

FTIR SPECTROSCOPIC STUDIES OF COAL LIQUEFACTION PRODUCTS

Jack Youtcheff, Paul Painter and Peter Given

Mineral Industries Research Lab
University of Alaska
Fairbanks, Alaska 99701

AND

Materials Science Department
The Pennsylvania State University
University Park, PA 16802

Recent work in our laboratories has been concerned with obtaining a better understanding of the phenomena associated with coal liquefaction (1). An initial study of three bituminous coals discussed the changes that occur in oxygen containing functional groups (2). It was concluded that the initial large loss of so-called "unaccounted" oxygen was a result of a cleavage of ether groups to form hydroxyls, which were subsequently removed by dehydroxylation. These same samples were also characterized by FTIR and the results of this portion of the work are presented in this communication.

As might be expected, the most interesting changes occurred in the aliphatic and aromatic CH stretching regions of the spectrum. Samples were prepared for infrared analysis using established KBr pellet techniques (1,3) and representative spectra of the three coals, PSOC 521 (HVC), PSOC 767 (HVB) and PSOC 757 (HVA) are presented in figure 1. Even though the aromatic CH stretching modes between 3100 and 3000 cm^{-1} are relatively weak, it can be seen that there is still a degree of overlap that can lead to errors when band areas are determined by simple integration. Accordingly, a curve resolving procedure, described in previous publications (1,3), was used to separate the two contributions. In addition, it was found that there was a change in the relative proportion of various aliphatic CH groups. In order to sort this out second derivative methods were used to define the initial positions of five bands that were curve-fit to the difference spectrum obtained by subtracting the aromatic CH stretching modes, as illustrated in figure 2. These bands do not represent individual components, but are themselves composites (4). Nevertheless, the bands near 2956 and 2867 cm^{-1} are largely due to methyl groups, the bands near 2923 and 2852 cm^{-1} have a major contribution from methylene groups, while the band at 2893 cm^{-1} can be assigned to methine CH moieties.

Liquefaction reactions were carried out at temperatures of 350, 370, 400 and 425°C for periods of 2, 12, 22 and 32 minutes, as described previously (1,2). Overall, the spectra of the liquefaction products from a particular coal were surprisingly similar, supporting the notion that structural rearrangement under these reaction conditions is relatively limited. The integrated area of the aromatic CH stretching modes increases with the severity of the liquefaction conditions, but it should be kept in mind that to some extent this is an apparent increase that is due to the loss of oxygen containing functional groups. The pattern of out-of-plane bending modes between 900 and 700 cm^{-1} shows little change in the distribution pattern of hydrogen in aromatic units, supporting the inference that the changes in this region are largely due to the loss of other groups and hence an increase in the per unit weight concentrations of those left behind.

Although this factor also affects the aliphatic CH stretching modes, the changes in this region are far more pronounced. The overall aliphatic CH content appears to initially increase with conversion, but then drops off somewhat

at conditions of high conversion. The data, however, shows considerable scatter and such conclusions are only tentative. There are much clearer changes in individual curve-resolved bands, (measured as a fraction of total aliphatic CH area, in order to eliminate and reduce errors in sample preparation, etc.), with the most marked differences being observed in the 2956 cm^{-1} band. The relative area of this band is plotted as a function of reaction time and conversion in figures 3 and 4, respectively.

The Ohio coal (PSOC 757) showed no temperature dependence in the plot against time, in contrast to the other coals. When the 2956 cm^{-1} band is plotted as a function of conversion (figure 4), the points for all temperatures tend to lie in a single band. Visual inspection suggests that the band or line is somewhat curved. However, linear regressions were performed and gave surprisingly high variance, particularly for the Oklahoma and Wyoming coals. Nevertheless, the slopes of these least-squares fits suggest that the number or type of bonds broken during liquefaction are different for the three coals. For a slope of zero to exist in figure 4, the distribution of aliphatics in the parent coal and products would have to be the same. This would result if no chemical reactions were involved, and conversion results from the physical dissolution of the coal. An increase in this slope is indicative of an increasing number of alkyl ethers or aliphatic systems cleaved in converting a particular coal. If the increase in relative area of this band stems from methyl-generating reactions, for the Ohio coal (PSOC 757), only a few bonds need to be broken to drastically enhance its conversion.

In figure 5, the amount of "ethers" cleaved (loss of unaccounted oxygen from references 1 and 2) is plotted against the area of the 2956 cm^{-1} band as a fraction of the total area for aliphatic C-H stretching vibrations. Correlations are readily apparent for the coals having a higher number of cleavable ethers, namely the Wyoming and Ohio coals with 7.7 and 5.1 cleavable ethers per 100 carbon atoms, respectively. A least-squares linear regression was performed on the values at the three lowest temperatures for the Wyoming coal (Figure 5 (b)). The slopes and the R^2 values for this correlation between ether removal and relative area of the 2956 cm^{-1} band show a high proportion of variance explained. If the correlation is accepted, the obvious inference is that ether cleavages generate methyl groups (i.e. $-O-CH_2-$ bonds are cleaved forming OH and CH_3). It should be noted that the slopes of the least-squares fit for the lowest three temperatures are quite similar, whereas the curves for the Ohio coal (figure 5 (c)) increase more steeply with increasing temperature. For the latter case, one could infer that at the lower temperatures, labile ethers (aliphatic and benzylic) are cleaved; proceeding to higher temperatures, the more refractory type of ethers (diaryl) are likely to be cleaved. The fact that the slopes are similar for the Wyoming coal suggests that similar types of ethers are broken under these conditions. The relatively small slopes suggest that these ethers are predominantly aliphatic or aralkyl. The lack of correlation at 425°C for this coal and the poor correlation at all temperatures for the Oklahoma coal (though a trend similar to that of the Ohio coal exists) arises perhaps because any trend is marked by alkyl cleavage and other reactions that do not involve loss of unaccounted oxygen.

In conclusion, the FTIR results indicate that extensive structural rearrangements are not occurring during liquefaction. Rather, a few selected bridging units are broken, resulting in the formation of various fragments of different solubility. The increase in methyl groups and previously reported loss of ether oxygen indicates

that bonds between aliphatic methylene units, benzylic ethers and aryl alkyl ethers are the principal sites of cleavage.

References

1. Youtcheff, J. S. and Given, P. H. "The dependence of liquefaction behavior on coal characteristics" and references therein. Final Report to DOE under Contract No DE-AC22-81-PC-40784, September 1983.
2. Youtcheff, J. S. and Given, P. H. *Fuel*, 61, 980 (1982).
3. Sobkowiak, M., Reisser, E., Given, P. and Painter, P. *Fuel*, 63, 1245 (1984).
4. Painter, P. C., Starsinic, M. and Coleman, M. M. in "Fourier Transform Infrared Spectroscopy", Vol 4. (edited by J. R. Ferraro and L. J. Basile) pp 169-243 Academic Press (1985).

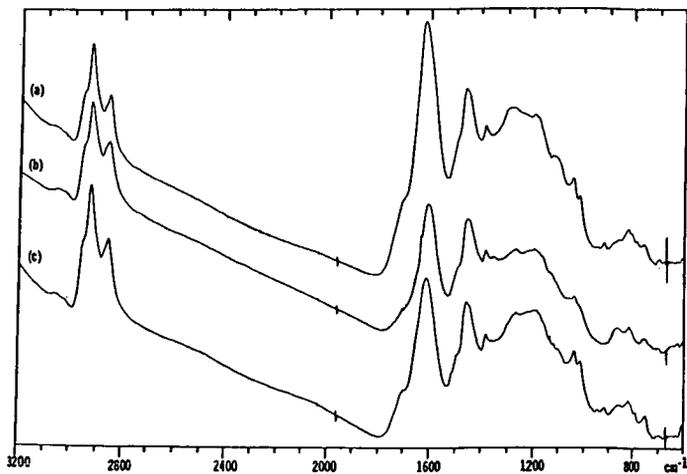


Figure 1. FTIR SPECTRA OF COALS (a) PSOC-521; (b) PSOC-767; (c) PSOC-757

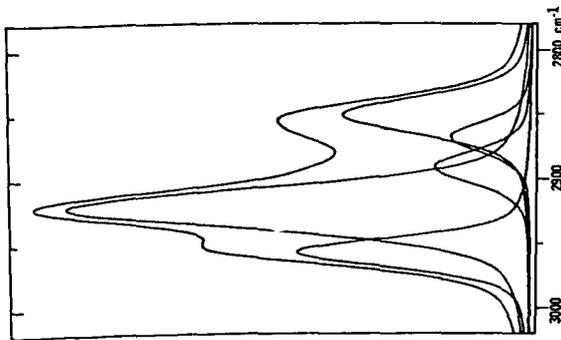


Figure 2. RESOLUTION OF THE DIFFERENCE SPECTRUM OF THE ALIPHATIC C-H STRETCH REGION INTO INDIVIDUAL BANDS (envelope synthesized by co-adding individual bands is superimposed)

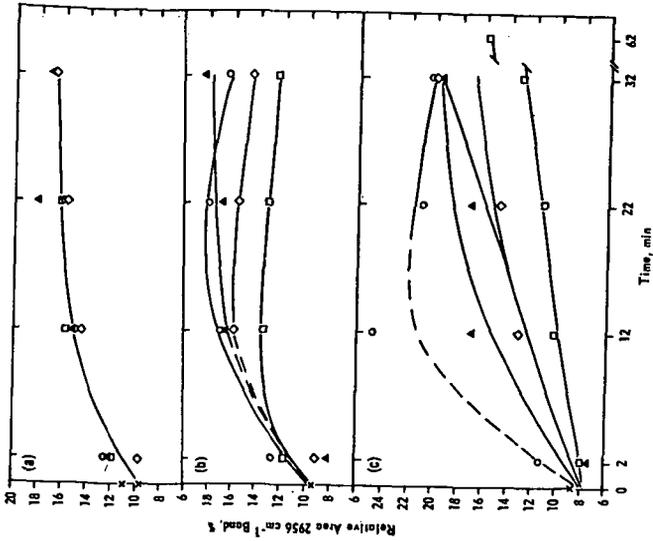


Figure 3. CHANGE IN RELATIVE AREA OF 2956 cm^{-1} BAND FOR COAL AS A FUNCTION OF TIME (a) PSOC-757; (b) PSOC-767 (c) PSOC-521
 o 425°C 400°C 370°C 350°C

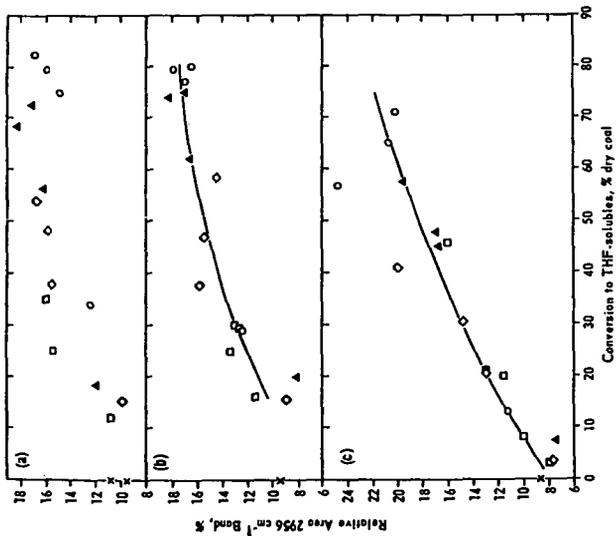


Figure 4. CHANGE IN RELATIVE AREA OF 2956 cm^{-1} BAND FOR COALS AS A FUNCTION OF CONVERSION TO THF-SOLUBLES, % DRY COAL
 (a) PSOC-757; (b) PSOC-767 (c) PSOC-521
 o 425°C 400°C 370°C 350°C

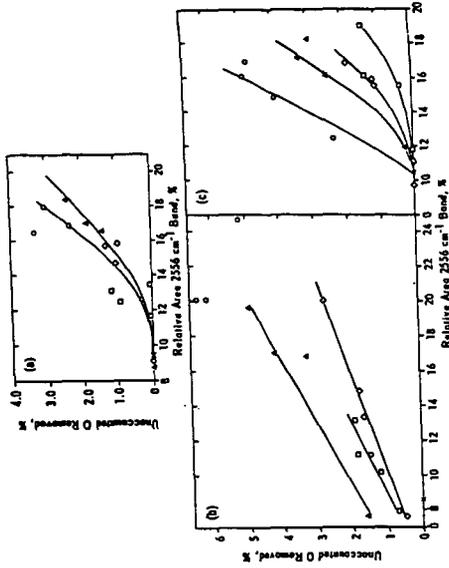


Figure 5. RELATION OF UNACCOUNTED O_1 REMOVED TO THE RELATIVE AREA OF 2956 cm^{-1} BAND
 (a) PSOC-767; (b) PSOC-521; (c) PSOC-757
 o 425°C 400°C 370°C 350°C