THE NATURE AND COMPOSITION OF COAL HUMIC ACIDS

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During the early stages of coalification the chemical substances in the decayed organs of higher plants are condensed into the humic acid-like substances. Classical theories of coal formation do not show characteristics of condensation product formed from the complex mixture of parent substances. These humic acid-like substances are ill defined substances of diverse origin and their composition is unknown. Although it has been known for many years that mild oxidation of bituminous coals yields humic acid-like material[1]. Reagents such as potassium permanganate, hydrogen peroxide and aqueous nitric acid have been used in the previous work[2]. The reagent selected here was aqueous performic acid which was generated by a reversible reaction between anhydrous formic acid and hydrogen peroxide. The mildness of the conditions, the speed of reaction and its simplicity were the factors for the reagent selection.

In this paper results are presented on humic acids which are extracted from thirty-eight different oxidized coals. Correlation equations are developed to predict the humic acid yields for coals of various origin. Elemental analyses of oxidized and parent coal are compared. Efforts are made to analyze changes in the amount and composition of mineral matter resulting from the chemical reaction. Petrographic changes as a result of oxidation is also studied. NaOH - soluble and insoluble materials are analyzed using FTIR. Infrared spectra of coals, humic acids and residues are interpreted and discussed.

EXPERIMENTAL PROCEDURE

The dried samples of coals (-80 mesh size) were dispersed in anhydrous formic acid (99 percent) (50 ml for 5 gms of each). The 30 percent hydrogen peroxide was then added, 2 ml at a time, at such a rate that the temperature rose to about 50°C. The mixture was then allowed to cool to room temperature for the next 24 hours with constant stirring. It was then filtered and the solid washed with water.

The dry residue, oxidized coal was then extracted with 1N NaOH in a stream of nitrogen gas at room temperature for another period of 24 hours with constant stirring. The insoluble residue was removed by centrifugation, washed and dried. The washings and NaOH soluble portion were collected and acidified to pH 1 and left overnight. The acid insoluble portion settled and most of the supernatent was siphoned from the precipitate. The precipitate was centrifuged and washed to about pH 5. Both the solids (NaOH soluble and insoluble) were dried in a vacuum oven at approximately 80°C for about 24 hours and analyzed on a Nicolet FTIR. KBr pellets of coals were prepared by mixing 1 mg of dry, finely ground sample with 300 mg of KBr.

Approximations were made of the mineral contents by determining (a) the high-temperature ash yields of humic acids and NaOH insolubles, (b) the yields of ash from the same materials in an oxygen-plasma low-temperature asher (LTA). Ultimate analysis of the oxidized products were obtained from the Commercial Testing and Engineering Co, Inc. Maceral analysis of oxidized product was done by coal petrography technique.

EXPERIMENTAL RESULTS

There is some difficulty in expressing the data on a completely sound basis, because of the complications introduced by the presence of mineral matter. There is a loss in weight of the mineral matter during oxidation. The mineral matter contents of coal and oxidized product are different. Neither the dmmf nor the mineral containing analyses can usefully be compared when expressed as percentages.

In Table 1 the weights of constituents in the sample taken for reaction are compared with their weights in the oxidized product. The losses shown for C, H, N in Table 1 contain no assumptions and are as good as the raw analytical data. Obviously there are uncertainties in the weights of organic sulfur and mineral matter, and hence in oxygen by difference. The results indicate that about 8-20 percent of the carbon and 0-15 percent of the hydrogen in the original coal is lost during the oxidation. The weight of oxygen is increased by 120-170 percent, and it appears to have doubled. It is clear that the data are not very satisfactory in this case. They should be considered qualitative in nature, nevertheless the data generated is first of its kind where efforts are made to interpret the data analytically for products of a chemical reaction of coals that considers the changes in the amount and composition of mineral matter resulting from the reaction.

The extraction of humic acids with sodium hydroxide is likely to disrupt partially the structure of the clay minerals and solubilize some material, which will not necessarily be completely reprecipitated by HCl with the humic acid. The sum of the LTA values for the humic acid and NaOH insolubles usually exceeded the mineral matter content of the coal by a considerable margin, suggesting that clay structures had been drastically altered. The sum of the high-temperature ashes bore a variable relation to the mineral matter content of the coal. In Figure 1 the yields of humic acids are expressed on the dry ash-free basis as a fraction of dmmf coal taken and are plotted against dmmf carbon contents. A tendency for the humic acid to increase with rank exists. The coals from Eastern Province tended to give the higher yields because this Province contains coals that in general are of higher rank than those of other Provinces. Regression analyses developed from the data showed that results for coals could be expressed by the equation.

$$\text{humic acid yield} = 3.15 \times \%C - 183$$

where the correlation coefficient is 0.95 for Rocky Mountain Province, 0.56 for Eastern Province and 0.22 for Interior Province coals. A correlation coefficient of 0.75 was found when all the data were used with respect to the Province of origin and can be expressed as

$$\text{humic acid yield} = 2.91 \times \%C - 163$$

As stated above, the hydrogen peroxide was added at such a rate as to limit the temperature rise due to the exothermic reaction. With Eastern coals the peroxide had to be added more slowly than with coals from the other Provinces, in order to avoid exceeding the temperature limit. It follows that the reaction with Eastern coals is more exothermic than with other coals.

Petrographic examination of the oxidized product do indicate that vitrinite had been greatly altered in appearance while sporinite and the inert macerals changed little or not at all. The apparently unaltered macerals could still be

recognized as such in the NaOH - insoluble materials which contain most of the inorganic material of the oxidized coal. The humic acid production arises from the vitrinite maceral which contain very minute quantities of mineral matter. Both of these materials (NaOH - insoluble and soluble) are analyzed by Nicolet FTIR and compared with that of coals.

The FTIR obtains spectra in digital form. The correction for the mineral matter and moisture is made[3,4]. The infrared spectra for the humic acids, NaOH - insoluble residue and coals are shown in Figures 2 to 4. Spectra obtained from coals and humic acids show a close similarity in the absorptions associated with the various C-H bonds and skeletal vibrations. Generally, the conclusions drawn from the absence of bands from the absorption spectrum are by no means less valuable than the information furnished by the existing bands. It is generally believed that coal contains no, or very few, C=O groups, isolated C=C and C≡C bands are absent. Aliphatic CH, CH_2 and CH_3 on the other hand do occur, as well as aromatic ring systems. -C-O- or C-O-C bands and associated OH and NH bands are probably also present.

DISCUSSION AND CONCLUSION

Infrared spectra of coals and humic acids demonstrate a very close similarity. The spectra from humic acids also resemble the spectra from coal tar[3], suggesting that the humic acids are the monomers derived due to the coal oxidation. Ash analysis and infrared analysis show that most of the organic matter ends up in the NaOH soluble part while most of the inorganic matter goes into the NaOH insoluble material.

Humic acid formation have been referred[5] earlier to "Regenerated Ulmins." This assumption needs further evidence. During the oxidation of coal, considerable oxygen enters the bonds of the coal molecule. Most of the vitrinites were greatly altered in appearance while sporinite and the inert macerals were changed little or not at all. The apparently unaltered macerals could still be recognized as such in the NaOH - insoluble material. The infrared spectra of NaOH - insoluble material looks like char, but the corrected spectra for the NaOH insoluble material show the absorption pattern similar to parent coal suggesting that the organic matter in that part is still highly polymerized similar to coal.

In all cases, the aliphatic C-H vibrations at 2850-2950 cm^{-1} are sharp, and the other C-H vibrations at 1450-1480 cm^{-1} and at 1375-1380 are there. Absorption near 1375 cm^{-1} is due to vibrations of the methyl group. When gem-dimethyl groups (ie, two methyl groups on the same carbon atom) are present, this band splits into a closely spaced doublet. Such splitting was observed in few spectra but not of an equal intensity. The aromatic absorption near 1600 cm^{-1} are very intense. Correlation of the magnitudes of the 1600 cm^{-1} peak with the hydroxyl content of a variety of coal, humic acid and even of the NaOH - insoluble material indicate that hydroxyl, in the form of phenolic hydroxyl contributes strongly to the peak.

Absorption due to C=O is very strong in all cases. These were at variable frequencies in the range 1660-1740 cm^{-1}, most often 1700-1730 cm^{-1}. The spectra of coals of bituminous rank do not show carbonyl absorption in the usual region (1660-1760 cm^{-1}). This absorption is quite clear in humic acids and entirely due to the presence of carboxyl groups which has been the result of oxidation.

A peculiar feature of the spectra is the ubiquity of absorption close to 1260 cm^{-1}. It is not quite intense but usually showed a multiplicity of peaks in the range 1250-1300 cm^{-1}. Primary and secondary alcohols, and phenols, may absorb in this region. Aromatic ethers also absorb here. The absorption appears to be due to some kind of C-O vibration, and such vibrations are often accompanied by other vibrations in the range 1000-1200 cm^{-1}. Indeed, bands were found at 1020-1030, 1070-1080 and 1170-1190 cm^{-1}. The striking point is that if any absorption in the region 1000-1300 cm^{-1} that was observed, was in the narrow ranges specified. This seems to suggest that a number of structural elements containing oxygen were widespread in coals and coal humic acids and differ surprisingly little from coal to coal.

A parallel situation is found with regard to another ubiquitous band in the range 795-820 cm^{-1}. This band is sharp in the spectra and sometimes intense. Weaker bands at higher frequencies (near 400-1000 cm^{-1}) were also seen.

The bending vibrations of aromatic C-H bonds are found near 870 cm^{-1} region, and their frequencies are used to identify substitution patterns in the benzene ring. Thus compounds with substituents in the 1, 4- or 1, 2, 3, 4-positions have an absorption near 830 cm^{-1} ($\pm$30 cm^{-1}), while 1, 2, 3-trisubstituted compounds absorb near 780 cm^{-1} ($\pm$20 cm^{-1}). Absorption near 750 cm^{-1} is ($\pm$20 cm^{-1}) characteristic of 1, 2-disubstituted compounds. No single pattern of substitution shows bands near both 750 and 830 cm^{-1}. The intensities of these bands is variable with pure compounds, but is often high. Weak shoulder is seen at 3030 cm^{-1} (aromatic C-H stretching) and the weak band near 1600 cm^{-1} (aromatic ring skeletal vibration?). No firm answer can be given, but probably the intensities are sufficiently consistent, since in pure aromatic compounds the 1600 cm^{-1} bond is sometimes quite weak. Sharp absorption at 1600 cm^{-1} in the spectra is due to -OH substitution on the aromatic ring[3,6].

The striking observation is that if these bands are present in a spectrum, they are always close to the same frequencies, and absorptions corresponding to other benzene substitution patterns than those mentioned are not seen at all. The implication is, once more, that certain structural elements or skeletons are of very frequent occurrence and differ surprisingly little from coal to coal which is in agreement with the other related published works[7,8].

ACKNOWLEDGMENT

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Figure 1
YIELDS OF HUMIC ACIDS AS FUNCTION OF CARBON CONTENTS OF COALS

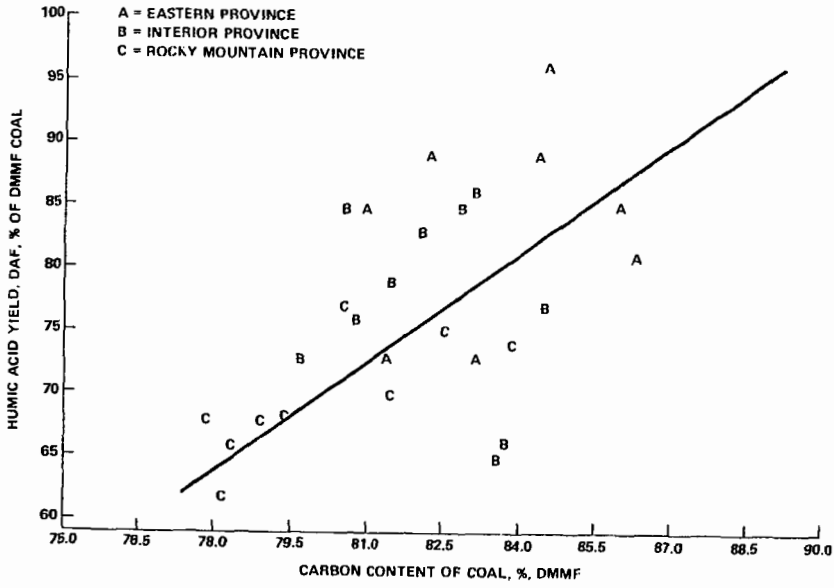

Table 1

Changes in Weight of Elementary Constituents Resulting from Performic Acid Oxidation

(The Figures Shown are Weights in Grams)

	PSOC 221 (HVA, Kentucky)			PSOC 278 (HVA, Ohio)		
	Original	Oxidized	Δ	Original	Oxidized	Δ
Whole Sample	5.037	4.870	-0.167	5.097	4.986	-0.111
C	3.763	3.140	-0.623	3.156	2.842	-0.314
H	0.289	0.250	-0.039	0.244	0.216	-0.028
N	0.073	0.065	-0.008	0.067	0.044	-0.023
S	0.102	0.082	-0.020	0.104	0.104	0
O (by diff.)	0.440	1.195	+0.755	0.352	0.961	+0.609
MM	0.343	0.140	-0.203	1.174	0.818	-0.356

	PSOC 284 (HVA, Illinois)			PSOC 314 (HVA, Utah)		
	Original	Oxidized	Δ	Original	Oxidized	Δ
Whole Sample	5.049	4.855	-0.194	5.032	4.769	-0.263
C	3.162	2.881	-0.281	3.625	2.914	-0.711
H	0.220	0.220	0	0.270	0.245	-0.025
N	0.070	0.054	-0.016	0.074	0.058	-0.016
S	0.058	0.058	0	0.030	0.025	-0.005
O (by diff.)	0.274	0.669	+0.395	0.451	1.019	+0.568
MM	1.266	0.975	-0.291	0.581	0.508	-0.073

Figure 2
INFRARED SPECTRA OF VARIOUS STAGES OF A COAL[3]

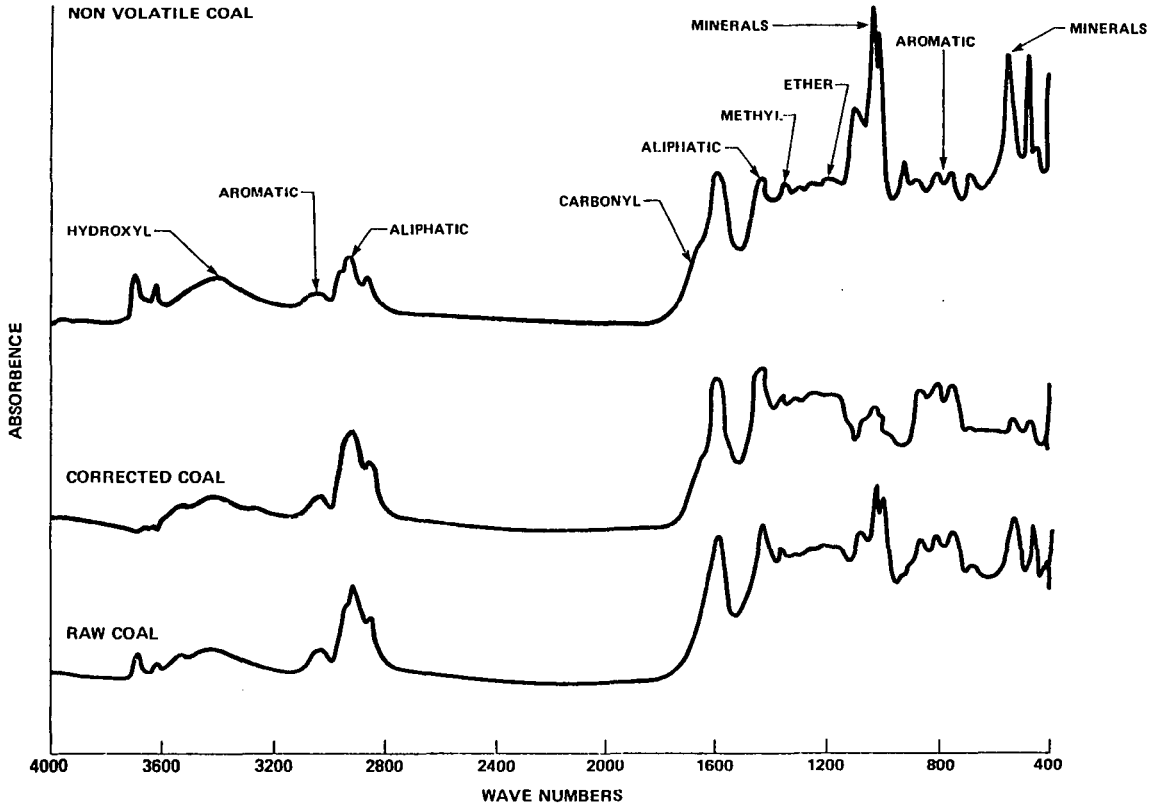

Figure 3
INFRARED SPECTRA OF (A) TEXAS LIGNITE (B) PSOC 168[3]

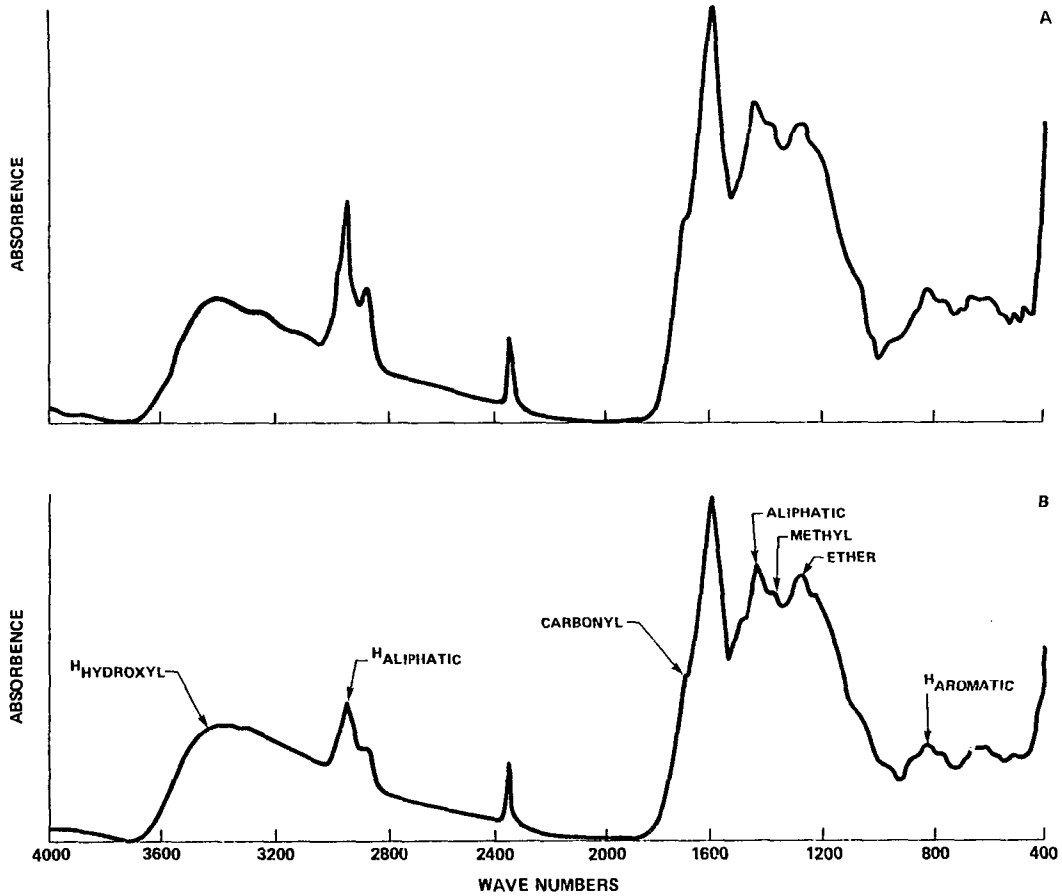
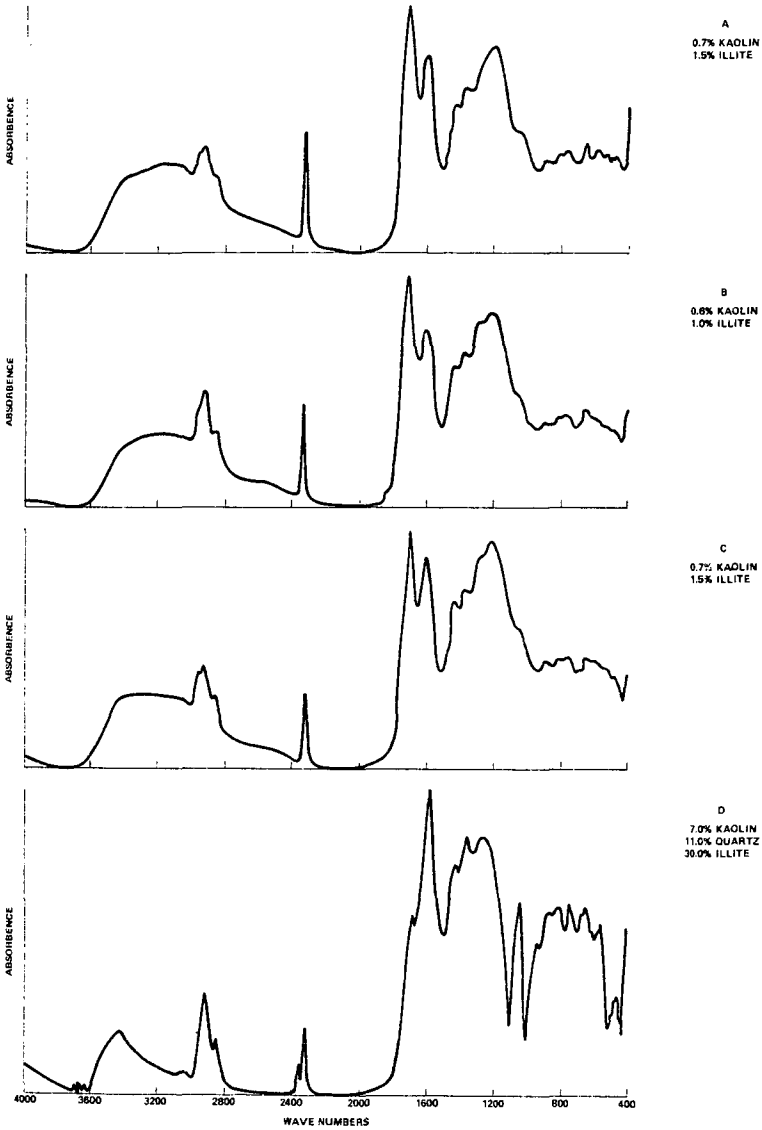
Figure 4
INFRARED SPECTRA OF (A) PSOC 282 HUMIC ACID, (B) PSOC 221 HUMIC ACID, (C) PSOC 295 HUMIC ACID, AND (D) PSOC 295 NaOH-INSOLUBLE