

Oxidative Degradation Studies and Modern Concepts of the
Formation and Transformation of Organic Constituents of Coals and Sedimentary Rocks

Ryoichi Hayatsu, Randall E. Winans, Robert L. McBeth
Robert G. Scott and Leon P. Moore

Chemistry Division
Argonne National Laboratory, Argonne, IL 60439 USA

INTRODUCTION

In our previous oxidative degradation studies (1-4) we have suggested that:
1) In addition to aromatic rich materials, Wyoming lignite coal also contains aliphatic rich materials that are similar to type I kerogen. These aliphatic rich materials are not considered to be directly related to exinite macerals, because petrographic analysis of the coal shows a very low content of exinite ($\sim 1\%$). 2) Lignin-like polymers are incorporated into macromolecular materials of low rank coals. 3) During catagenesis (coalification processes) most of these aliphatic rich materials and lignin-like polymers are extensively transformed or degraded.

In our effort to better understand the transformation of aliphatic rich materials and lignin-like polymers during catagenesis, oxidative degradation studies of lignite, subbituminous and bituminous coals were carried out using different oxidants. For comparison with coal oxidation, Green River kerogen and softwood and hardwood lignins were oxidized. In order to determine how phenolic structures in lignins and lignin-like polymers have been altered during the evolutionary stages of diagenesis, catagenesis and metagenesis, lignin or lignite coal was heated with clay minerals to produce artificial coalification products. Since the naturally occurring low temperature transformations may require millions of years, they cannot be duplicated in the laboratory and our artificial catagenetic reactions must, therefore, be somewhat accelerated by higher temperatures (150-200°C). However, even temperatures in this range may be considered realistic, because many coals may have been subjected to such temperatures due to depth of burial (5). An oxidative degradation study of these artificial coalification products provided some evidence which helps elucidate the alteration of phenolic structures during catagenesis.

EXPERIMENTAL TECHNIQUES AND RESULTS

Sample. All samples used in this study are shown in Table 1. Prior to the oxidation reactions and other experiments, solvent soluble trapped organic materials were removed from the samples as described previously (2,6).

Oxidation. Since the oxidation procedures used have been reported in detail in our earlier work (1,2), they are described only briefly in this paper. A summary of the oxidation results is shown in Table 2. a) KMnO_4 oxidation with buffer-control: A sample (3g) methylated with d_6 -dimethylsulfate or dimethylsulfate was oxidized at 80°C with buffer-controlled permanganate (300 ml of 4.3% aq. KMnO_4 and 11.5g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) with stirring for 14-20 hours (1st step oxidation); the insoluble residue was further oxidized under the same conditions as the 1st step (2nd step). The residue of the second step was oxidized further in a third step until most of the carbon in the sample was oxidized. b) CuO-NaOH oxidation: A non-methylated sample (5g) was oxidized with alkaline cupric oxide (51.9g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 37.3g of NaOH and 185 ml H_2O) in a rocking stainless steel autoclave at 200° for 10 hours. This oxidation was carried out in a nitrogen atmosphere.

Artificial catagenesis. A mixture of sample (2.5g of lignin or lignite coal) and 0.5g of montmorillonite clay mineral pretreated with 5% HCl was dried at 100°C for 12 hours under vacuum, and was then placed in a 45cm x 2cm i.d. quartz tube sealed at one end and joined to a metal valve at the other end. The sealed end

was inserted to a depth of about 10cm in a tubular furnace which was heated at 150°C for the lignin sample and 200°C for the coal sample. These experiments were carried out in the absence of oxygen. During the heating, water and volatile materials were evaporated and condensed on the wall of that part of the quartz tube that was outside the furnace and which remained at room temperature. After the reaction, the mixture was extracted with benzene-methanol (3:1); the extract was equal to 6.3% by weight of the original softwood lignin for 14 days heating and 9.1% for 28 days heating. The insoluble residue was dried at 100°C for 12 hours; 66.3% of the carbon in the original sample remained in the insoluble residue (artificial product 1) after 14 days heating and 57.8% after 28 days heating (artificial product 2). Artificial catagenetic reaction of Wyoming lignite (100°C for 2 days, 150°C for 8 days and finally 200°C for 20 days) produced organic solvent soluble material (6.7 wt%) and insoluble residue (artificial product 3; 84.2% of carbon in the original sample).

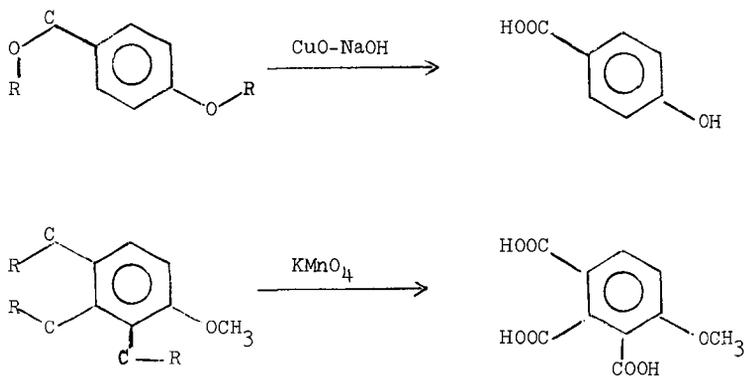
Separation and identification. Insoluble non-volatile samples or products were analyzed by solid probe MS. For each sample, about 50-70 spectra were generally taken between 25°C and 500°C. Oxidation products were esterified and analyzed by GCMS and HRMS. Non-volatile products were examined by LC, solid probe MS and HRMS.

Aliphatic rich material. In the past, a number of oxidation studies have been done to characterize the nature of aliphatic structures in coal. However, with few exceptions (7,8) only short-chain aliphatic mono and dicarboxylic acids have been reported as oxidation products. These results have suggested that non-aromatic carbon in vitrinite rich coal is present in the form of short methylene chain linkages between aromatic ring clusters, short alkyl side chains, alicyclics and hydroaromatics. For lignite coal, as previously reported (2,3), this view is no longer adequate since in the stepwise buffer-controlled permanganate oxidation products of the lignite, relatively large amounts of unbranched aliphatic dicarboxylic acids ranging from C₄-C₂₁ (with C₉ most abundant) have been identified. Branched dicarboxylic acids (C₅-C₁₀) and tricarboxylic acids (C₆-C₈) were identified also but in lower concentrations. Phthalic acid was the most abundant aromatic acid in the first step oxidation products, but benzenetricarboxylic acids (1,2,4- and 1,2,3-) were the most abundant acids in the 2nd and 3rd step oxidation products. These long-chain dicarboxylic acids identified are believed to be derived from material that is similar to type I kerogen. In the buffer-controlled oxidation of Kaiparowitz subbituminous coal, a series of unbranched aliphatic dicarboxylic acids up to C₁₄ was identified in smaller amounts than those in the lignite. The most abundant oxidation products for any of these stepwise oxidations, were the 1,2,4- and 1,2,3-benzenedicarboxylic acids. Very little or no long-chain dicarboxylic acids (C>8) were detected in the oxidation products of high volatile and low volatile bituminous and anthracite coals. However, there are some exceptions. For example, long-chain aliphatic dicarboxylic acids are produced from the oxidation (HNO₃ or Na₂Cr₂O₇) of HVC (9) and HVA (6) bituminous coals. However, these coals are cannel or cannel-like coals which are believed to have formed through different evolutionary paths from those of humic coals.

Oxidation results of Green River kerogen concentrate with buffered permanganate or chromic acid showed that more than 80% of the oxidation products are aliphatic carboxylic acids (monocarboxylic acid up to C₂₉; dicarboxylic acid up to C₂₀). The distribution pattern of these products is similar to that of the first step oxidation products obtained either from buffered permanganate or chromic acid oxidation of the lignite. CuO-NaOH oxidation of the kerogen also produced long-chain dicarboxylic acids (up to C₁₈ with max. at C₉) with lesser amounts of phenolic and benzenedicarboxylic acids. Of particular interest is the fact that this kerogen appears to be a type of kerogen resulting from contributions of both algal and higher plant materials.

Lignin-like polymer. As shown in our previous papers (1), large amounts of p-hydroxy-, 3,4-dihydroxybenzoic acids and 4-hydroxybenzenedicarboxylic acids which are regarded as lignin oxidation products were identified in the CuO-NaOH oxidation products of low rank coals. However, we have found that the same oxidation of high

rank coals gave much lower yields of phenolic acids with no predominance of 4-hydroxy isomers. Stepwise buffer-controlled permanganate oxidation of methylated lignite, subbituminous and HVC bituminous coals has been found to produce phenolic acids in good yield (in particular at the later steps) together with large amounts of benzenecarboxylic acids. It is interesting to note that, while the CuO-NaOH oxidation of these coals gives higher yields of total phenolic acids than the permanganate oxidation does, the latter generally produces more monohydroxybenzenetri- and tetracarboxylic acids as the oxidation products. This shows that the CuO-NaOH oxidation is more effective at breaking up ether bonds but much less efficient for degradation of aromatic structures bonded by C-C linkages than the permanganate is. Perhaps these phenolic polycarboxylic acids found result from the oxidative degradation of more crosslinked portions of the macromolecular structures as shown in the example below.



R= alkyl or aryl

Although many oxidation studies on lignin have been carried out, for comparison, we oxidized methylated softwood and hardwood lignins with stepwise buffered permanganate. As expected, phenolic acids were major oxidation products (see Table 2); for example, the most abundant acids obtained from softwood lignin were p-methoxy-, 3,4-dimethoxy-, 3,4,5-trimethoxybenzoic acids, 4,5-dimethoxy-1,2-benzenedicarboxylic acid and its isomers, and 4,5-dimethoxybenzenetricarboxylic acids. Benzenecarboxylic acids and short-chain aliphatic dicarboxylic acids were obtained in much smaller amounts. A few oxygen-containing heterocyclic acids were also identified in negligible amounts.

The permanganate oxidation of artificial product 1 resulted in a distribution pattern of aromatic acids produced that is intermediate between those of the lignite and the subbituminous coal. The results are that: 1) the most abundant acids are benzenetricarboxylic acids, 2) the yield of phenolic acids was 11% by wt of the total oxidation products (cf. >75 wt% for the lignins), 3) as in the case for coals, no trimethoxybenzoic acid, which is one of the major products of lignin oxidation, was found, 4) furan, benzofuran, dibenzofuran and xanthone carboxylic

acids were identified, which are found in the oxidation products of low rank coals, but not lignins; 5) no long-chain aliphatic carboxylic acids were detected. The distribution pattern of the oxidation products obtained from artificial product 2 was very similar to that of the LV bituminous coal; that is, very small amounts of phenolic acids were produced and large amounts of benzenecarboxylic acids. Benzo and dibenzofurancarboxylic acids were also found.

These results were also confirmed by solid probe MS analysis of softwood lignin and its artificial products. As expected, major mass peaks obtained from the lignin were due to mono- di- and trihydroxyphenols and their methyl and/or methoxy derivatives. On the other hand, prominent peaks from artificial product 1 consisted mainly of fragments of monohydroxyphenol derivatives and alkylbenzenes. Less intense peaks corresponding to indanes, indenenes, naphthalenes, dihydroxyphenols and oxygen containing heterocyclics were also seen. These mass spectra were very similar to those of lignite or subbituminous coals except for the lack of longer chain hydrocarbons, and N and S-containing heterocyclics. Of phenolic compounds, only monohydroxy derivatives were detected (as minor peaks) in the mass spectra of artificial product 2 as well as in the spectra of high rank coals. It is interesting to note that artificial product 3 prepared from lignite coal showed very similar analytical results (solid probe MS, IR, H/C and O/C ratios) to those of LV bituminous coal. This evidently shows that lignin-like polymers in lignite coal are extensively degraded by either natural catagenetic processes or artificial coalification reactions. It is known that during pyrolysis experiments (300-600°C) on lignin or model compounds, reactions such as demethoxylation or rearrangements of phenyl propane units, etc. can occur and furan and benzofurans (but not dibenzofuran) can be formed (10). Our artificial reactions occur at much lower temperatures, therefore, it is apparent that montmorillonite clay accelerated the catagenetic processes.

CONCLUSION

From the present and previous studies, we conclude that: 1) at least this lignite and subbituminous coal contain aliphatic rich materials which might have been derived from lipids. Such materials are no longer identifiable in higher rank coals except cannel coal, because of extensive degradation during catagenesis. Indeed, trapped volatile compounds extracted from bituminous coals are predominantly aliphatic hydrocarbons which are considered to be degradation products from the macromolecular materials. However, lignite and anthracite coals contain much less of these hydrocarbons (11,12). As Tissot and Welte (5) have also mentioned, during catagenesis aliphatic carbon chains and alicyclics in kerogen are released successively forming crude oil and gas. 2) During diagenesis and early catagenesis lignin polymers are transformed to lignin-like polymers which are incorporated into the low rank coal macromolecules. At a later stage of catagenesis, these polymers have lost their lignin-like nature as a result of continued and extensive transformation.

Higher plants are composed largely of cellulose and lignin. Lipids and lipid-like substances and proteins are also present as minor components. Lignin is more resistant to decay than cellulose which is easily removed by hydrolysis during diagenesis and early catagenesis. Thus, lignin or lignin-like polymers are preferentially concentrated together with other phenolic materials and lipids during the formation of peat and low rank coal. Since cellulose or carbohydrates are known to produce furans and benzofurans by thermal degradation at over 300°C (13,14), we may not be able to exclude the possibility that some of the oxygen-containing heterocyclics found in the structures of coal macromolecules were derived from cellulose. However, on the basis of the following results, we believe that the major source of these heterocyclics is the abundant lignin material.

We have found that artificial catagenetic reactions readily transform lignin polymers into lignin-like polymers which have oxygen-containing heterocyclic structural constituents such as furan, benzofuran, dibenzofuran and xanthone. In addition, demethoxylation of lignin structural units was found to occur easily during the reactions. Somewhat stronger conditions (longer reaction time or a little higher temperature) employed for preparation of artificial products 2 and 3, which may correspond to later catagenesis stages, resulted in additional transformation and loss of lignin-like characteristics. This may be the first clear experimental demonstration of the way that clay minerals can affect the course and result of catagenesis.

ACKNOWLEDGEMENT

This work was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences of the U.S. Department of Energy.

REFERENCES

1. Hayatsu, R., Winans, R.E., McBeth, R.L., Scott, R.G., Moore, L.P. and Studier, M.H., *Advances in Chemistry Series on "Coal Structure"* (Am. Chem. Soc.) in press; see also *Nature* 278, 41 (1979).
2. Hayatsu, R., Winans, R.E., Scott, R.G. and McBeth, R.L., *Fuel*, in press.
3. Hayatsu, R., Winans, R.E., Scott, R.G., McBeth, R.L., and Vandegrift, G.F., *Fuel*, in press.
4. Hayatsu, R., Scott, R.G., McBeth, R.L. and Winans, R.E., *ACS, Div. of Organic Coatings and Plastic Chem.*, Preprint 43, 401 (1980).
5. Tissot, B.P. and Welte, D.H., *Petroleum Formation and Occurrence* (Springer-Verlag, New York, 1978).
6. Hayatsu, R., Scott, R.G., and Winans, R.E., *Oxidation of Coal in "Oxidation in Organic Chemistry"*, Part D (W.S. Trahanovsky, ed., Academic Press, New York) in press.
7. Allan, J. Ph.D. Thesis, Univ. of Newcastle upon Tyne (1975).
8. Young, D.K. and Yen, F.T., *Energy Science* 3, 49 (1976).
9. Deno, N.C., Curry, K.W., Jones, A.D., Keegan, K.R., Rakitsky, W.G., Richter, C.A., and Minard, R.D., *Fuel*, in press.
10. Sigleo, A.C., *Science* 200, 1054 (1978); see also *Geochim. Cosmochim. Acta* 42, 1397 (1978).
11. Raj, S., Ph.D. Thesis, Pennsylvania State Univ. (1976).
12. Hayatsu, R., Winans, R.E., Scott, R.G., Moore, L.P., and Studier, M.H., *Fuel* 57, 541 (1978).
13. Shafizadeh, F., Sarkanen, K.V. and Tillman, D.A., *Thermal Uses and Properties of Carbohydrates and Lignins* (Academic Press, New York, 1976).
14. Brazhnikov, V.V., and Mukhin, L.M., *Chromatog. Rev.* 15, 151 (1971).

Table 1

Elemental Analysis of Samples (maf %)

No.	Sample ^{a)}	C,	H,	N,	S,	O, (by Diff.)	H/C	O/C
1	Lignite (Sheridan Wyoming)	66.4	4.8	1.5	1.1	26.2	0.87	0.29
2	Subbituminous (Kaiparowitz)	77.4	5.6	1.2	0.3	15.5	0.87	0.15
3	HVC bituminous (IL #2)	73.9	5.2	1.4	2.4	17.1	0.84	0.23
4	Softwood lignin ^{b)}	65.6	5.9	<0.1	<0.1	28.5	1.08	0.33
5	Hardwood lignin ^{b)}	63.1	5.8	<0.1	<0.1	31.1	1.10	0.37
6	Artificial product 1	69.7	5.2	<0.1	<0.1	25.1	0.90	0.27
7	Artificial product 2	78.3	5.0	<0.1	<0.1	16.7	0.77	0.16
8	Artificial product 3	84.3	4.9	1.3	0.9	8.6	0.69	0.08
9	Green River kerogen	77.5	10.1	2.4	1.4	8.6	1.56	0.08

a) For samples not listed here, see Ref. 1. b) Samples provided by Dr. R.J. Preto, (North Carolina State University, Raleigh)

Table 2

Summary of Buffer Controlled Permanganate^{a)} and CuO-NaOH^{b)} Oxidation Products

Sample wt % ^{c)}	1	2	3	4	5	6	7	9
Organic acids	52.1 (35.3)	41.3	51.5 (19.6)	19.3	21.2	57.2	52.1	57.8 (20.3)
Humic Acid-like material	25.1 (55.3)	16.8	45.4 (62.5)			21.6	20.3	
Insoluble residue ^{d)}	14.2 (11.0)	37.6	11.3 (21.0)	26.3	27.1	14.5	30.3	(49.3)
Wt% of Identified Acids								
Aliphatic Dicarboxylic Acid <C ₇	11.0 (1.8)	9.5	6.3 (1.0)	2.5	2.2	4.3	2.4	11.8 (13.2)
Aliphatic Dicarboxylic Acids ≥C ₈	14.2 (0.8)	9.7	1.1 (<0.1)	<0.1	<0.1	<0.1	<0.1	69.3 (53.0)
Phenolic acids	11.3 (66.6)	10.4	8.3 (54.1)	87.3	74.8	11.0	1.5	3.4 (8.6)
Benzenecarboxylic Acids	54.7 (26.0)	55.3	58.9 (36.2)	7.6	13.5	58.4	70.3	5.2 (9.3)
Oxygen-containing Heterocyclic Acids	6.7 (<1.0)	5.8	6.2 (<1.0)	<1.0	1.3	7.8	4.9	<0.1 (<1.0)
Others	2.1 (3.8)	9.3	19.2 (7.7)	2.6	8.2	18.5	20.9	10.3 (14.9)

a) Total amounts (wt%) of 3 step oxidation products are shown.

b) Data obtained from CuO-NaOH oxidation are shown in parentheses.

c) Wt% was obtained from a sample on a dry, ash free basis. Elemental analysis showed the presence of ash (1.5-5%) in organic acid fraction and humic acid-like material respectively.

d) Insoluble residue consists of non-oxidized sample and partially oxidized material which is not soluble in solvents; wt% was estimated from carbon analysis of the residue.

e) Wt% was estimated from the GC. For non-volatiles, solid probe MS and HRMS were used.

f) Polynuclear aromatic, S- and N- containing heterocyclic, aliphatic monocarboxylic acids and unidentified compounds.

Blank spaces represent isolations and identifications that have not been done or for which experimental results have not yet been obtained.