would be consistent with pyrolysis studies showing a decrease in methoxylated lignin phenols and an increase in phenols, cresols, and catechol. It is also consistent with the NMR data showing a decrease in methoxyl carbon and a constant value for the fraction of aryl-O carbons relative to total aromatic carbons.

As lignin in buried wood is gradually transformed to lignite and the lignin structural units are modified to catechol-like structures, the samples show gradually decreasing proportions of pyrolysis products that are directly of lignin origin (e.g. methoxyphenols) and increasing proportions of phenol and catechol-based products which most likely originated from lignin. If one assumes that this trend is related to increasing degrees of coalification, then the loss of methoxyphenols could be used in a quantitative sense to denote increasing rank. It is particularly noteworthy that some lignite samples of Cretaceous age still have a suite of lignin-derived pyrolysis products that suggest that lignin is not extensively altered. This implies a generally high geochemical stability for lignin.

It is difficult to determine from the pyrolysis data if the catechol-like structures in lignite samples are linked by aryl ether bonds as in lignin which shows such a linkage (β -O-4) between the C-4 phenol and the β -carbon on the propyl side chain. However, the NMR data would imply that the catechol-like structures are, in fact, linked in such a manner. Significant intensity in the range of 60-100 ppm is attributable to aliphatic C-O carbons as would be expected from above linkages.

As the xylem tissue is coalified further, lignin pyrolysis products disappear entirely and the catechol-like structures typical of lignite undergo further modification. The data appear to show that catechol-like structures are losing one hydroxyl group per aromatic ring. Pyrolysis products of xylem tissue having a rank of subbituminous coal are principally phenol, the cresols, dimethylphenols, C₃-phenols, and C₄-phenols. The presence of substantial 2,4-dimethylphenol is indicative of the fact that the carbon linkage at C-4 associated with the three-carbon side-chain of lignin is retained. The lack of ¹³C NMR signals in the range of 60-100 ppm suggests that the three-carbon side chain of lignin has been modified, probably by cleavage of the β -O-4 linkage.

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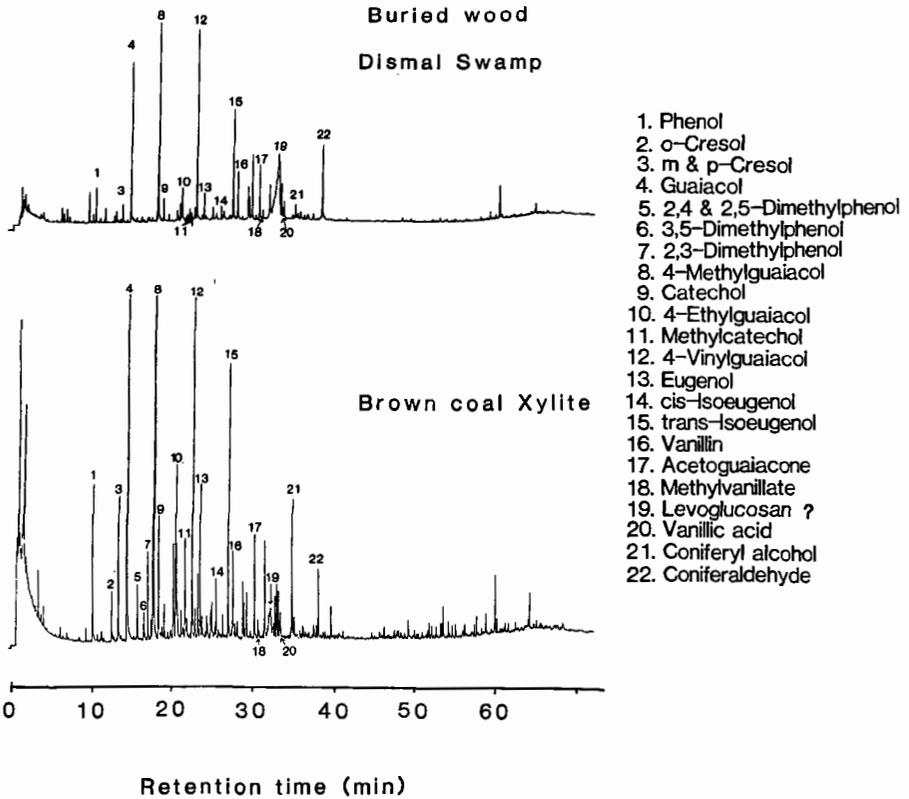


Figure 1. Py/gc-ms traces of buried wood described by Hatcher *et al.*(3) and a sample of a Podocarpacea log (xylite) described in the text.

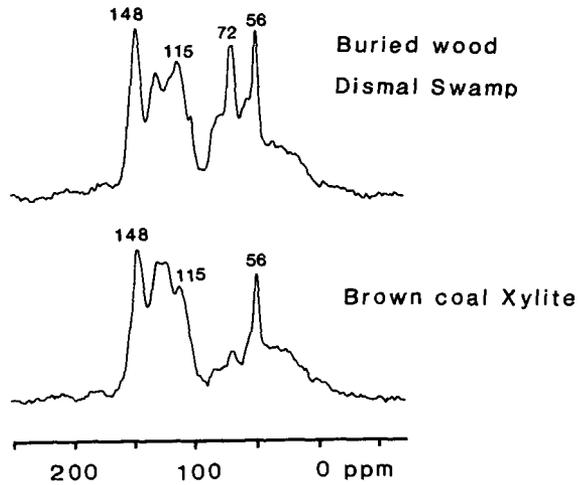


Figure 2. Solid-state ^{13}C NMR spectra of buried wood and Podocarpacea log. Spectra are reproduced from previous publications (4,8).

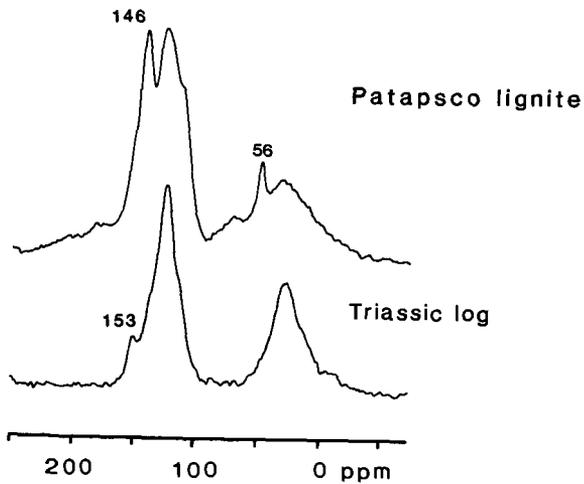


Figure 3. Solid-state ^{13}C NMR spectra of samples described in previous reports (3,8) and in the text.

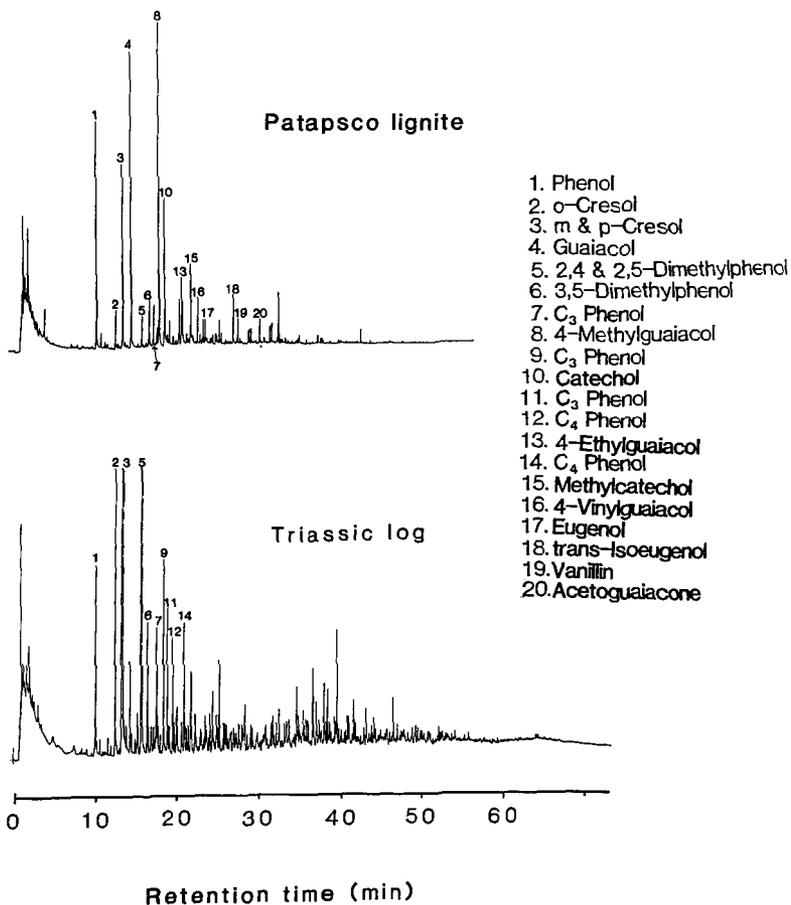


Figure 4. Py/gc-ms traces for the lignite from the Patapsco Formation and for the Triassic log of subbituminous rank.