# THE ORGANIC CONSTITUTION OF WILCOX LIGNITE

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The distribution of functional groups in low rank coals has been the subject of a body of investigations [summarized by Meyers (1982) and Spiro and Kosky (1982)] oriented towards a description of the kinetics and mechanism of thermal conversion processes. Use of the new technique of Californium-252 Plasma Desorption Mass Spectrometry (CFPDMS) as a probe to the structural features of coal have been described by Lytle, Tingey and Macfarlane (1982). The interpretation of CFPDMS spectra has necessitated a functional group characterization of the coal substrate by conventional spectroscopic and chemical techniques. CFPDMS requires the use of organic soluble fractions, and we have utilized DMSO extracts as they seem quite representative of the organic functionalities present. Dry Wilcox Lignite (WL) and some of its solubility fractions have been so characterized, including its DMSO solubles (SD), DMSO insolubles (ID), humic acids (HA), a sample demineralized (DM) by the method of Bishop and Ward (1958), the DMSO extract of this (SDM), and the insoluble residue (IDM). The coal sample used was obtained from a drill core near Rockdale, Texas.

Extraction of WL with DMSO for 24 hours at room temperature gives a 20% yield of extract. Humic acids were obtained by aqueous NaOH extraction and precipitation with HCl. Removal of residual DMSO in the solubles and insolubles can be accomplished by HI treatment with subsequent removal of dimethyl sulfide and HI, but at the cost of some iodine incorporation, ether cleavage, and mineral matter loss.

Acidic Group Titration

Titration for carboxylic acid content, (COOH), were carried out on WL, SD, DM, and SDM according to the methods of Schafer (1970a, 1970b); total acidity was determined on SDM and IDM. The results are reported on a daf basis in Table 1. An enrichment in (COOH) in the DMSO extracts of Wilcox lignite and the demineralized lignite amounts to 0.16 and 0.4 meg(COOM)/g respectively. Carboxylate bound cation content (COOM) is estimated from

$$\text{meq(COOM)/g} = (\text{COOH})_{\text{Demineralized}} - (\text{COOH})_{\text{Dry}}$$

Thus the bound cation content of WL and SD is some 1.5 and 1.8 meq(COOM)/g respectively. From the total acidity data, the concentration of hydroxyl and pyrrole hydrogen (OH,> NH) is estimated from

$$(\text{OH},> \text{NH}) = \text{total acidity} - (\text{COOH})$$

For the demineralized samples, DM and SDM, this amounts to 4.9 and 5.0 meq(OH, > NH)/g.

Nuclear Magnetic Resonance

Solid state C 13 NMRCPMS spectra for selected solubility fractions were obtained by the NMR Center at Colorado State University. Aromaticities derived from the spectra shown in Figure 1 for WL, ID, SD, and HA are 0.53 0.55, 0.52, and 0.72. The higher aromaticity of HA is due to both the enhanced height of the 123 ppm absorption due to the truly aromatic carbons, and to the profusion of carboxylates and aromatic oxygen functions in the skirt downfield of 150 ppm.

Proton NMR of SD in $d_6$-DMSO exhibits the proton populations shown in Table 2. The chemical shift of hydrogen attached to, or alpha to, oxygen atoms is not at all clear. What is apparent is that the high oxygen content

of this fraction gives rise to peaks in the 3.0-4.0 ppm region of the proton NMR spectrum.

Oxygen bound carbon also accounts for absorption in the downfield flanks of both aromatic and aliphatic peaks in the carbon 13 NMR spectra. Use of shift reagents (Shue and Yen (1983)) is under study in identifying the functionalities involved.

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR spectra of WL, ID, SD and HA were obtained on a Digilab 20C spectrometer in KBr discs. Although grossly similar in appearance, the spectra reveal some notable differences. Aliphatic absorptions at 2825 and 2920 $cm^{-1}$ appear in all the spectra, but the 2825 $cm^{-1}$ peak is much more intense in WL and ID. SD exhibits a prominent band at 2970 $cm^{-1}$, absent in the others. The carbonyl absorption at 1700 $cm^{-1}$ appears as a shoulder in WL and ID, but is nearly as intense as the coal band (1600 $cm^{-1}$) in SD and HA. SD shows a pair of intense bands at 1260 and 1010 $cm^{-1}$, tentatively assigned to the asymmetric and symmetric aryl alkyl ether C-O-C stretch. Both bands are small in HA. In WL and ID, the 1260 $cm^{-1}$ absorption is small, and the 1010 $cm^{-1}$ absorption is masked by the kaolinite doublet at 1010 and 1035 $cm^{-1}$. Of the aromatic out of plane bending modes, only the 860 $cm^{-1}$ band (isolated hydrogen) is present in all the fractions. The diminuitive aromatic C-H stretching band (3000-3100 $cm^{-1}$) in all the fractions, and the low population of aromatic protons (15.3%) seen in the $^{1}H$-NMR spectrum of SD, suggests that the aromatic moieties are sparse and highly substituted. An unidentified absorption at 800 $cm^{-1}$ appears in all the spectra, but is quite intense in SD.

Pertrifluoroacetic Acid Oxidation (PTFA)

The PTFA reaction described by Deno (1979) has been reinvestigated by Hessley et al (1982) in the analysis of Wyodak coal. In our laboratory, that procedure has led to low and variable product yields when applied to Wilcox lignite. Using a chloroform cosolvent during the oxidation moderates the degradation of aliphatic reaction products. This modification was developed by Lawrence Shadle at Pennsylvania State University. Wilcox lignite yields one hundred methyl esters, as detected by GC/MS, of which fifty comprise over 90% of the product. Fragmentation patterns indicate that the majority of the products are methyl esters of branched and napthenic hydrocarbons in the molecular weight range of 200 to 400. Methyl laurate is prominent among the straight chain esters present. Aromatic esters and oxirane carboxylates have not been detected among the products. Proton NMR of the crude acids of WL, SD, ID and HA discloses the presence of variable amounts of $C_2$ to $C_5$ mono- and dicarboxylic acids. No aromatic absorptions are seen in these spectra, with the notable exception of a 7.3 ppm absorption from SD.

Californium Plasma Desorption Mass Spectrometry (CFPDMS)

In the CFPDMS experiment described by Macfarlane and Torgerson (1976), a fission fragment of Cf-252 impinges on a thin film of substrate, forming high molecular weight ions whose mass is measured by a TOF mass spectrometer. Collision results in a localized hot spot for one picosecond, reaching temperatures of some $10^4$ $\underline{o}$ K. Extracts of Wilcox lignite typically show positive and negative ions in clusters in the mass range of m/z 400 to 800. Isolated clusters of peaks are seen at low signal intensity up to m/z 2000. Although identification of these peaks is only tentative at this time, one of the

fragments does behave as a carboxylate functionality. In the positive ion spectrum of SD, peaks at m/z 646, 668 and 684 occur in a ratio of 8:5:1. The negative ion spectrum exhibits a peak at m/z 644. By analogy with the behavior of known carboxylic acids and their salts, these peaks correspond to structures $RCOOHH^+$, $RCOOHNa^+$, $RCOOHK^+$ and $RCOO^-$ respectively. The positive ion peaks at m/z 645 and 668 are also seen in the spectrum of HA.

Functional Description of Wilcox Lignite

On the basis of the ultimate analysis of Wilcox lignite, the organic constitution can be formulated as $C_{100}H_{76}O_{21}NS$. The titration data indicates 0.6 (COOH)/g., 1.6 meq(COOM)/g., and 4.9 meg.(OH, > NH)/g. In the $C_{100}$ formulation, this corresponds to one carboxylic acid, three carboxylate salts, six hydroxyls and one pyrrole. The remaining seven oxygen atoms are semiarbitrarily distributed among two aryl alkyl ethers, three quinone carbonyls and one ester. By this accounting, eight of the carbons in the $C_{100}$ formulation appear in the downfield skirt of the aromatic C-13 NMR absorption. From this we project forty eight aromatic carbons (not bound to oxygen) and forty three aliphatic carbons. Hydrogen atoms not bound to heteroatoms are assigned according to their integrated populations in the NMR spectrum of SD. Table 3 compiles this distribution within the $C_{100}$ formulation.

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## References


Bishop, M. and Ward, D.L. (1958) "The Direct Determination of Mineral Matter in Coal": Fuel 37, 191.

Deno, N.C., Griegger, B.A., Jones, A.D., Rakitsky, W.G. and Stroud, S.G. (1979) "Coal Structure and Coal Liquefaction"; Final Report to Electric Power Research Institute from Pennsylvania State University, AF-960, RP-779-16.

Hesslly, R.K., Benjamin, B.M. and Larsen, J.W. (1982) "Deno Oxidation. Isolation of High Molecular Weight Aliphatic Material from Coals and Further Model Compound Studies"; Fuel 61, 1085.

Lytle, J.M. Tingey, G.L. and Macfarlane, R.D. (1982) "Californium-252 Plasma Desorption Mass Spectrometry of Solid Coal": Anal. Chem. 54, 1881.

Macfarlane, R.D. and Torgerson, D.F. (1976) "$^{252}$Californium Plasma Desorption Time of Flight Mass Spectrometry": Int. J. of Mass Spec. and Ion Physics.

Meyers, R.A. (1982) "Coal Structure": Academic Press, New York.

Schafer, H.N.S. (1970a) "Carboxyl Groups and Ion Exchange in Low Rank Coals": Fuel 49, 197.

Schafer, H.N.S. (1970b) " Determination of Total Acidity of Low Rank Coals": Fuel 49, 271.

Spiro, C.L. and Kosky, P.G. (1982) "Space Filling Models for Coal. 2. Extension to Coals of Various Ranks": Fuel 61, 1080.

Shue, F.F. and Yen, T.F. (1983) "Application of Lanthanide NMR Shift Reagents for Functional Group Studies of Shale Bitumen Asphaltenes" Fuel 62, 127.

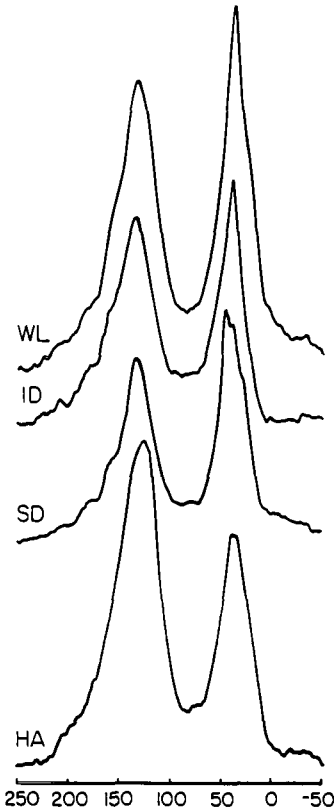


Figure 1. $^{13}$NMR CP/MAS Spectra of Wilcox Lignite (WL), its DMSO Insolubles (ID), DMSO Solubles (SD) and Humic Acids (HA). Scale is in ppm.

Table 1. Acidic Group Concentration of Wilcox Lignite Fractions (meq/g., daf)

| Sample | (COOH) | Total Acidity |
|---|---|---|
| Wilcox Lignite, (WL) | .55 | --- |
| DMSO Solubles of WL, (SD) | .71 | --- |
| Demineralized WL, (DM) | 2.1 | 7.0 |
| DMSO Solubles of DM, (SDM) | 2.5 | 7.5 |

Table 2. Proton Population (Area %) in Wilcox Lignite DMSO Solubles, by H-NMR

| Proton Type | δ(ppm) | % |
|---|---|---|
| H(AR) | 4.5-9.0 | 15.3 |
| H(α2) | 3.3-4.5 | 14.2 |
| H(α1) | 2.0-3.3 | 24.0 |
| H(N) | 1.5-2.0 | 12.0 |
| H(β) | 1.0-1.5 | 20.8 |
| H(γ) | 0.5-1.0 | 13.7 |

Table 3. Accounting of Functional Groups and Atoms in the $C_{100}H_{76}O_{21}NSM_3$ Formulation of Wilcox Lignite Organic Matter. M = Na, Ca, etc.

| Group | Population in the $C_{100}$ Formulation | Atoms Present in Specified Groups | | | | | |
|---|---|---|---|---|---|---|---|
| | | C | H | O | N | S | M |
| -COOH | 1 | 1 | 1 | 2 | | | |
| -COOX | 3 | 3 | | 6 | | | 3 |
| -OH | 6 | | 6 | 6 | | | |
| >N-H | 1 | | 1 | | 1 | | |
| R-O-Ar | 2 | | | 2 | | | |
| >C=O | 3 | 3 | | 3 | | | |
| RCOOR | 1 | 1 | | 2 | | | |
| Aromatic C | 49 | 49 | | | | | |
| Aliphatic C | 43 | 43 | | | | | |
| H(AR) | 10.4 | | 10 | | | | |
| H(α2) | 9.9 | | 10 | | | | |
| H(α1) | 16.3 | | 16 | | | | |
| H(N) | 8.2 | | 8 | | | | |
| H(β) | 14.1 | | 14 | | | | |
| H(γ) | 9.3 | | 10 | | | | |
| Thiophene(?) | | | | | | | |

Table 4. Analyses* of Wilcox Lignite and its Solubility Fractions (% Dry Basis).

| Sample | C | H | O | N | S | Halogen | Ash |
|---|---|---|---|---|---|---|---|
| WL | 62.75 | 4.45 | 19.38 | 1.28 | 1.32 | 0.83 | 14.16 |
| SD | 68.38 | 5.17 | 18.22 | 1.41 | 1.80 | 1.04 | 2.98 |
| ID | 64.89 | 4.67 | 17.92 | 1.28 | 1.50 | 1.06 | 8.09 |
| HA | 66.83 | 4.02 | 23.17 | 1.41 | 2.54 | 0.88 | 1.26 |
| DM | 70.49 | 5.01 | 19.57 | 1.48 | 1.97 | 0.78 | 0.23 |

*Huffman Laboratories, Inc.