

SOME ASPECTS OF THE STRUCTURE AND REACTIONS OF NORTHERN GREAT PLAINS LIGNITES

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The lignites of the Northern Great Plains are in the Fort Union Region, which contains the largest reserves of lignite of any coal basin in the world. The Fort Union Region encompasses areas of North Dakota, South Dakota, Montana, and Saskatchewan. The identified resources of lignite in this region amount to 422 Gt (465 billion short tons), of which 24 Gt (26 billion short tons) constitute the demonstrated reserve base (1).

Until about 1970, the utilization of lignite was limited, accounting for no more than 1-2% of the total annual U.S. coal production. In recent years the production of low-rank coals has increased dramatically, so that by 1980 production represented about 24% of the total national coal production. It has been estimated that in another ten years, low-rank coals could amount to half the total coal production (1).

It has long been recognized that lignites possess unusual properties which can have profound effects on utilization. Such properties include high moisture content, high quantities of oxygen functional groups in the carbon structure, an alkaline ash, and inorganic cations attached to carboxylic acid groups. The rapid expansion of lignite utilization in recent years has brought with it an increasing realization of the importance of developing a better understanding of the organic and inorganic structures in lignite and of how those structural features influence lignite reactivity or processing behavior. Here we present results from some current studies in progress in our laboratories on lignite structure and reactivity.

Comparison of Northern Great Plains Lignites with Bituminous Coals

The predominant position of bituminous coal in the total U.S. coal production has resulted, not unreasonably, in the properties of bituminous coals being more extensively studied and thus better known to the general coal research community than those of lignites.

The average proximate and ultimate analyses of Fort Union lignites are summarized in Table 1, together with average values for a Pittsburgh seam bituminous coal. The data in Table 1 were taken from references (2) and (3) for lignite and bituminous coal, respectively. The important points to note are the much higher moisture content, higher oxygen, and lower heating value of the lignite.

Usually, lignitic ash contains a much higher proportion of alkali and alkaline earth elements, and consequently lower proportions of acidic oxides such as silica and alumina, than does ash from bituminous coals. These differences are illustrated by the data in Table 2, as taken from reference (1). The data on spruce bark ash are taken from reference (4) and show the similarity of lignitic and woody ashes. Of interest are the contrasts between the lignite and bituminous averages first with regard to silica and alumina and, second, to lime, magnesium, and sodium oxide.

TABLE 1
 AVERAGE ANALYSES OF NORTHERN GREAT PLAINS LIGNITE
 AND BITUMINOUS COAL SAMPLES, AS-RECEIVED BASIS

	<u>Northern Great Plains Lignite</u>	<u>Pittsburgh Seam Bituminous</u>
<u>Proximate, %</u>		
Moisture	37.2	2.3
Volatile Matter	26.3	36.5
Fixed Carbon	30.3	56.0
Ash	6.2	5.2
<u>Ultimate, %</u>		
Hydrogen	4.9	5.5
Carbon	71.9	78.4
Nitrogen	1.1	1.6
Oxygen	21.0	8.5
Sulfur	1.1	0.8
<u>Heating Value, MJ/kg</u>	15.9	32.6

TABLE 2
 AVERAGE ASH COMPOSITIONS OF NORTHERN GREAT PLAINS LIGNITES
 AND BITUMINOUS COALS, SO₃ - FREE BASIS

	<u>Spruce Bank</u>	<u>Lignite</u>	<u>Bituminous</u>
<u>Acidic Components:</u>			
SiO ₂	32.0	24.9	48.1
Al ₂ O ₃	11.0	14.0	24.9
Fe ₂ O ₃	6.4	11.5	14.9
TiO ₂	0.8	0.5	1.1
P ₂ O ₅	-	0.4	0.0
<u>Basic Components:</u>			
CaO	25.3	31.1	6.6
MgO	4.1	8.7	1.7
Na ₂ O	8.0	8.2	1.2
K ₂ O	2.4	0.5	1.5

Organic Structural Relationships

Lignite is an early stage in the coalification process and thus could be expected to retain some characteristics of wood. This relationship is illustrated by the electron micrographs shown as Figures 1 and 2. Pieces of plant debris, presumably twigs or rootlets, can be seen in Figure 1. Remains of the cellular structure are visible in Figure 2; the close similarity to the structure of softwood may be seen by comparing reference (5) for example.

On the molecular level, the distinguishing features of the organic structure of lignite are the lower aromaticity (or fraction of total carbon in aromatic structures), compared to bituminous coals; aromatic clusters containing only one or two rings; and the prevalence of oxygen-containing functional groups. A proposed structural representation, modified slightly from the original version (6), is given in Figure 3. We do not claim that this represents the structure of Northern Great Plains lignite, but rather use it as an illustration of major structural features.

The aromaticity has been studied by pressure differential scanning calorimetry (PDSC). The details of the experimental technique and of the methods for calculating aromaticity from a PDSC thermogram have been published elsewhere (7). Briefly, the PDSC experiment provides for controlled combustion of a 1-1.5 mg sample of -100 mesh coal in a 3.5 MPa atmosphere of oxygen. The sample is heated at 20°C/min in the range 150° to 600°C. The instrument response is a thermogram plotting heat flux, Δq , versus temperature, the integrated value thus being the heat of combustion. For most coals, and many organic compounds and polymers, the thermogram in this region consists of two peaks, which, from comparison to the behavior of model compounds, arise primarily from combustion of the aliphatic and aromatic portions of the sample. The aromaticity may be deduced from a comparison of peak heights.

The aromaticity for several samples of Northern Great Plains lignites, as measured on run-of-mine material, lies in the range of 0.61 to 0.66. For comparison, a sample of Australian brown coal available to us was found to have aromaticity of 0.56; a sample of Minnesota peat had an aromaticity of 0.50. Samples of vitrinite concentrates from the Northern Great Plains lignites were more aromatic, with values in the range of 0.72 to 0.74.

The temperature at which the maximum of the aromatic peak occurs has been shown to be a function of the extent of ring condensation (7), the maximum shifting to higher temperatures with increasing condensation. In support of the studies on coal structure, we have measured the PDSC behavior of over 30 organic compounds (most of which have been suggested as coal models or have been identified in the products of coal processing) and about 50 polymers. The maxima of the aromatic peaks in the thermograms of Northern Great Plains lignites generally fall into the same temperature range (375°-400°C) as those for compounds or polymers having benzene or naphthalene rings. One example is given in Figure 4, in which the PDSC thermograms of Gascoyne (N.D.) lignite and poly(4-methoxystyrene) are compared. We conclude that the aromatic ring systems therefore are mostly one- or two-ring systems.

Much less is known about the hydroaromatic structures or aliphatic bridges between ring systems. A methylene bridge is often suggested as a typical aliphatic bridging group, and was originally shown in the proposed structural representation (6). However, considerations based on thermochemical kinetics predict a half-life of 10^6 years for bond cleavage of diphenylmethane in tetralin at 400°C (8). Exhaustive analyses of the products from liquefaction of Northern Great Plains lignite at 400°C and higher in the presence of tetralin, (see (9) for example) have never identified diphenylmethane or related compounds. Absence of diphenylmethane constitutes strong circumstantial evidence for the relative unimportance of methylene linkages between aromatic clusters.

Oxygen is distributed among carboxylate, phenol, and ether functional groups. The carboxylate concentration has been measured by reaction of demineralized coal with calcium acetate following the procedure of van Krevelen and co-workers (10). A study of the carboxylate concentrations is still in progress; preliminary data for the Northern Great Plains lignites indicate carboxylate concentrations ranging from 1.75 to 1.93 meq/g on a dry basis. Concentrations of phenolic or ether functional groups have not yet been measured. Electron spectroscopy for chemical analysis (ESCA) provides a means for discriminating between carbon atoms incorporated in C=O and C-O structures by a Gaussian-Lorentzian decomposition of the carbon 1s spectrum (11). Figure 5 provides a comparison of the decomposed carbon 1s spectra of Beulah (N.D.) lignite and polyethylene terephthalate. At present, the ESCA data cannot be resolved into phenolic and etheric carbons. However, it can be shown that the ratio of carbon in carboxylate groups to that in (phenol plus ether) groups is about 0.62 (11). The presence of methoxy groups has been qualitatively confirmed; as-yet unpublished work by E.S. Olson and J.W. Diehl demonstrates the production of methanol from sodium periodate oxidation of Beulah lignite.

Little consideration has yet been given to the three-dimensional structure. A preliminary examination of lithotypes of Beulah lignite has been conducted by laser Raman spectroscopy (11). The lithotype having a higher concentration of carboxylic acid groups has a weaker band at 1600 cm^{-1} . If this band is assigned as a graphite mode (12), results suggest that the relatively bulky carboxylate groups, with their associated counterions, may disrupt, or preclude, three-dimensional ordering.

Distribution of Inorganic Constituents

In lignites the inorganic constituents are incorporated not only as discrete mineral phases, but also as relatively mobile ions, presumably associated with the carboxylic acid functional groups. The distribution of inorganic constituents has been studied principally by the chemical fractionation procedure developed by Miller and Given (13).

Extraction of the coal with 1M ammonium acetate removes those elements present on ion exchange sites, which are presumed to be carboxylic acid functional groups. Sodium and magnesium are incorporated almost exclusively as ion-exchangeable cations. For a suite of Northern Great Plains lignites tested, 84 to 100% of the sodium originally in the coal and 88 to 90% of the magnesium are removed by ammonium acetate extraction. Figure 6 is an electron micrograph showing an electron backscatter image due to the presence of sodium intimately associated with the organic material. Calcium is largely present in cationic form, 48 to 76% being extracted. Some potassium is also extracted in this step, in amounts ranging from 20 to 57%.

Further treatment with 1M hydrochloric acid then removes elements present as acid-soluble minerals or possibly as acid-decomposable coordination compounds. This acid extraction removes essentially all of the calcium and magnesium not removed by ammonium acetate. This finding is suggestive of the presence of calcite or dolomite minerals, which are known to be present in Northern Great Plains lignites (14). The hydrochloric acid extraction behavior of other major metallic elements is quite variable, which suggests significant differences in the mineralogy of the samples. Of those elements not extracted at all by ammonium acetate, some iron, aluminum, and titanium are removed by hydrochloric acid.

The portions of elements which are not removed by either reagent are considered to be incorporated in acid-insoluble minerals, particularly clays, pyrite, and quartz. This group includes all of the silicon, the remaining sodium and potassium, and the residual iron, aluminum and titanium. The acid-insoluble minerals are present as discrete phases. Frequently the mineral particles are quite small (see Figure 7, for example) and very highly dispersed through the carbonaceous material, to such

an extent that only about 15-30% of the discrete mineral matter is separable in a traditional float/sink experiment.

Effects of Structure on Reactivity

The small aromatic clusters, the high concentration of organic oxygen functional groups, and the presence of inorganic species as ion-exchangeable cations are unique features of low-rank coals. Each of these features should influence the reactivity of low-rank coals, thereby giving low-rank coals distinctly different reactions when compared to bituminous coals. The reactivity indeed has unique features. As yet, however, little has been done in a deliberate way to develop an understanding of the connections between structure and reactivity.

The carboxylic functional group is thermally labile and is driven off by heating to 450°C (15). Although the volatile matter content of lignite is higher than that of bituminous coals, much of the material released from lignite is carbon dioxide rather than hydrocarbon gases or tars. Thus only about 17% of the calorific yield occurs in volatile products from Northern Great Plains lignites at 500°C, compared with 30% for some bituminous coals (16). Since this thermal decomposition removes much of the oxygen from the coal, in a liquefaction reaction the removal of oxygen would require no net consumption of external hydrogen.

Oxygen functional groups can promote β -bond scission (8), which may be an important process in the degradation of the coal structure. The role of ether, carboxyl, and other groups in wood pyrolysis and combustion has been discussed (17); it seems reasonable to assume that analogous reactions would occur in low-rank coals. Other possible roles for oxygen functional groups include ether cleavage, cleavage of aliphatic bridges linked to aromatic rings bearing a phenolic group, and the enhancement of the ability of free radicals to form adducts with potential solvent or reactant molecules. The relationship of organic structure to reactivity should be a fertile field for research.

Sodium is the best-studied of the inorganic constituents of Northern Great Plains lignite. The combustion of the sodium carboxylates generates sodium-containing vapor species which can then be deposited on boiler tubes. The relationship of the sodium content of the coal to the formation of ash deposits on boiler tubes is well known. While the ash deposition problem can be severe and expensive for commercial installations (18), the mobility of cationic sodium holds out the promise for sodium removal or reduction by ion-exchange processes (19). The possible role of the ion-exchangeable sodium in the catalysis of liquefaction reactions has been studied by Given (20).

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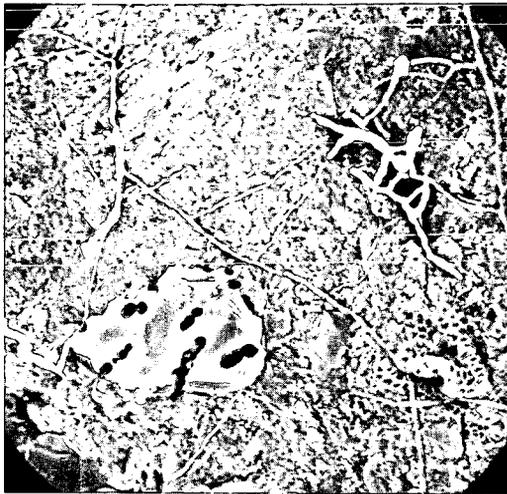


FIGURE 1. Electron micrograph of ion-etched Beulah lignite, showing rootlets or other plant debris. 7800x.

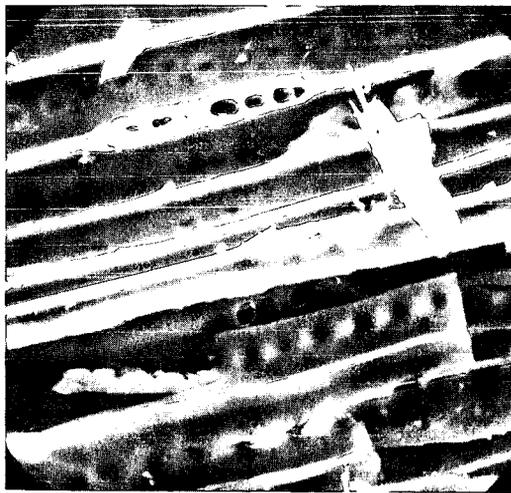


FIGURE 2. Electron micrograph of woody lithotype of Beulah lignite showing cellular structure. 390x. Compare softwood structure in reference (5).

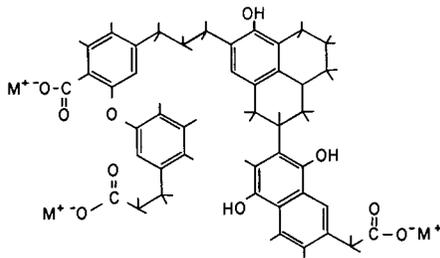


FIGURE 3. Proposed representation of structural features of lignite. Adapted with minor modification from reference (6).

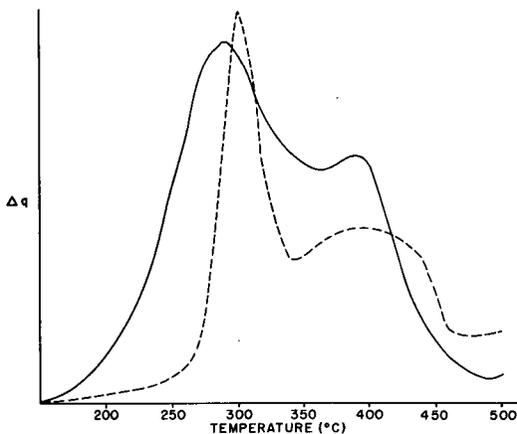


FIGURE 4. PDSC thermograms of Gascoyne lignite (solid line) and poly(4-methoxystyrene) (dashed line). Plot is of heat flux in arbitrary units versus temperature, °C.

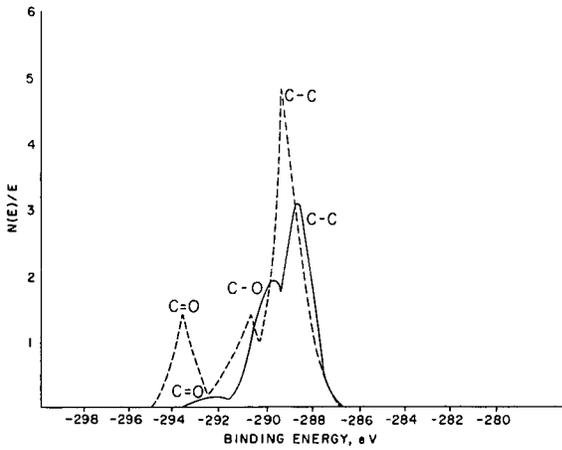


FIGURE 5. Decomposed ESCA carbon 1s spectra of Beulah lignite (solid line) and polyethylene terephthalate (dashed line). Plot is of number of electrons per energy in arbitrary units versus binding energy in electron volts. The lignite spectrum has been corrected for sample charging (11).



FIGURE 6. Electron micrograph of Beulah lignite showing organic region enriched in sodium (circular structure in lower center of view).

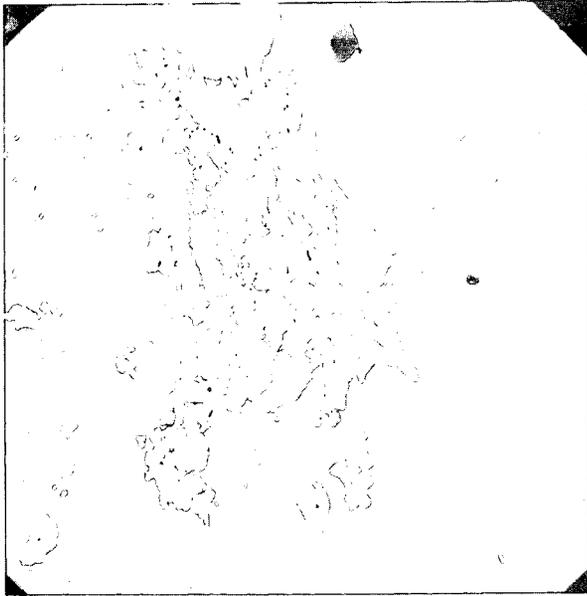


FIGURE 7. Electron micrograph of pyrite particles intergrown in carbonaceous structure of Beulah lignite, suggesting difficulty of removal by float/sink. 200x.