

DIRECT INVESTIGATION OF REACTING COALS BY  
DIFFUSE REFLECTANCE INFRARED SPECTROMETRY

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Introduction

A few years ago we showed that it was possible to measure the diffuse reflectance (DR) infrared spectrum of solids at high signal-to-noise ratio (SNR) with no sample preparation required other than pulverization (1). The key factors in our design were the use of a Fourier transform infrared (FT-IR) spectrometer incorporating a mercury cadmium telluride (MCT) detector, and the design of a highly efficient optical configuration for collecting diffusely reflected radiation and passing it to the detector. At that time, we suggested that the study of coal might be among the more important applications of DR spectrometry, although we initially believed that in order for good spectra to be obtained it was necessary to grind the samples with about ten times their weight of an alkali halide diluent (2). Subsequently, we demonstrated that equally good spectra could be obtained when no diluent was added, and several applications of DR infrared spectrometry to coal chemistry were described in a recent publication from this laboratory (3). Today it is possible to obtain commercial accessories for DR spectrometry for most commonly used FT-IR spectrometers from at least four different sources.

In view of the structural information potentially obtainable from the infrared spectra of neat powdered coals, we have studied the feasibility of monitoring the chemical changes which occur while reactions are taking place. This work necessitated two instrumental developments before truly useful data could be obtained. These were the construction of a cell and optical configuration suitable for the study of gas-solid reactions at high temperature and the further refinement of the assignment of infrared spectra of coals, especially after resolution enhancement.

Optics and Cell

The first DR infrared spectra measured during a reaction were described by Niwa *et. al.* (4,5). Their spectra were measured on a grating spectrometer and had a very low SNR. Subsequently (6), we described a small cell for controlling the atmosphere around a heated powder which could be installed in the optics reported in our first paper on DR spectrometry (1). Although the spectra measured with this cell had a far higher SNR than those of Niwa *et. al.*, the cell still had several disadvantages, in that it had to be very small, its temperature could not be raised above about 200°C, and temperatures had to be estimated rather than measured directly. The optical efficiency was reduced by the window geometry and, in addition, a substantial fraction of the radiation reaching the detector had never interacted with the sample, leading to a high level (~20%) of stray light.

Subsequently, a superior cell was introduced by Harrick Scientific Corporation (Ossining, N.Y.) with improved upper temperature limits, optical efficiency and stray light specifications. However, this cell still had one significant drawback for the study of reacting coals, in that it had only one inlet/outlet gas line, so that if tars were formed they would condense on the windows, completely obscuring the infrared beam from the detector.

To circumvent this problem and to permit improved operating specifications, a completely redesigned cell was constructed. Separate inlet and outlet gas lines were installed; the use of a wide-bore outlet tube permitted a vacuum of  $10^{-4}$  torr to be obtained. The base of the sample cup is fritted so that inert or reactive gases can be drawn through the sample, preventing tar deposits on the window. The

input beam and diffusely reflected output beam are passed through a single 50cm diameter KCl window. The sample is heated by a nichrome wire coiled around the cup. The temperature of the sample can be measured by a thermocouple inserted into the powdered coal, and temperatures up to 600°C (1100°F) have been reached, which should allow the study of most important reactions of coals. To avoid overheating, the body of the cell is water-cooled.

To accommodate this cell, we designed a fundamentally different optical configuration for DR infrared spectrometry, which permits a large cell to be installed with little or no loss in optical efficiency. If a non-absorbing sample (such as powdered KCl) is placed in the cell, the SNR of the interferogram measured with an FT-IR spectrometer operating at full throughput (0.06 cm<sup>2</sup> steradian) with a medium-range MCT detector ( $\lambda_{\text{max}}=15\mu\text{m}$ ) can be so large in the region of the centerburst that the dynamic range of the analog-to-digital converter may be exceeded unless a screen is placed in the beam. This cell and optics are described in details in the Ph.D. dissertation of Hamadeh (7), and are shown schematically in Figure 1.

### Resolution Enhancement

Absorption bands in the infrared spectra of coals may be rather broad, so that detailed chemical information may be masked by the overlap of neighboring bands. Conversion of the spectrum to the second, or even the fourth, derivative has permitted the separation of small shoulders in the spectra of coals (3,6,8) but the interpretation of second- and fourth-derivative spectra is made difficult by the possibility that secondary lobes from intense sharp peaks may be mistaken for a real spectral feature in complex spectra. An alternative, and we believe preferable, technique for resolution enhancement where the effect of secondary lobes should be minimized is Fourier self-deconvolution (FSD). Here the absorption spectrum is converted to its Fourier transform, multiplied by an exponential function, and truncated if necessary to remove the high frequency noise components. The inverse transform then yields a spectrum in which the width of all spectral features has been reduced (9). Care must be taken, however, to avoid the use of an exponent in the multiplier which is too large since side-lobes will be generated which are analogous to those of second-derivative spectra.

To illustrate the potential of Fourier self-deconvolution in coal spectrometry, the progressive resolution enhancement of the spectrum of an oxidized low volatility bituminous coal in the region of the carbonyl stretching bands is shown in Figure 2. In the upper spectrum it can be seen that side-lobes have been generated and the noise level of the spectrum is increased to the point that it is difficult to distinguish a real feature from a noise spike. We have recently developed a technique to determine the optimum level of resolution enhancement consistent with an acceptable noise level and side-lobes (10), and we believe that the degree of resolution enhancement of all spectra shown or used in subsequent sections of this paper is quite conservative, and could probably have been improved upon if these optimization procedures had been applied rigorously.

### Spectral Assignments

This increased resolution leads to some benefits and some problems. The benefits are obvious when the newly resolved bands can be unequivocally assigned to definite vibrational modes. For example, the spectra of most coals contain two bands between 3000 and 2800 cm<sup>-1</sup>; these may be assigned to the symmetric and asymmetric stretching modes of aliphatic C-H groups. Each band often shows evidence of being composed of two unresolved or partially resolved components which can be completely resolved by FSD; these components can be assigned to vibrations of methylene and methyl groups. By studying the ratio of the intensities of these bands, the relative rates of reaction of CH<sub>2</sub> and CH<sub>3</sub> groups can be monitored, for example during air oxidation (vide infra).

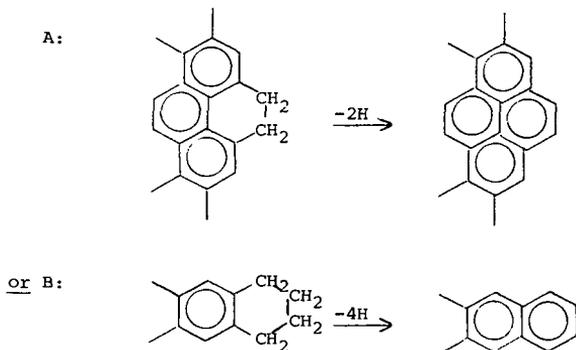
The disadvantage of the enhanced information content is encountered when the newly resolved spectra cannot be interpreted with certainty. In Figure 2, as many as nine bands may be resolved in the carbonyl stretching region alone. Some of these, e.g. the two anhydride bands at 1845 and 1775  $\text{cm}^{-1}$ , are easily assigned. Others, especially the bands between 1735 and 1675  $\text{cm}^{-1}$ , are much less easy to assign with any degree of certainty.

We are hoping to increase the certainty of these band assignments by correlating the infrared spectra with both solution-phase  $^1\text{H}$  and solid-phase  $^{13}\text{C}$  NMR spectra. The correlating of solution-phase  $^1\text{H}$  spectra of that fraction of each coal soluble in pyridine- $d_5$  with the diffuse reflectance spectrum of the solute remaining after complete evaporation of the solvent is certainly useful, but one can never be sure that the structure of the coal remains unchanged after solvent elimination. The SNR of CP-MAS  $^{13}\text{C}$  NMR spectra measured on a 60 MHz spectrometer was too low to permit useful conclusions to be made, and we are hoping that spectra to be measured on a 90 MHz spectrometer with a wide magnet gap prove more helpful.

#### Low Temperature Oxidation

The potential of DR spectrometry for monitoring coal reactions will be illustrated by the low temperature (150°C) air oxidation of a low volatile bituminous coal. This reaction is very slow - much slower than the types of reactions which we ultimately hope to study (which can have half-lives of only a few seconds) - but the data still give a good indication of the type of results which can be obtained. Deconvolved spectra measured at different times after oxidation was initiated are shown in Figure 3. The increase in absorption around 1700 and 1250  $\text{cm}^{-1}$  is evident, showing that oxygen reacts to form both double and single carbon-oxygen bands, with C=O formation being the more rapid reaction. The existence of anhydride groups is not obvious in the early spectra, but the 1845  $\text{cm}^{-1}$  band builds up rapidly after a few days, indicating that oxidation to carboxylic acids is an initial step, followed by condensation of neighboring  $-\text{CO}_2\text{H}$  groups when their concentration is sufficiently high.

The increase in aromaticity can be inferred from a plot of the ratio of the intensity of the aromatic C-H stretching band at 3070  $\text{cm}^{-1}$  to that of the symmetric methyl stretching band (2872  $\text{cm}^{-1}$ ) against time of oxidation, see Figure 4. The mechanism of this reaction can be inferred from a plot of the ratio of the intensities of the asymmetric methylene and methyl stretching mode against time of oxidation, see Figure 5. The faster rate of disappearance of  $\text{CH}_2$  groups indicates that one possible mechanism by which aromaticity is increased is by oxidative dehydrogenation of hydroaromatic methylene groups:



In Reaction A, an aromatic ring with two neighboring C-H groups would be formed whereas in Reaction B the newly formed aromatic ring would have four neighboring C-H groups. It is possible to determine which reaction has the higher probability by studying the spectral region between 950 and 650  $\text{cm}^{-1}$ . Three strong bands of approximately equal intensity may be observed in this region, at approximately 880, 815 and 760  $\text{cm}^{-1}$ . These bands are due to the aromatic out-of-plane C-H deformations, and may be assigned as follows, after Bellamy (11):

880  $\text{cm}^{-1}$  band: Isolated C-H groups, i.e. 1,2,3,4,5-pentasubstituted ring; 1,2,3,5 and 1,2,4,5-tetrasubstituted ring; 1,2,4, trisubstituted ring (in conjunction with 815  $\text{cm}^{-1}$  band).

815  $\text{cm}^{-1}$  band: Two neighboring C-H groups, i.e. 1,2,3,4-tetrasubstituted ring; 1,2,4-trisubstituted ring (in conjunction with 880  $\text{cm}^{-1}$  band); para-disubstituted ring.

760  $\text{cm}^{-1}$  band: Four neighboring C-H groups, i.e. ortho-substituted ring.

An increase in the intensity of the 815  $\text{cm}^{-1}$  band relative to that of the 760  $\text{cm}^{-1}$  band on dehydrogenation would indicate that Reaction A is favored over Reaction B, and vice versa. In Figure 6, it is shown that the rate of increase of the 760  $\text{cm}^{-1}$  band is greater than that of the 815  $\text{cm}^{-1}$  band, indicating that Reaction B is favored. It is noteworthy that this type of conclusion also gives an indication of the structure of low volatility bituminous coals, since the dimethylene structural unit in the reactant for Reaction A has been generally believed to be more prevalent in coals of this rank than the tetramethylene hydroaromatic unit in the reactant for Reaction B.

### Conclusions

We believe that these data indicate the feasibility of monitoring structural changes occurring during reactions such as oxidation, pyrolysis and hydrogenation, with or without catalysts present, in situ by diffuse reflectance infrared spectrometry. Our current cell allows reactions to be studied at temperatures as high as 600°C. Reaction products may be continuously swept out of the cell, permitting characterization by a wide range of other instrumental techniques. Reactions occurring at high pressure are less easy to monitor at this time, but it should not be too difficult to redesign the cell so that pressures to 1000 psig are permissible.

### References

1. M. P. Fuller and P. R. Griffiths, Anal. Chem., **50**, 1906 (1978).
2. M. P. Fuller and P. R. Griffiths, Amer. Lab., **10**(10), 69 (1978).
3. M. P. Fuller, I. M. Hamadeh, P. R. Griffiths and D.E. Lowenhaupt, Fuel, **61**, 529 (1982).
4. M. Niwa, T. Hattori, M. Takahashi, K. Shirai, M. Watanabe and Y. Murakami, Anal. Chem., **51**, 46 (1979).
5. T. Hattori, K. Shirai, M. Niwa and Y. Murakami, Anal. Chem., **53**, 1129 (1981).
6. P.R. Griffiths and M. P. Fuller, in Advances in Infrared and Raman Spectroscopy, Vol. 9, (R. Clark and R. Hester, eds.), Wiley-Interscience, New York (1982), pp. 63-127.
7. I. M. Hamadeh, Ph.D. dissertation, Ohio University, Athens, Ohio (1982).
8. P. C. Painter, R. W. Snyder, M. Starsinic, M. M. Coleman, D. W. Kuehn and A. Davis, Appl. Spectrosc., **35**, 475 (1981).
9. J. K. Kauppinen, D. J. Moffatt, H. H. Mantsch and D. G. Cameron, Appl. Spectrosc., **35**, 271 (1981).
10. W. J. Yang and P. R. Griffiths, unpublished results (1982).
11. L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Chapman and Hall, London (1954).

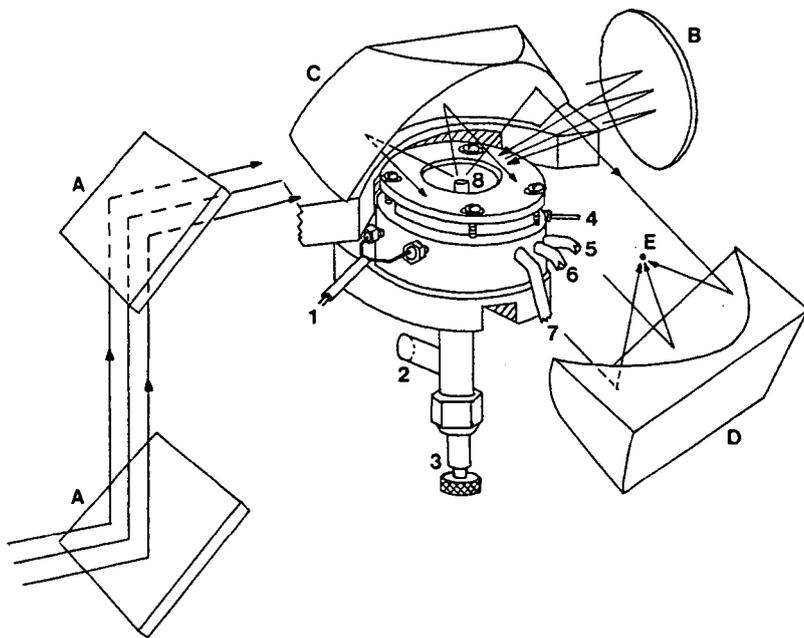


Figure 1: Schematic of cell designed for the study of gas-solid reactions. The level of the collimated beam from the interferometer is raised by the two plane mirrors (A) and focused onto the sample by the off-axis paraboloidal mirror (B). The diffusely reflected beam is collected and collimated by the paraboloidal mirror (C) and refocused by the other segment of the same paraboloidal blank (D) onto a downward-looking MCT detector at E. The components of the cell are as follows: (1) Heater leads, (2) Line to vacuum pumps, (3) Screw for sample removal, (4) Gas inlet line, (5) (6) Water inlet and outlet lines, (7) Manometer connection, (8) Sample.

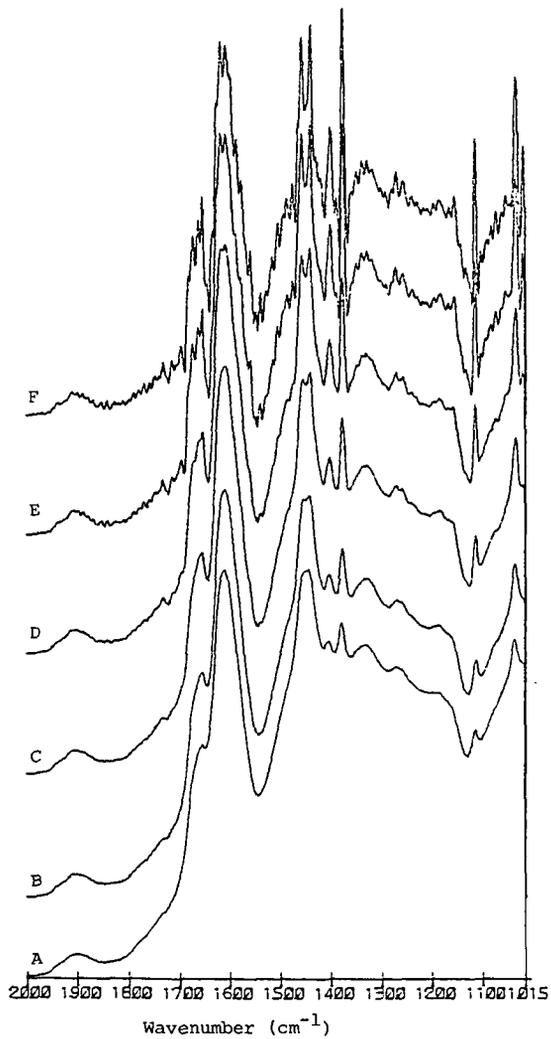


Figure 2: Effect of progressive resolution enhancement of the DR spectrum of a low volatility bituminous coal. The original spectrum is the lowest trace (A). Spectra used in this paper were computed with the parameter used for spectrum D.

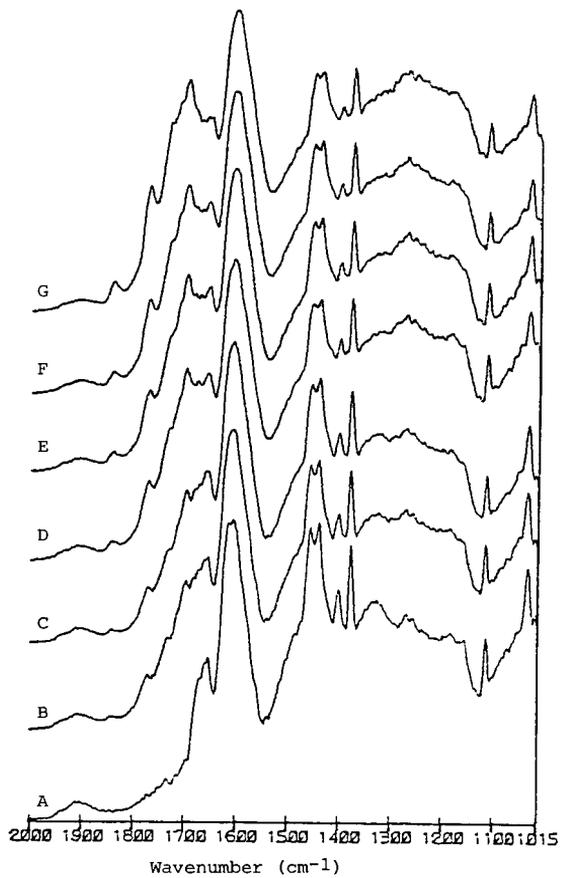


Figure 3: Resolution-enhanced spectra of a low volatility coal subjected to 150°C air oxidation for (A), 0; (B), 2; (C), 4; (D), 6; (E), 8; (F), 10; (G), 12 days.

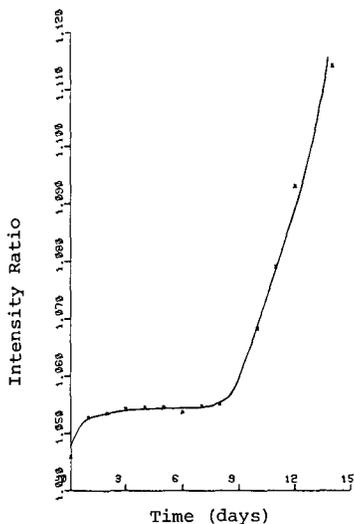


Figure 4

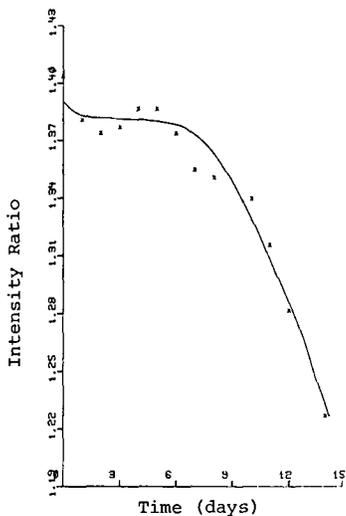


Figure 5

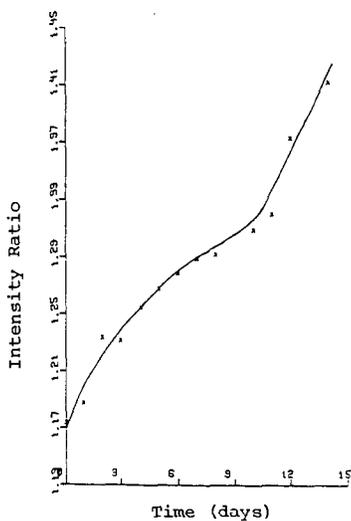


Figure 6

Figures 4, 5 and 6: Plots of ratio of band intensities in the DR spectra of a low volatility coal (PSOC 620, Bedford Co., PA) against time of oxidation at 150°C.

Figure 4: Aromatic C-H stretch (3070  $\text{cm}^{-1}$ ) vs symmetric methyl stretch (2872  $\text{cm}^{-1}$ );

Figure 5: Asymmetric methylene stretch (2920  $\text{cm}^{-1}$ ) vs asymmetric methyl stretch (2962  $\text{cm}^{-1}$ );

Figure 6: 760  $\text{cm}^{-1}$  aromatic C-H out-of-plane deformation vs 815  $\text{cm}^{-1}$  band.