

DETERMINATION OF PHENOLIC STRUCTURES IN LOW RANK COALS: ELUCIDATION OF TRANSFORMATION PROCESSES OF LIGNIN AT THE EARLY STAGE OF COALIFICATION

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INTRODUCTION

Because lignin is considered to be a major precursor of coal vitrinite, chemical alteration studies of lignin structure are important for elucidating coalification processes as well as for understanding the chemical structure of vitrinite. Many investigators have attempted to elucidate the chemical processes in the coalification lignin. For example, Wayman et al. (1) have reported that a 100-million-year-old conifer consists of lignin-like material which is about one-third demethylated. Extensive cleavage of lignin ether linkages was also observed. Recently, based on ^{13}C NMR study, Hatcher (2) has concluded that the defunctionalization reactions of lignin-derived aromatic structures occur sequentially during coalification. A similar pathway has been suggested by Wilson (3). From a comparative NMR study of [$\beta\text{-}^{13}\text{C}$]lignin and its coalified products, Botto (4) has suggested that transformation of lignin is initiated by the heterolytic bond cleavage of labile β -aryl ether groups.

The present study continues our investigation of transformation processes of plant organic material to coal during early stages of coalification. To understand alteration of phenolic structures in lignin, and natural and synthetic coals have been characterized by using two-step depolymerization procedure of alkaline hydrolysis followed by silver oxide oxidation. In parallel experiments, lignin model compounds and a polymer have been transformed using thermal catalytic reaction conditions that mimic natural catagenetic metamorphism.

EXPERIMENTAL

Samples. The elemental compositions are presented in Table 1. Prior to the oxidations, all coal samples were exhaustively extracted with benzene-methanol (3:1) and CHCl_3 under reflux, and these were demineralized with HCl-HF at room temperature. A softwood lignin was isolated from pine.

Alkaline Hydrolysis. Each sample (0.5-1.0 g) was hydrolyzed with 12% NaOH aq. solution in an autoclave at 180°C for 4 hours. The air in the autoclave was replaced by nitrogen. The yields of alkaline hydrolyzed fractions from all samples are shown in Table 1. The soluble hydrolyzed fraction (after acidity) consists of humic acid-like material (soluble in alkali only but not HCl and organic solvents) and small molecules (soluble in organic solvents); dried at 60°C under vacuum.

Oxidation. Each alkaline hydrolyzed fraction was methylated with dimethyl- d_6 sulfate (5) before oxidation. A methylated- d_3 sample (0.3 ~ 0.4 g) was oxidized with alkaline silver oxide (freshly prepared 6 g of Ag_2O and 60 ml of 16% NaOH

TABLE 1. Elemental and Maceral Compositions of Samples.

No.	Sample	Elemental Composition per 100 Carbons	Soluble ^a	Insoluble ^b	Loss (by difference)
1	Victorian Brown Coal (Pale Lithotype)	$C_{100}H_{89}O_{34}N_{0.5}S_{0.2}$	64.3	28.7	7.0
2	Beulah-Zap Lignite (APCS #8)	$C_{100}H_{80}O_{21}N_{1.4}S_{0.4}$	57.5	28.5	14.0
3	Wyodak-Anderson Subbituminous (APCS #2)	$C_{100}H_{86}O_{18}N_{1.3}S_{0.2}$	53.0	31.4	15.6
4	Illinois #6 seam hvC Bituminous (APCS #3)	$C_{100}H_{77}O_{13}N_{1.5}S_1$	12.7	79.9	7.4
5	Blind Canyon hvB Bituminous (APCS #6)	$C_{100}H_{88}O_{11}N_{1.7}S_{0.2}$	32.7	58.8	8.5
6	Upper Freeport mv Bituminous (APCS #1)	$C_{100}H_{86}O_{6.8}N_{1.8}S_{0.3}$	8.6	84.5	6.9
L	Lignin	$C_{100}H_{108}O_{33}$	69.3	22.0	8.7
SY	Synthetic Coal	$C_{100}H_{86}O_{23}N_{1.2}S_{0.3}$	54.4	29.3	16.3

^aThe soluble, in experimental hydrolyzed fraction (after acidity) consists of humic acid-like material (soluble in alkali only but not HCl and organic solvents) and small molecules (soluble in organic solvents); dried at 60°C under vacuum.

^bInsoluble residue was determined after washing with HCl, H₂O and organic solvents, dried at 80°C under vacuum.

aqueous solution) at 80°C for 10 hours. After filtration, the reaction mixture was acidified with 10% HCl, concentrated, and extracted with benzene-methanol (3:1) and ether-methanol (3:1). Finally the solvent extractable material was esterified with diazomethane for GCMS analysis.

Thermal Catalytic Reaction. As shown in Table 2, six lignin model compounds and a polymer were used. Each sample (0.5 g) and montmorillonite K-10 (Aldrich Chemical Co.) were placed in a 25 x 2 cm i.d. glass tube. After evacuation, the tube was sealed and then heated at 150°C for two weeks. After the reaction, the mixture was extracted with refluxing benzene-methanol (3:1) and then CHCl₃.

In general, phenolic groups are strongly adsorbed on the surface of clay minerals. Therefore, it is necessary to treat the reaction mixture with 6N-HCl (reflux for 6 hrs.) before extraction with organic solvent. The solvent insoluble residue was treated with concentrated HCl-HF (1:1) at room temperature to remove the clay. A synthetic coal was prepared by heating a mixture of lignin, amino acids and K-10 at 150°C for two months (6-7).

Characterization and Identification Procedures. The analytical procedures used in this study have been described in detail previously (5,7-8).

RESULTS AND DISCUSSION

We have found that the alkaline hydrolysis effectively solubilizes lignin and low rank coals. The most likely mechanism of solubilization is the cleavage of ether linkages except aryl methyl and diaryl ethers. As expected, high oxygen containing samples (L, No. 1-3 and SY in Table 1) were hydrolyzed appreciably and produced significant amounts of solubilized materials.

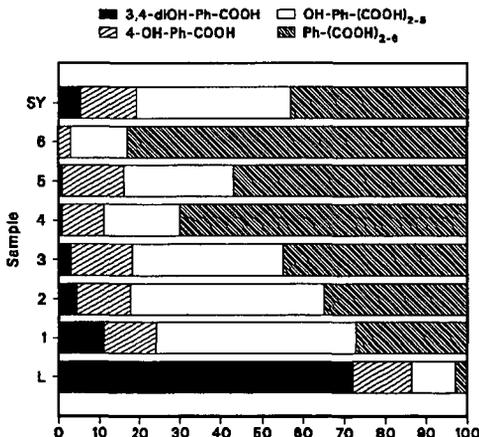
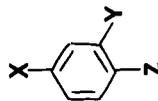


Figure 1. Relative abundances of the phenolic- and benzene-carboxylic acids obtained from silver oxide oxidation of alkaline solubilized materials; determined by GCMS as methyl esters.

TABLE 2. Summary of the Thermal Catalytic Reaction of Lignin Models.

Run	Model			Yield of Product wt%		Soluble Products (GCMS Analysis)	
	X	Y	Z	Soluble	Insoluble Polymers	Major	Minor
1	CH ₂ OH	OME	OH	38	42	C ₁₋₃ alkyl-catechols	dimers
2	O-nBu	H	H	53	10	C ₁₋₇ alkyl-phenols	dimers, trimers
3	OCD ₃	H	{CH-CH ₂ } _n	27	61	C ₁₋₃ alkyl, CD ₃ -phenols	dimers
4	OCH ₂ Ph	H	H	45	41	hydroxyl-diphenylmethanes	dimers
5	H	OH	OCH ₂ Ph	63	16	benzylcatechols	dimers, trimers
6	CH ₂ OCH ₂ Ph	H	H	42	37	C ₁₋₂ alkyl-diphenylmethanes	triphenylalkanes
7	OPh	H	H	79	13	starting material	monomeric and dimeric phenols

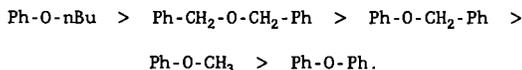


A summary of the silver oxide oxidation products from d_3 -methylated solubilized materials is shown in Fig. 1. The yields are 63-89 wt%. The major product from oxidation of lignin is 3-methoxy-4-methoxy- d_3 -benzoic acid. This result is in excellent agreement with the latest softwood lignin model (9) and other oxidation studies (e.g. 10). On the other hand, the oxidation of coal samples shows much smaller yields of dimethoxybenzoic acid. The GCMS analyses of coal oxidation products indicated that the concentration of 3,4-dimethoxy- d_6 derivative is much higher than that of 3-methoxy-4-methoxy- d_3 compound which is lignin's major product; $(OCD_3)_2/OCD_3OCH_3$ ratios are 0.16 for lignin and 4.7 - 7.5 for coal samples.

Most informative was the identification of large amounts of phenol-polycarboxylic and benzene-polycarboxylic acids in the oxidation products of low rank coals (Nos. 1-3). These acids are found in very little or negligible concentration in the oxidation products of lignin or slightly altered lignin. These observations apparently show that phenolic structures in lignin are considerably changed even at early stages of coalification.

With increasing rank (HV bituminous coals), the yield of phenolic acids decreases; benzenecarboxylic acids become the most abundant products. Polynuclear aromatics such as naphthalene carboxylic acids have also been found as minor products.

As shown by the results of thermal catalytic reactions of lignin models in Table 2, it is apparent that the reactions proceed by intra- and inter-molecular rearrangements of ethers. Aryl methyl and aryl butyl ethers (runs 1-3) rearrange to alkyl phenols; benzyl ethers were found to be converted to diphenylmethane derivatives through cleavage of ether linkages and benzylation. The reactivity of ethers under the reaction conditions used in this study are shown to increase in the following series:



These results imply that ether linkages in lignin structures (benzyl aryl type ethers; β -O-4, α -O-4 and γ -O-4) are labile and readily cleaved with accompanying intra- and inter-molecular rearrangements at early stages of coalification. Botto has observed (4) the occurrence of such rearrangement reactions from ^{13}C NMR studies of [β - ^{13}C] lignin samples coalified by the thermal catalytic reactions.

In this and previous (6-7) studies, we have also found that the oxidation results of synthetic coals obtained from lignin closely resemble those of the oxidation of samples No. 1 and 2 (Fig. 1), and other coals and vitrinites (6-7). Both natural and synthetic coals produce phenolic- and benzene-polycarboxylic acids as major oxidation products.

An important problem has been understanding how phenolic structures in lignin are altered to benzene and other aromatic structures such as naphthalene and tetralin. In our preliminary studies, we have found that phenols and phenyl ethers undergo catalytic hydrogen transfer reactions with terpenoids found in

low rank coals and sedimentary rocks. The terpenoids are apparently acting as hydrogen donors. These reactions are believed to be catalyzed by clay minerals.

One of our experiments indicates that the reaction of p-hydroxy-polystyrene and d-limonene in the presence of montmorillonite K-10 produce alkyl benzenes and p-cymene together with alkyl phenols. Such hydrogen transfer reactions may reveal the processes by which benzene rings are formed at the expense of lignin-phenols. It is considered that somewhat transformed lignin may also contain hydrogen donors such as hydroaromatics. Indeed, Botto has suggested (4) formation of hydroaromatic structures such as dihydrofurans during coalification of lignin. Detailed results for this study will be reported.

SUMMARY

The present study indicates that natural alteration processes from lignin to low rank coal are highly diverse and involve many types of organic reactions. Among them are clay catalyzed intra/inter-molecular rearrangement, hydrogen transfer and transalkylation reactions (11-14) which occur simultaneously rather than sequentially.

ACKNOWLEDGMENT

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