

Structural Characterization of Coal: Lignin-Like Polymers in Coals

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INTRODUCTION

Although lignins are major constituents of vascular plants from which coals are derived, their roles in the coalification process and resulting coal structures have not been defined. On the basis of chemical and biological degradations, lignins are considered to be polymers of propylphenyl compounds, coniferyl alcohol and related alcohols (1-3). Because of their great abundance, high resistance to biological degradation and characteristic occurrence in land plants, isolation of coal degradation products related to these lignin compounds should shed some light on the roles, if any, played by lignins during coalification and in the final structure of coals. To date such studies have had only limited success.

Although fulvic and humic acids have been degraded successfully with alkaline solutions to produce lignin-related phenols (4-6), this method has not proved to be useful for coals. Reductive degradations of soil and coal-derived humic acids with sodium amalgam have been reported to produce a variety of phenolic compounds (9-10); however, several investigators have found that this procedure gives only a few phenols in very small amounts, because of the degradation of phenolic rings (11-12).

Many oxidative degradations have also been carried out to break coal down into simpler species; however, isolation and identification of phenols such as p-hydroxybenzene derivatives, vanillic and syringic groups, which are characteristic lignin oxidation products, have not been definitely confirmed yet. In general, commonly used oxidants destroy phenolic rings or give complex products (13-15). Some of the oxidants such as nitrobenzene produce reaction by-products that may interfere with the analysis of the oxidation products (16-18). To obtain lignin oxidation products from coals, we resorted to the alkaline cupric oxide oxidation method which has been successfully applied to analysis of lignins in plants (16), fulvic and humic acids (18-19), and land-derived marine sediments (16).

EXPERIMENTAL

Seven coals were used in this study (Table 1). To remove trapped organic materials (20-21), four coals (samples 1-4) were extracted with benzene-methanol (3:1, refluxing for 48 hours) and 2.5% aq.-NaOH (20-35°C for 16 hours) before oxidation. Since the alkaline extractable material was found to be negligible for samples 5-7 these coals were only extracted with benzene-methanol.

Each coal sample (5g) was oxidized with alkaline cupric oxide (51.9 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 37.3 g of NaOH and 185 ml of H_2O) at 200°C for 8-10 hours* by the method of Greene et al. (22). After the reaction mixture had cooled, it was centrifuged. The alkaline supernatant was acidified with HCl to pH 2. After concentration of the acidic solution, the slushy residue was repeatedly extracted with benzene-ether (1:3). The residue was further extracted with methanol. Materials soluble in alkali only were also isolated from all samples. To recover non-oxidized coal, the alkaline insoluble residue was treated several times with concentrated HCl, and finally washed with water. A summary of the oxidation products is shown in Table 2.

Solid probe mass spectrometric analysis (20) showed that the benzene-ether extracts consist mainly of organic acids. Therefore, these extracts were derivatized with d₆-dimethylsulfate to yield d₃-methyl labelled derivatives. The derivatives were analyzed by GC-TOFMS and high resolution MS using techniques which have been previously described (20). Authentic samples of phenolic acids derivatized with d₆-dimethylsulfate or diazomethane were also analyzed by GCMS for reference.

Gas chromatograms of the derivatives obtained from samples 1 and 2 are shown in Fig. 1a and in Fig. 1b with numbered peaks identified in Table 3. The methanol extracts and fractions soluble in alkali only were found to consist essentially of humic acid-like materials by solid probe MS.

To obtain detailed information of the CuO-NaOH oxidation, control experiments with 15 model compounds and a polymer were carried out using the procedure employed for the coals. The results are shown in Table 4.

RESULTS AND DISCUSSION

As shown in Table 2 and in Table 3, most informative is the identification of large amounts of p-hydroxy and 3,4-dihydroxybenzoic acids in the oxidation products of samples 1 and 2. These are regarded as lignin oxidation products. It is interesting to note that, while no o- and m-hydroxybenzoic acids were found in the oxidation products of samples 1 and 2, all three isomers were identified in small amounts in other rank bituminous coals (samples 3, 5, 6). From sample 3, 3,4-dihydroxybenzoic acid was also isolated in small amount, however this compound was not detected in the oxidation products of other bituminous coals (samples 4-6).

It is interesting that bituminous (sample 4) gave organic acids qualitatively similar to those of lignite coal (see Table 2).

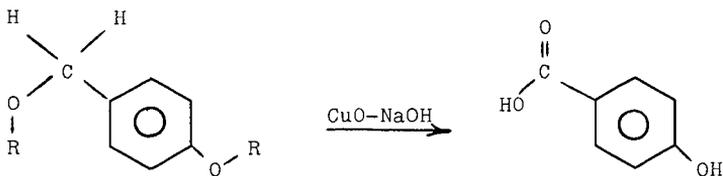
* In general, lignin, plant materials, fulvic and humic acids and marine sediments are oxidized at 170°C for 3-4 hours, however this condition has been found to be not strong enough to oxidize coals.

identified compounds were p-hydroxybenzoic acid, 4-hydroxy-1,3-benzenedicarboxylic acid, benzene di and tricarboxylic acids. No o- or m- isomer of hydroxybenzoic acid was detected. We have found that solvent extractable hydrocarbons obtained from this coal consist mainly of n-alkane (C₁₁ to C₃₁). This is quite different from other results which showed that aromatic hydrocarbons were the major solvent extractable material of several bituminous and anthracite coals (20,23). Indeed, petrographic analysis shows that this coal has a high content of sporinite (14.3 wt %) and low content of vitrinite (30.2 wt %) (24). Anthracite coal (sample 7) did not yield any organic solvent extractable oxidation products.

Some acids not found in oxidation products of lignins, land plants and marine sediments were found in the oxidation products of coals. Among these were phenolic di and tricarboxylic acids and hydroxynaphthalenecarboxylic acids. From some soil fulvic and humic acids, phenolic polycarboxylic acids have been found in the oxidation products together with considerable amounts of fatty acids. Therefore, phenolic esters of fatty acids are considered to be present in these soil acids (5,18). However, little or no fatty acids were observed in the coal oxidation products.

Trihydroxybenzoic acid or its methoxy derivatives (syringic group) which are obtained from the oxidation of lignins, fulvic and humic acids and marine sediments were not found in any of our oxidation products. We have found that the authentic syringaldehyde and 2,6-dimethoxyphenol were largely degraded by the oxidation (Table 4). This may account for the fact that we did not observe them, however the syringic groups may have been degraded during coalification.

All phenolic acids identified were found as OCD₃-derivatives. The mass spectra showed the complete absence of OCH₃-group. It is confirmed that no isotope exchange of the H in OCH₃ with D occurred under our procedures. Although partial demethylation reaction during the oxidation cannot be excluded from the control experiment (see Table 4), it is probable that the phenolic acids found were derived mainly from the fission of ether linked aromatic systems as shown in the example below rather than from aryl methoxy units.



R = alkyl (C \geq 2), aryl

Indeed, it is known that very little or no methoxy groups are present in bituminous coals (25-26). In the lignite coal (sample 1) aryl methoxy groups are not present in significant amounts (26).

Nonhydroxy benzene, naphthalene, pyridine and thiophene carboxylic acids and humic acid-like materials found in the oxidation products might be derived from non-lignin or extensively transformed lignin polymers.

The oxidation of methyl groups of aromatic compounds has been found to be ineffective. Therefore, relatively large amounts of methyl-substituted phenolic and benzene carboxylic acids were isolated from the coal oxidation. Our control experiments also indicated that, while the CuO-NaOH oxidation of alcohol, aldehyde, ketone, quinone and ether is effective, methyl groups and methylene bridges are not oxidized significantly.

CONCLUSIONS

1. Although one cannot rule out the possibility that plant polyphenols (27) could be one of the important precursors for coal formation, the present work shows that lignin-like polymers have been incorporated into the macromolecules of coals, and are still identifiable in lower rank coals. Evidence for this is the identification of p-hydroxy- and 3,4-dihydroxy-benzoic acids which are known lignin oxidation products.

2. The lignin-like polymers contain more highly cross-linked structures increased in aromaticity compared with the original lignins. Phenolic polycarboxylic acids and hydroxynaphthalene-carboxylic acids which were identified are not found in the CuO-NaOH oxidation products of lignins and plant materials.

3. It is obvious that extensive transformation of lignin-like polymers occurred perhaps through reactions (28-29) such as demethylation, demethoxylation, dehydrogenation, oxidation, cleavage of ring structures, re-condensation, etc. during coalification from lignite to bituminous and anthracite coals. This is shown by the fact that (a) lower rank coals gave higher yields of the CuO-NaOH oxidation products; (b) higher phenolic acid/benzenecarboxylic acid ratio is shown for the lower rank of coals; (c) very little or no dihydroxy-benzoic acid was identified in the oxidation products of higher rank coals (samples 3-6); (d) more naphthalene- and heterocarboxylic acids are found in the oxidation products of higher rank coals. Finally, major parts of lignin-like polymers are transformed into non-lignin type polymers at later stage of coalification. Indeed, the later coalification product, anthracite coal (sample 7) did not yield any phenolic acid by the oxidation.

4. In a previous paper (21) we characterized aromatic acids trapped in lignite coal, and have found that these acids are qualitatively quite similar to those obtained from the present oxidation of the same pretreated coal. This indicates that the trapped acids were derived mainly from the oxidative degradation of lignin-like polymers during the coalification. We have also observed that no trapped organic acid is isolated from the anthracite coal which no longer contains lignin-like polymers.

ACKNOWLEDGEMENT

This work was supported by the Division of Basic Energy Sciences of the Department of Energy.

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Table 1
 Elemental Analysis of Samples* (maf %)

No.	Sample	C	H	N	S	O (by diff)	H/C
1	Lignite (Sheridan Wyoming)	66.4	4.8	1.5	1.1	26.2	0.87
2	Bituminous (IL. #2)	73.9	5.2	1.4	3.4	16.1	0.84
3	Bituminous (IL #6)	77.7	5.4	1.4	4.1	11.4	0.83
4	Bituminous (Ohio PSOC#297)	80.5	5.6	1.6	2.9	9.4	0.83
5	Bituminous (Pitt. #8)	82.0	5.5	1.4	3.7	7.4	0.70
6	Bituminous (Penn. PSOC#258)	86.5	4.8	1.3	2.6	4.8	0.67
7	Anthracite (Penn. PSOC#85)	91.0	3.8	0.7	1.2	3.3	0.50

* All samples were pretreated to remove solvent extractable trapped organic materials and were dried at 110-120°C for 16-18 hours under vacuum before oxidation.

Table 2
Summary of CuO-NaOH Oxidation Products

Wt % of fraction ^b	Sample No. ^a						
	1	2	3	4	5	6	7
Organic acid (Benzene-ether extract)	35.3	19.6	17.1	7.0	14.7	1.3	-
Humic acid A (Methanol extract)	54.3	61.0	46.2	9.3	39.5	69.5	-
Humic acid B (only aq. alkali soluble)	≤ 1.0	≤ 1.5	16.1	51.0	20.2	2.0	7.5
Non-oxidized coal ^c	11.0	21.0	22.2	30.4	26.5	32.0	95.0
Wt % of identified acids ^d							
Phenolic	66.6	54.1	14.6	41.0	8.3	5.8	-
Benzene carboxylic	26.0	36.2	69.4	50.2	62.7	76.7	-
Naphthalene carboxylic	2.0	3.3	6.2	5.5	22.9	10.6	-
Heterocyclic ^e	-	1.6	3.5	2.0	2.0	3.2	-
Aliphatic dibasic	2.6	1.0	1.4	-	≤ 1.0	≤ 1.0	-
Others	2.8	3.8	4.9	1.3	3.5	3.0	-
Ratio of Phenol/Benzene Acid	2.56	1.49	0.21	0.82	0.13	0.07	-

^aSee Table 1 for information.

^bWt % was obtained from coal sample on a dry, ash free basis.

^cSmall amount of insoluble Cu-salts are present.

^dWt % was obtained from each benzene-ether extract. Determination was made from the gas chromatograms of their methyl esters.

^eThiophene- and pyridine carboxylic acids for samples 2-6, and pyridine tricarboxylic acids for sample 1.

- Not found.

Table 3

Organic Acids Identified as Their d_3 -methyl Esters by GC-MS and
High Resolution MS

Peak No.	Compound
1	Succinic acid
2	C ₃ -dibasic acid
3	Benzoic acid
4	Methylbenzoic acid
5	p-Hydroxybenzoic acid
6	Hydroxytoluic acid
7	1,2-Benzenedicarboxylic acid
8	1,4-Benzenedicarboxylic acid
9	1,3-Benzenedicarboxylic acid
10	Methylbenzenedicarboxylic acid
11	Dihydroxybenzoic acid
12	Pyridinedicarboxylic acid
13	3,4-Dihydroxybenzoic acid
14	Dimethylbenzenedicarboxylic acid (naphthoic acid, minor)
15	Hydroxybenzenedicarboxylic acid (4-hydroxy-1,3-benzenedicarboxylic acid, largest peak)
16	Methylhydroxybenzenedicarboxylic acid
17	1,2,4-Benzenetricarboxylic acid
18	1,2,3-Benzenetricarboxylic acid
19	1,3,5-Benzenetricarboxylic acid
20	Methylbenzenetricarboxylic acid
21	Pyridinetricarboxylic acid
22	Naphthalenedicarboxylic acid
23	Hydroxybenzenetricarboxylic acid
24	1,2,4,5-Benzenetetracarboxylic acid
25	1,2,3,4-Benzenetetracarboxylic acid
26	1,2,3,5-Benzenetetracarboxylic acid
27	Methylbenzenetetracarboxylic acid
28	Dihydroxy-diphenyldicarboxylic acid (T)
29	Hydroxynaphthalenedicarboxylic acid
30	Benzenepentacarboxylic acid

T indicates that identification is tentative.

Table 4

CuO-NaOH Oxidation of Model Compound at 200°C for 8-10 Hours

Compound	Type of Reaction	Major Product ^a	Yield mol %
4-Methylbenzyl alcohol	-CH ₂ OH → -COOH	4-Methylbenzoic acid	93
β-Naphthyl methylcarbinol	-CH ₂ OH → -COOH	β-Naphthoic acid	77
Benzaldehyde	-CHO → -COOH	Benzoic acid	95
4-Methoxybenzaldehyde	-CHO → -COOH	4-Hydroxybenzoic acid	89(45)
2,6-Dimethoxyphenol	-OCH ₃ → -OH	b	-
Syringaldehyde	-CHO → -COOH	3,4,5-Trihydroxybenzoic acid	4.5 ^c
Dibenzoylmethane	-CO-CH ₂ - → -COOH	Benzoic acid	76
1,4-Naphthoquinone	-CO-C → -COOH	Phthalic acid	91
Phenylacetic acid	-CH ₂ -CO- → -COOH	Benzoic acid	68
Diphenyl ether	-O- → -OH	Phenol	67
Dibenzyl ether	-H ₂ C-O-CH ₂ - → -COOH	Benzoic acid	81
Diphenyl methane	-C-C- → -COOH	Benzoic acid	11
Poly-(4-methoxystyrene)	-C-C → -COOH	4-Hydroxybenzoic acid	6 ^d
1-Methylnaphthalene	-C-C → -COOH	1-Naphthoic acid	3
2,4-Dimethoxytoluene	-C-C → -COOH	2,4-Dihydroxybenzoic acid	5(58)
3,4-Dimethoxytoluene	-C-C → -COOH	3,4-Dihydroxybenzoic acid	7(52)

^aAll products were derivatized with d₆-dimethylsulfate or diazomethane, and analyzed by GCMS.

^bAbout 16.9 wt % of the oxidation product was obtained under the same conditions (170°C for 4 hours) employed for plant materials, humic acids and marine sediments. The product consisted mainly of polymerized material. Very small amount of trihydroxy compounds (2-3%) was detected by GCMS.

^cMost of syringaldehyde was degraded.

^dShown as wt %.

^eNumber in parenthesis shows % of demethylation from -OCH₃ group.

FIGURE CAPTION

Fig. 1a. Gas chromatogram of methyl esters of the organic acid fraction from lignite; Fig. 1b, from bituminous coal. The analysis was carried out on a Perkin-Elmer 3920B gas chromatograph interfaced to a modified Bendix model 12 time-of-flight mass spectrometer with a variable split between a flame ionization detector and the source of the mass spectrometer. The separation was made on a 15.2 m x 0.51 mm SCOT column coated with OV 17 and temperature programmed from 100-250°C at 4°C min⁻¹.

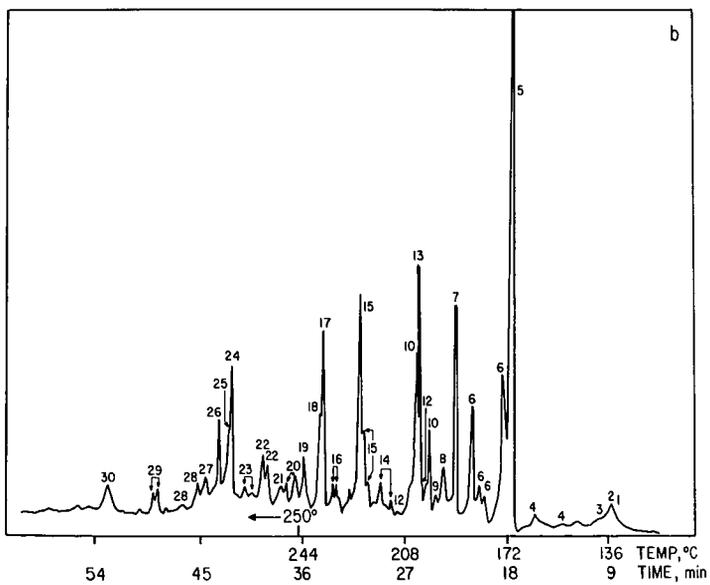
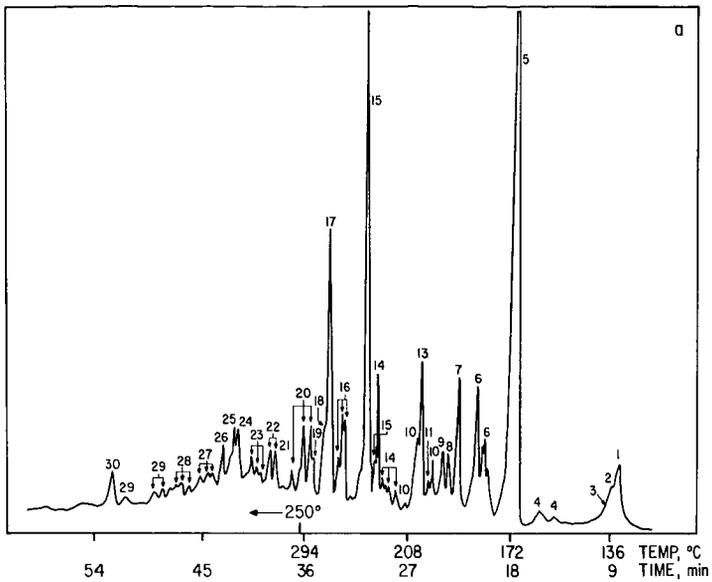


Figure 1