

CHEMISTRY AND STRUCTURE OF COALS: AIR OXIDATION STUDIES
RELATED TO FLUIDIZED BED COMBUSTION

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Efficient use of coals as feedstocks and thermal energy requires comprehensive understanding of the physical and chemical structure of the starting materials and the changes wrought in the processing steps. Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy is being developed^{1,2} as a facile, nondistructive, rapid, highly informative means of measuring and monitoring the chemical structure of coals

Figure 1 shows how well the DRIFT technique can be used to rank coals with respect to the hydroxyl content and hydrocarbon type and content for unweathered powders of the greater maturity increasing from top to bottom. Figure 2 shows the wealth of information as related to carbonyl content, polynuclear aromaticity and mineral type and mineral content for the various coal powders and the simulated end members of the coalification process (cellulosic fibers and graphite).

Figure 3 is an example where the changes due to oxidation are readily discerned. This partial oxidation involved loss of the aliphatic hydrogen ($2800-3000\text{ cm}^{-1}$) and simultaneous carbonyl formation ($1600-1900\text{ cm}^{-1}$) with little or no loss of hydroxyl ($3600-2000\text{ cm}^{-1}$), aromatic hydrogen ($3200-3000\text{ cm}^{-1}$), polynuclear carbon ($1650-1550\text{ cm}^{-1}$), nor polyaromatic hydrogen ($900-700\text{ cm}^{-1}$). Studies of catalytic effects due to inorganic constituents are facilitated by DRIFT as shown in Figure 4 where quantitative measures are obtained for the amount and nature of argillic components inherent in and/or admixed with the run of the mine coals.

The DRIFT technique uses the coal as a solid piece and/or as powder with no mulling agents (CCl_4), support medium (KBr), or other extraneous materials that can contribute erroneous spectral features and serve as barriers for *in situ* reaction studies. Figures 5 and 6 illustrate the additional information that one can obtain by noting spectral changes wrought on oxidation. The dehydrogenation process involves oxidation of only the aliphatic hydrocarbon initially and only at the latter stages the oxygen attack involves unsaturated olefinic and aromatic species

(3035 cm^{-1}). Also there is little or no loss of phenolic, carboxyl alcoholic, etc. entities (3650-2400 cm^{-1}) until the later stages of reaction. Figure 6 shows more details of the oxygen insertion process where the initial oxidation forms somewhat isolated carbonyls (1705 cm^{-1}) with higher degrees of reaction progressively forming analogs of carboxylic acids (1745 cm^{-1}), acid anhydrides (1775 cm^{-1}) and organic carbonates (1845 cm^{-1}) as a synergetic continuum of oxygen enrichment prior to the final evolution as gaseous carbon dioxide. Steady state conditions seem to prevail where the process proceeds continuously at the steady state concentrations noted in the upper difference spectrum. DRIFT spectroscopy uniquely allows one to monitor the concentration of virtually all of the entities required to fully elucidate the oxidation mechanism proposed by batch techniques.^{3,4} Additional details of interpretation and experimental techniques are given elsewhere.

Mercury porosimetry, vapor sorption, microscopy, and helium picnometry aid appreciably in our heat and mass transport modelling under conditions relevant to fluidized bed reactors of the Tennessee Valley Authority. The original rigid structure of the coal swells and expands as volatile bubbles grow and flow out of the tarlike mass where the -3+4 mesh particles are introduced into the hot (1500°F) reactor. The volatiles burn vigorously and the residual char slowly burns away to leave residual ash. Data will be given to show the nature of the porosity (internal/external, open/closed, macro/micro, etc.) as determined by the various techniques and the relevance to existing and proposed processes.

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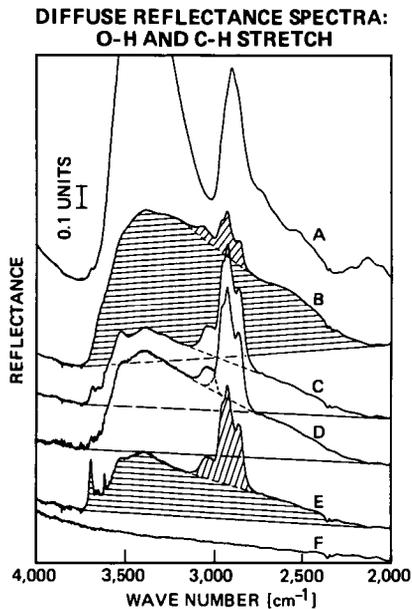


Figure 1. Hydrogen stretch region of DRIFT spectra of; A. cellulosic fibers, B. Lignite, C. Subbituminous Coal, D. C-bituminous coal, E. A-bituminous coal, and F. Graphite. All samples are equilibrated with 30 ppm moisture in the argon purge.

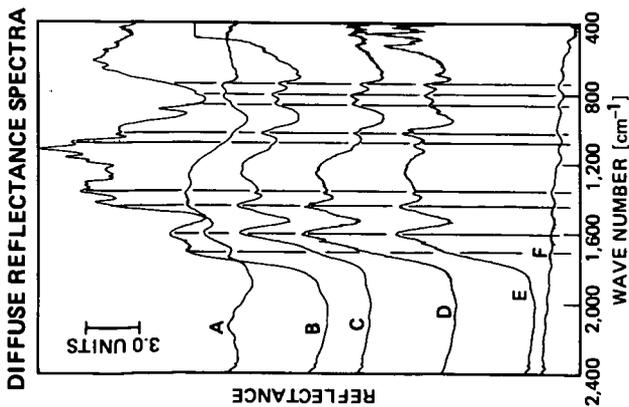
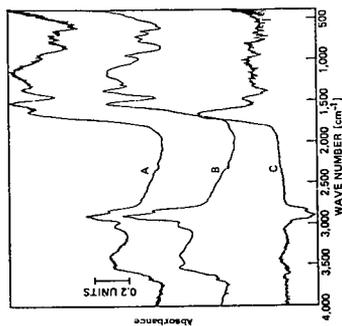


Figure 2. Low energy DRIFT Spectra: Legend Same as Figure 5. Vertical lines (left to right) denote characteristic bands for (1) carbonyl, (2) polynuclear aromatic rings, (3) methylene, (4) mineral, and (5) aromatic hydrogen groups, respectively.



DRIFT Spectra of Wyodak Coal.
 A. Sample after 24 hr of oxidation in 2.7 kPa at 395°C
 B. Dried unoxidized sample
 C. Difference Spectrum (A-B)

Figure 3. DRIFT Spectra. A. Partially oxidized coal powder 1 hour, 2.7 kPa of air at 395°C. B. Original coal powder dried in vacuum at 400°C. C. A-B with no scaling factor to show the changes due to oxidation.

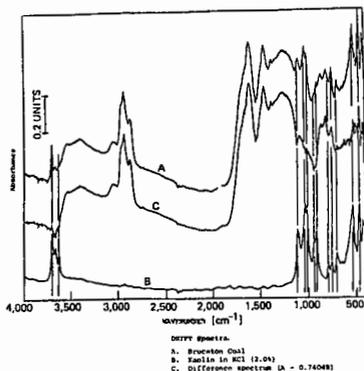


Figure 4. Correction for Minerals. A. DRIFT spectrum for powdered coal. B. DRIFT spectrum of 20% kaolin dispersed in powdered KCl. C. A-0.7404B for each of the individual 3600 data points.

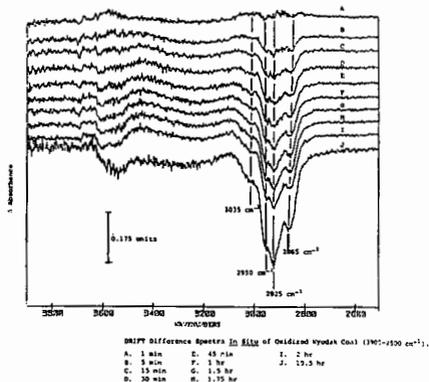


Figure 5. DRIFT Difference Spectra for ca 19 hours continuous oxidation of coal. These difference spectra show the loss of hydrogen from C-H and, in later stages, OH units of coal.

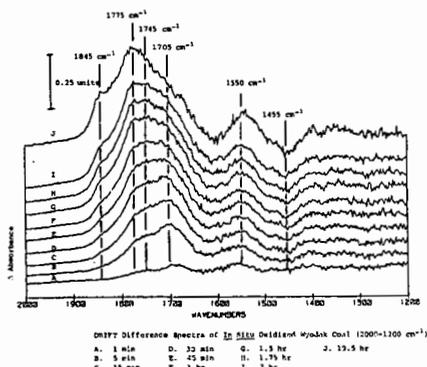


Figure 6. DRIFT Difference Spectra for Carbonyl Region. The amount and nature of the oxygenated specie changes markedly. A general increase in carbonyls is noted and shift to higher frequencies is evident.