

FOURIER TRANSFORM INFRARED STUDIES OF COAL OXIDATION

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INTRODUCTION

It is well-known that even minor amounts of oxidation can dramatically change the properties of caking and coking coals. In a number of studies (1,2) it has been noted that there is an increase in the reactive oxygen groups, -OH, COOH and C=O, upon low temperature oxidation. However, in recent work (1,3-5) changes such as the loss of swelling properties of coking coals upon low temperature oxidation have been attributed to the formation of ether cross links. In fact, Wachowska, et al. (5) could determine no change in the carbonyl content of Balmer 10 coal upon oxidation at 100°C, using chemical methods of analysis.

In contrast to these results, an FTIR study of the weathering of a Canadian coking coal (6) and preliminary work on the laboratory oxidation of a caking coal (7,8) demonstrate that carbonyl and carboxyl groups are formed in the early stages of the oxidation. In this paper we will report further studies of coal oxidation by FTIR, with particular emphasis on the detection of hydroxyl groups and the changes that occur in reacting oxidized coal with potassium in THF.

RESULTS AND DISCUSSION

The utility of FTIR in the study of the oxidation of coal is illustrated in Figure 1, which compares the infrared spectrum of a sample of unoxidized PSOC 337 coal to the spectrum of the same sample subsequent to heating in air at 150°C for two hours. A weak shoulder appears near 1690 cm^{-1} upon oxidation. All spectra were recorded on a Digilab FTS 15B spectrometer using 400 'scans' (co-added interferograms) at a resolution of 2 cm^{-1} . Figure 1 also shows the difference spectrum obtained by subtracting the spectrum of the unoxidized sample from that of the oxidized. The criteria used to determine the "correct" degree of subtraction was the elimination of the kaolinite bands at 1035 and 1010 cm^{-1} , since this clay should be relative unaffected by low-temperature oxidation. It can be seen that this subtraction results in the elimination of the aromatic C - H stretching mode near 3050 cm^{-1} and the aromatic C - H out-of-plane bending modes between 700 and 900 cm^{-1} . This is to be expected in that direct oxidative attack of the aromatic nuclei is unlikely under the oxidation conditions used in this study and confirms the choice of kaolinite bands as a subtraction standard.

In contrast to the aromatic C - H bands, the aliphatic C - H stretching modes near 2900 cm^{-1} appear negative, or below the baseline, demonstrating a loss in CH_2 groups upon oxidation. This observation is not particularly novel, as methylene groups in the benzylic position are well known to be sensitive to oxidation and are probably the initial site of oxidative attack. However, the difference spectrum reveals new detail in the 1700 to 1500 cm^{-1} region of the spectrum. The 1685 cm^{-1} band, which appeared as a weak shoulder in the original spectrum of the oxidized coal, is now resolved as a separate band. Furthermore, a prominent new band near 1575 cm^{-1} is now revealed in the difference spectrum. This band is not detectable in the original spectrum. The 1685 cm^{-1} absorption is probably due to an aryl alkyl ketone, while the 1575 cm^{-1}

mode can be assigned to an ionized carboxyl group, COO^- .

In addition to the difference bands at 1685 and 1575 cm^{-1} , there is a weak broad absorption centered near 1200 cm^{-1} . This band was not differentiated from background scatter at lower levels of oxidation (7,8). Modes in this frequency range are usually assigned to aromatic C-O stretch, as in phenols or ethers. However, there are a number of other functional groups that absorb in this region of the spectrum (e.g., O-H bend, various CH_2 bending modes), so that specific assignments cannot be made unambiguously.

In addition to the problems associated with assigning specific bands to ethers, there is a problem in measuring OH groups using the standard KBr preparation method. Friedal (9) discussed in some detail the difficulty in removing water absorbed on the KBr discs during sample preparation and noted that heating to 175°C is required to completely remove water bands, which nevertheless reappear upon cooling. Consequently, in order to determine changes in hydroxyl and ether groups upon oxidation we decided to combine FTIR with chemical methods of analysis. Samples were acetylated in order to determine hydroxyl groups and reacted with potassium in THF, as described by Wachowska, et al. (5), in order to cleave ether bonds.

Durig and Sternhell (9) reported an infrared study of acetylated coal twenty years ago. Although some useful linear plots were obtained, the method was complicated by the overlap of the acetyl bands with those of the original coal. This made the determination of baselines and the measurement of peak intensities (and hence reactive OH groups) subject to possible error. The problem is illustrated in Figure 2, which compares the infrared spectrum of an Arizona HVC coal (PSOC 312) to that of the same sample subsequent to acetylation. FTIR is capable of solving many problems of this type (band overlap) by simple spectral subtraction. Figure 2 also shows the difference spectrum obtained by subtracting the spectrum of the original coal from that of the acetylated product. The characteristic acetyl bands are now relatively well-resolved and it is a straight-forward task to draw an appropriate baseline and measure peak heights, or even make integrated absorption measurements of, for example the 1370 CH_3 mode. We have 'calibrated' the intensities of these bands, so that we can obtain a measure of the number of reactive OH groups, but this work will be reported elsewhere. In this study our initial aim was to determine qualitatively the change in OH content upon oxidation. Figure 3 compares the infrared spectrum of acetylated fresh PSOC 337 coal to the spectrum of the acetylated oxidized (150°C , 2 hours in air) coal. Difference spectra of the type shown in Figure 2 were obtained and intensity measurements of the acetyl bands indicated a reduction in the number of reactive OH groups under these conditions of oxidation. This reduction can be seen in Figure 3, which also shows two difference spectra (acetylated oxidized - acetylated fresh sample). Two different subtraction criteria were used, first the elimination of the coal 1600 cm^{-1} band and second the subtraction to the baseline of the aliphatic CH bands near 2900 cm^{-1} . In both difference spectra there are negative bands characteristic of the acetyl group, near 1770 , 1370 and 1200 cm^{-1} , indicating a loss of reactive OH group content upon oxidation. At this time we are not convinced that this reduction in the number of OH groups is a direct consequence of oxidation. At elevated temperatures there is also the possibility of condensation reactions between phenolic OH groups. We are still in the process of investigating this point thru the study of coals oxidized at lower temperatures.

As we noted above, in a number of studies it has been concluded that the formation of ether cross links are critical to loss of coking ability. For example, it has been observed that the swelling behavior of coking coal can be

partially regenerated by treating with potassium in THF, a reagent that should cleave C-O bonds but not C-C bonds (5). We therefore considered it valuable to apply FT-IR to the characterization of the chemical changes occurring upon reaction of potassium in THF with oxidized coal. The spectrum of an oxidized coal (3.3% oxygen uptake) is compared to the spectrum of the same sample treated with potassium in THF in Figure 4. We were surprised by the observation that this treatment apparently leads to an increase in the degree of oxidation of the sample, as measured by the increased intensity of the shoulder near 1695 cm^{-1} . This is confirmed by the difference spectrum, shown in the same figure, which is remarkably similar to the difference spectrum shown in Figure 1. The criteria for obtaining this difference spectrum differs from that used previously, in that, because kaolinite is lost from the sample during the course of the reaction, it is no longer a suitable subtraction standard. Instead, we subtracted the aliphatic C-H modes near 2900 cm^{-1} to the baseline. Because of the weak intensity of this band, this subtraction is only approximate. Nevertheless, the carboxyl band, now appearing near 1580 cm^{-1} , is again revealed.

We postulated that the increased oxidation of the sample might occur in the final stage of the reaction procedure, where the coal is dried at 70°C (7,8). Consequently, we modified the procedure so that the final product was dried under vacuum at room temperature. The results remained the same. For example, the spectrum of the unoxidized coal is compared in Figure 5 to the spectrum of the same sample after reaction. Again a carbonyl band appears as a shoulder near 1695 cm^{-1} . However, there is also an apparent decrease in intensity of the band near 1265 cm^{-1} (which was not observed in the spectra of samples dried at 70°C ; see Figure 4), suggesting that some C-O bonds are being cleaved. The reaction of coal with potassium in THF therefore appears more complex than considered in previous studies and does not lead to cleavage of C-O bonds alone. It is important to note that Wachowska, et al. (5) detected an increase in oxygen content of both fresh and oxidized coal upon reaction, an increase that manifests itself in our study as an increase in carbonyl and carboxylic acid groups.

Finally, we were surprised by the observation that in our oxidized samples⁻¹ the carboxylic acid groups are in the salt form, thus giving bands near 1575 cm^{-1} one possibility is that there has been an exchange with potassium ions in the KBr matrix used for sample preparation. Alternatively, -COO^- groups have a counterion (e.g. Ca^{++}) derived from the mineral matter. Miller (10,11) has reported that in the low temperature ashing process used in mineralogical analysis organic sulfur is fixed as inorganic sulfate in the form of bassanite, but only if there are carbonate or -COO^- groups present. If the carboxyl groups are converted to the acid form, -COOH , then organic sulfur is no longer fixed. We have observed similar results in FTIR studies (12,13) and also observed a corresponding fixation of organic nitrogen as inorganic nitrate. If we examine the infrared spectra of the low-temperature ash of a coking coal samples as a function of degree of oxidation (6) we can see bands characteristic of bassanite (near 605 and 660 cm^{-1}) and nitrate (1386 cm^{-1}) in the spectra of oxidized samples which are absent or extremely weak in the spectra of the ash of unoxidized samples, as illustrated in Figure 6. Previously, Pearson and Kwong (14) have noted an empirical correlation of bassanite concentration with the degree of oxidation of a coking coal. This can now be explained by the presence of -COO^- groups in these coals which allow the fixation of organic sulfur as inorganic sulfate. These results also demonstrate that in the oxidized coals used in this study carboxyl groups are present in the salt form, presumably through interaction with the mineral matter present in the coal.

CONCLUSIONS

In the early stages of coal oxidation the principal products appear to be carbonyl and carboxyl groups. Oxidation at 150°C appears to result in a slight loss of phenolic OH, possibly through condensation reactions to give ethers.

REFERENCES

1. Ignasiak, B. S., Clugston, D. M. and Montgomery, D. S. Fuel 51, 76 (1972).
2. Carbonization Research Report 64, February 1979. The British Carbonization Research Association, Chesterfield, Derbyshire, England.
3. Wachowska, H. and Angelova, G. Fuel, 56, 422 (1977).
4. Ignasiak, B. S., Nandi, B. N. and Montgomery, D. W. Fuel, 49, 214 (1970).
5. Wachowska, H. M., Nandi, B. N. and Montgomery, D. S. Fuel, 53, 212 (1974).
6. Painter, P. C., Snyder, R. W., Pearson, D. E. and Kwong, J. Fuel, 59, 282 (1980).
7. Painter, P. C. and Snyder, R. W. ACS Division of Fuel Chemistry preprints (1980).
8. Painter, P. C., Coleman, M. M., Snyder, R. W., Mahajan, O., Komatsu, M. and Walker, P. L., Jr. Applied Spectroscopy (In press).
9. Friedel, R. A. in Applied Infrared Spectroscopy, p. 312. Edited by Kendall, D. N. Reinhold, New York (1966).
10. Miller, R. N. Ph.D. Thesis, 1977, The Pennsylvania State University.
11. Miller, R. N., Yarzab, R. F. and Given, P. H. Fuel, 58, 4 (1979).
12. Painter, P. C., Coleman, M. M., Jenkins, R. G. and Walker, P. L. Jr. Fuel, 57, 125 (1978).
13. Painter, P. C., Youtcheff, J. and Given, P. H. Fuel 59, 523 (1980).
14. Pearson, D. E. and Kwong, J. Fuel, 58, 63 (1979).

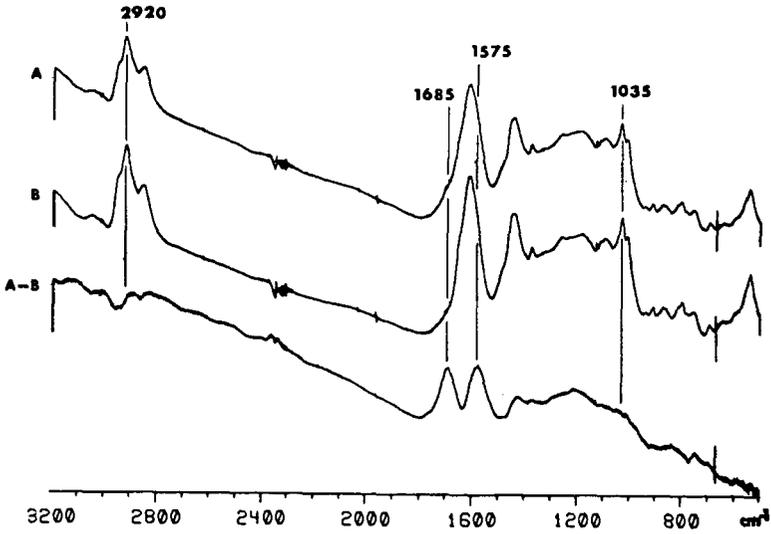


Figure 1: A: FTIR spectrum of coal (PSOC 337) oxidized at 150°C for 2 hours.
 B: FTIR spectrum of the original coal (PSOC 337).
 A-B: Difference spectrum.

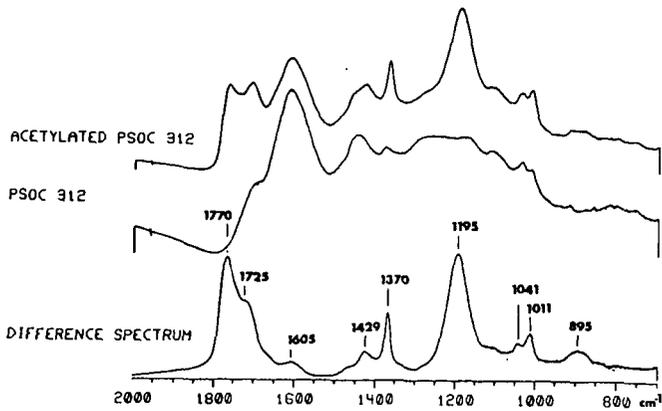


Figure 2: Top: FTIR spectrum of an acetylated Arizona coal (PSOC 312).
 Middle: FTIR spectrum of the original coal (PSOC 312).
 Bottom: Difference spectrum.

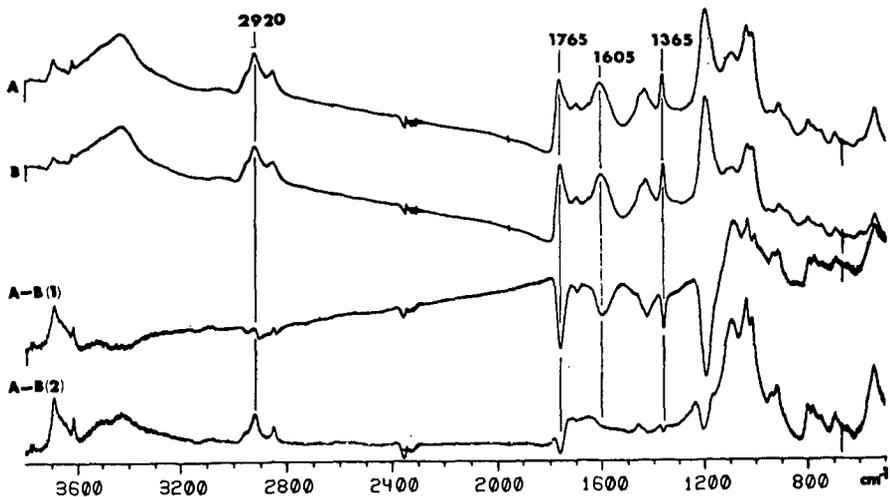


Figure 3: A: FTIR spectrum of acetylated coal (PSOC 337) oxidized at 150°C for 2 hours.
 B: FTIR spectrum of acetylated, fresh coal (PSOC 337).
 A-B: (1) Difference spectrum subtracting 2920 band to the baseline.
 A-B: (2) Difference spectrum subtraction 1605 band to the baseline.

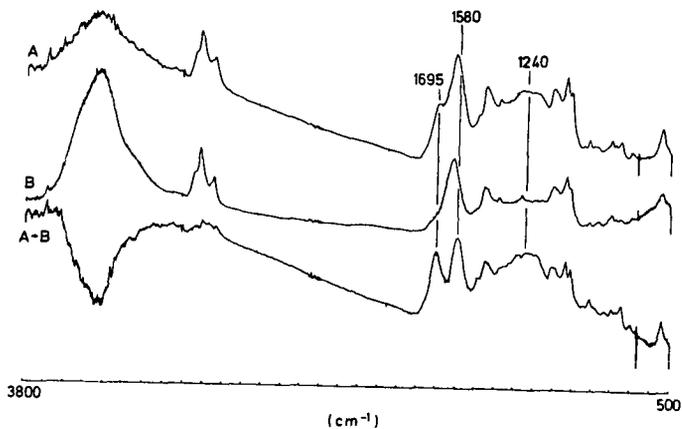


Figure 4: A: FTIR spectrum of oxidized coal after treatment with potassium in THF.
 B: FTIR spectrum of oxidized coal.
 A-B: Difference spectrum.

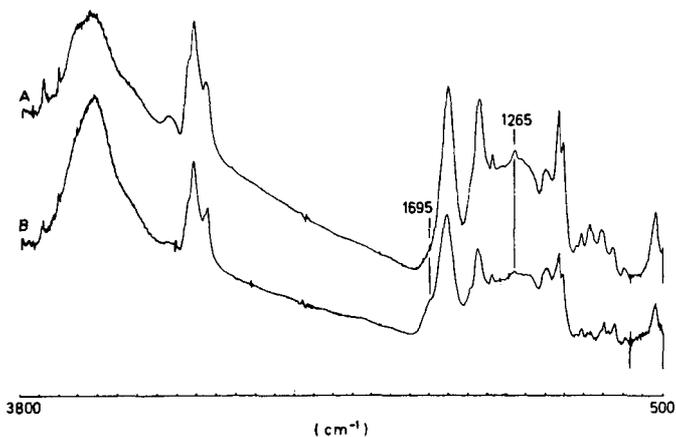


Figure 5: A: FTIR spectrum of fresh, unoxidized coal.
 B: FTIR spectrum of unoxidized coal after treatment with potassium in THF.

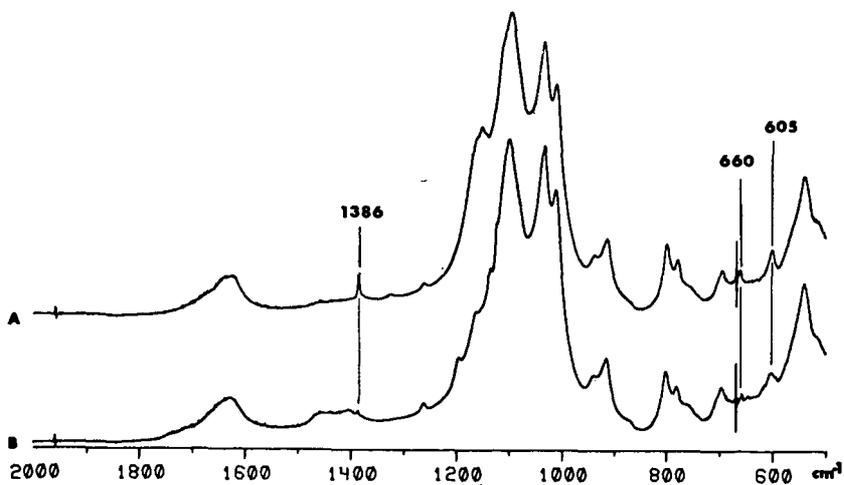


Figure 6: A: FTIR spectrum of low temperature ash (LTA) from highly weathered Canadian coking coal.
 B: FTIR spectrum of low temperature ash (LTA) from a less weathered Canadian coking coal.