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ASPECTS OF COAL WEATHERING AS STUDIED BY SPECTROSCOPIC TECHNIQUES

by

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ABSTRACT

The oxidation or weathering of coals, either in situ or during transportation and stockpiling, is a process having a generally deleterious effect on technological behaviour whether it be carbonization, combustion or liquefaction. A fundamental knowledge of the processes involved is an intriguing one and of considerable interest to the organic chemist. On a theoretical level it can shed some light on the molecular structure of coals while at the practical level it can be used to characterize the extent of oxidation.

Spectroscopic techniques (e.g. FTIR, ^{13}C nmr) have been applied to this problem with varying degrees of success. Indeed confusion, or at least controversy, concerning the mechanism of coal oxidation seems to have increased as a result of recent work rather than have diminished. Some results concerning recent work on carefully characterized coal samples (fresh and oxidized) will be presented in an attempt to clarify some points of interpretation. The evidence comes mainly from FTIR and ^{13}C nmr work performed by ERL in collaboration with St. F.X. University and NRC, Ottawa. It is shown that good correlations between infrared parameters and chemical composition make possible the assessment of the extent of oxidation of a coal sample. This is particularly easy when using photoacoustic detection.

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INTRODUCTION

The low temperature oxidation of coal has received a great deal of attention in the last few years. The reasons for this accrued interest are multiple. Oxidation, either in-situ or during transportation and stockpiling has a generally deleterious effect on technological processes such as carbonization, combustion and liquefaction. It is therefore of considerable practical interest to know how to characterize the degree of oxidation of coals so as to have some idea of how coals will perfom in a particular process. A fundamental knowledge of the mechanism involved is of considerable interest to the organic chemist since it could shed some light on the intriguing problem of the molecular structures in coal. These goals have been, of course, only partially achieved.

One of the most important elements in any study of coal reactivity is proper care in the obtaining of a meaningful sample and adequate characterization of the coal itself. This characterization should consist of, at least, proximate, ultimate, and petrographic analyses. Coals exhibit an astonishing variety of behaviour based on differences in rank, geological history and petrographic composition. Unless proper care is taken to characterize the coals anomalous behaviour cannot be properly explained or even reproduced by an independent laboratory.

In this paper we will discuss a bituminous coal from eastern Canada (high-volatile A) in fresh and oxidized states characterized by a variety of physical and chemical techniques and examined using Fourier Transform Infrared Spectroscopy and solid state ^{13}C nmr with cross polarization and magic-angle spinning. Some less detailed results on other Canadian coals and Illinois #6 will also be mentioned.

RESULTS AND DISCUSSION

Oxidation or weathering generally has an unfavourable effect on the technologial properties of coal. Liquefaction studies on fresh and oxidized bituminous coal show that the conversion yields are lowered as a result of oxidation and the oxidized coal has more of a tendency to produce mesophase and coke than the fresh coal.(1) In combustion, high levels of unburnt carbon in fly-ash due to weathering have been observed.(2) It is well-known that the swelling tendency of bituminous coals is reduced upon prolonged exposure to air and in certain cases by in-situ weathering.(3) Such observations provide the rationale for studies on coal weathering.

Table I provides proximate, ultimate, dilatometric and petrographic analyses of DEVCO Harbour 26, high volatile A bituminous coal. In addition, data for the same coal after 192 hrs. oxidation in air at 105°C are given. Oxidation for this duration is just sufficient to reduce the dilatation to a nil value, but no more. This is seen from Figure 1 where the dilatation curves for various oxidation times at 105° are given. The data of Table I show that while the oxygen content of the coal increases by 2.8% after 192 hrs. of oxidation the atomic H/C ratio remains the same, within experimental error. This implies that while oxygen is being taken up by the sample neither carbon nor hydrogen are being lost, unless they are being lost in precisely the same amounts. Thus it would appear then that the chemical changes taking place that are responsible for the swelling are very subtle indeed and difficult to detect.

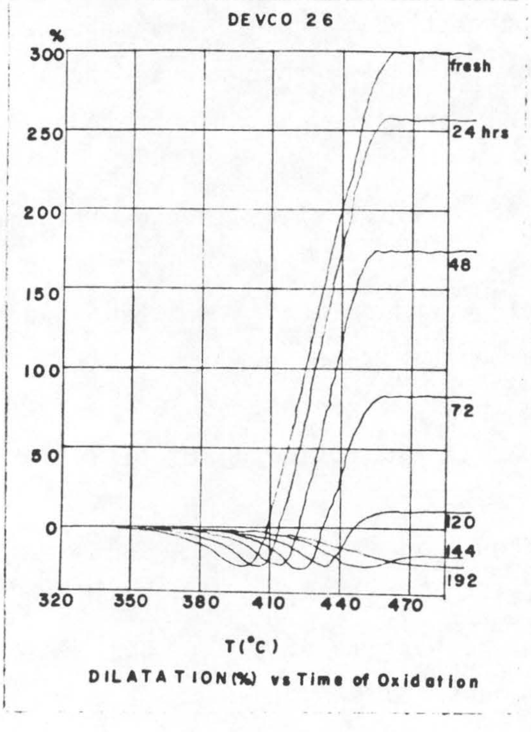


FIGURE 1. Ruhr Dilatometer Curves of DEVCO Harbour 26 Coal as a function of oxidation (@ 105°C).

In Figure 2 we see that there is a rather good linear correlation between the softening temperature (from the Ruhr dilatometer) and the duration of oxidation. The softening temperature then becomes a useful parameter for assessing the degree of oxidation of those coals having measurable plastic properties. This, of course, applies to only a limited range of coal rank.

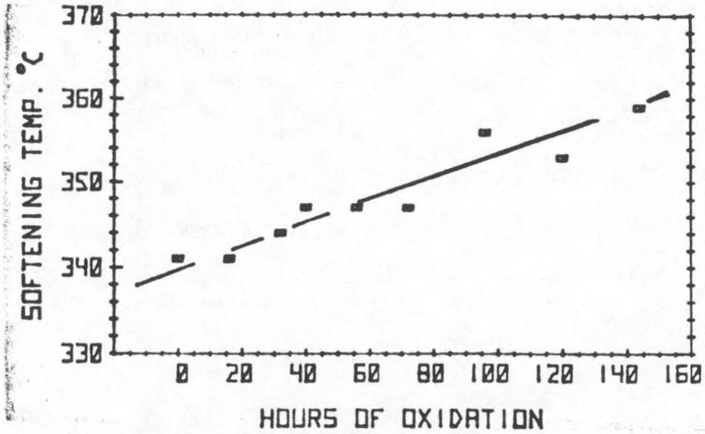


FIGURE 2. Softening temperature (Ruhr dilatometer) variation with oxidation @ 105°C.

It is possible to follow the uptake of oxygen by the coal during the course of weathering. A variety of methods are currently available for doing this. We have opted in favour of a pyrolysis technique using the Perkin-Elmer 240 Elemental Analyser which gives the total amount of organic oxygen.(4) Figure 3 gives the variation of total organic oxygen content as a function of time along with the corresponding variation in dilatation.

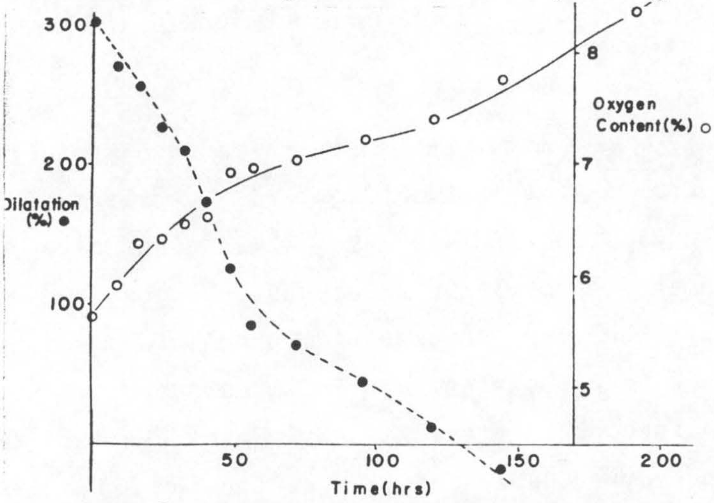


FIGURE 3. Dilatation and oxygen content variation with oxidation @ 105°C.

If total organic oxygen is plotted against dilatation, the result is a surprisingly good straight line (Figure 4). This is true both for Harbour 26 and for a vitrinite concentrate from a western Canadian medium-volatile bituminous coal (Balmer). This correlation raises a caveat concerning mechanistic interpretation of coal oxidation based on partial investigations of oxygen containing functional groups. It is probable that parallel reactions incorporating oxygen functionality are taking place. Since the total organic oxygen correlates with loss of swelling tendency it is likely that partial organic oxygen based on analysis for one particular functional group would do so as well. The causal relationship between loss of coking and change in oxygen functionality in such a case would however be difficult to establish.

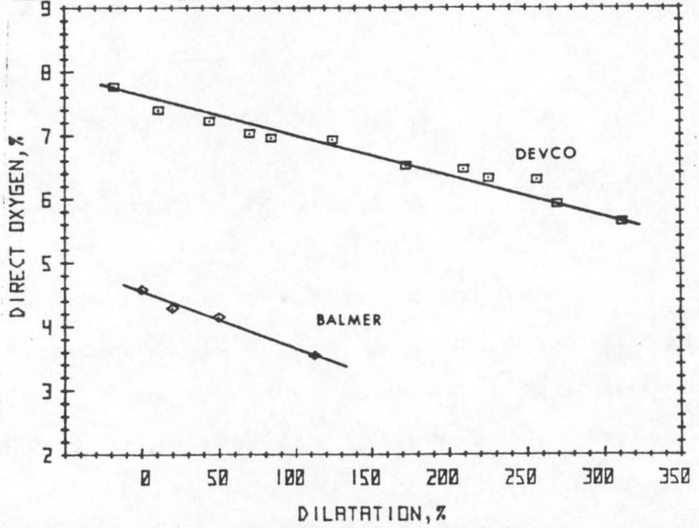


FIGURE 4. Linear relationship between oxygen uptake (wt.%) and dilatation for two coals, eastern Canadian (DEVCO) and western Canadian (Balmer).

Determination of oxygen containing functional groups in high rank coals is not a simple matter. Quantitative analysis for -OH groups is possible (5), if laborious, while quantative analysis for carboxyl groups and carbonyl groups appears not possible at the present time. Exchange reactions using barium or calcium acetates can detect the presence of carboxyl groups in bituminous coals but they give low values due to incomplete exchange. Using the standard techniques we were unable to find any evidence for the presence of carboxyl groups either in the fresh or oxidized coal (Table 1). Oxidation at higher temperatures (140° and 190°) involves the formation of carboxyl groups but at 105° such formation is outside the limits of detection by chemical exchange. On examination of the variation of organic oxygen in the coal as a function of temperature (Figure 5) shows that there is a qualitative difference between what occurs at 105° and what occurs at the higher temperatures examined. Even extremely prolonged oxidation at 105° could never produce the oxygen levels observed at 140° and 190° after only 8 days oxidation.

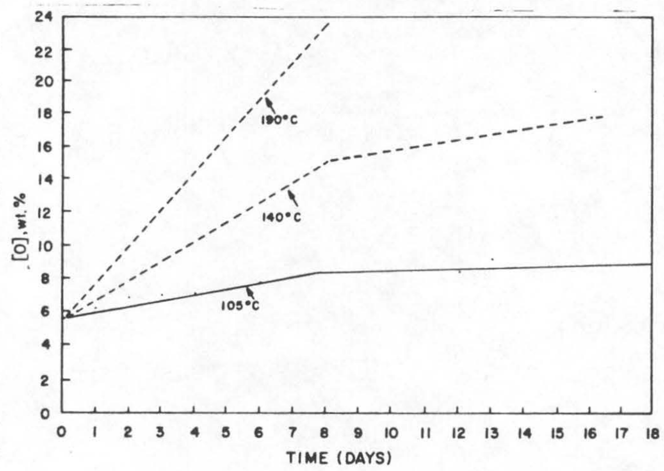


FIGURE 5. Oxidation of DEVCO Harbour 26 coal at 105°, 140° and 190° in air.

Fourier Transform Infrared Spectra

The DEVCO Harbour 26 sample was examined using Fourier Transform Infra-Red Spectroscopy with photo-acoustic detection. In this discussion we will centre our attention on the 1600 cm^{-1} band and its modifications as a function of oxidation (carbonyl formation), although other spectral features (O-H stretch and C-H stretch) may also be considered. Two appropriate techniques have been developed to indicate the extent of oxidation from an evaluation of the increasing high-frequency assymmetry of the 1600 cm^{-1} band by (i) peak half-width, or by (ii) half-peak integrated intensity.

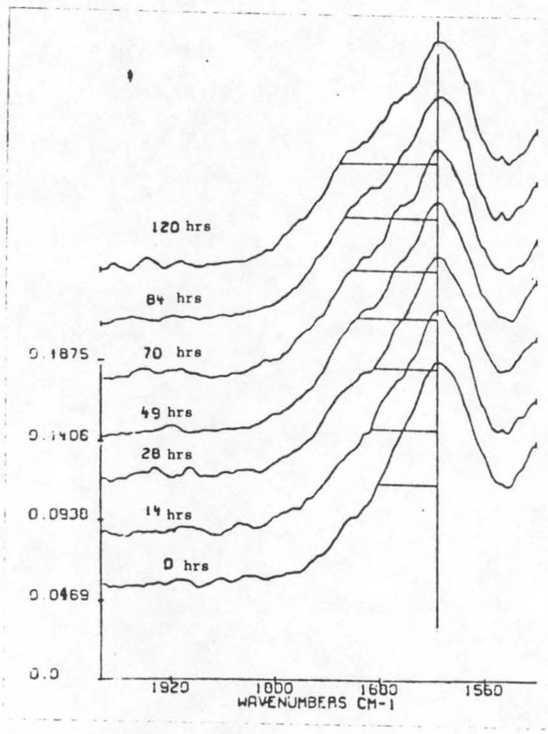


FIGURE 6. FT-IR Spectra of DEVCO Harbour 26 Coal Oxidized @ 105° for indicated time.

FTIR spectra of the coal samples whose dilatation (Ruhr) is given in Figure 1 are displayed in Figure 6 where an increase in the high-frequency assymmetry of the 1600 cm^{-1} band is observed as a function of oxidation time. This is shown graphically in Figure 7. It is clear that such an analysis can be used to evaluate the 'extent of oxidation' of a coal sample provided enough information is available to set up a calibration curve. However, the 'mechanistic' interpretation of these data is subject to caution in the light of the data in Figure 4.

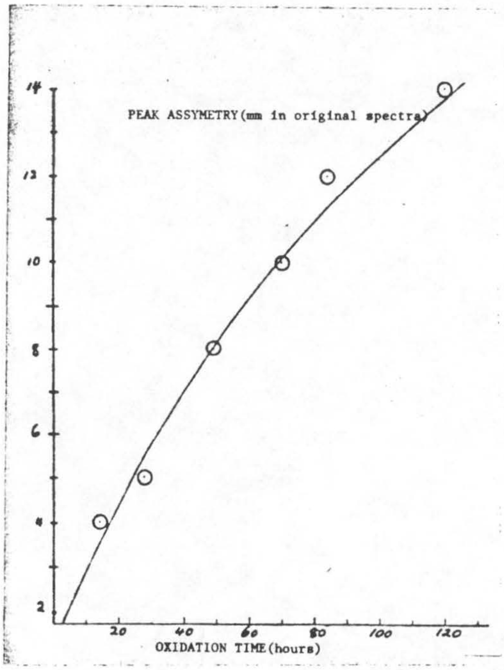


FIGURE 7. Relationship between high frequency assymmetry of the $1600\ cm^{-1}$ band for oxidized DEVCO coals.

Useful correlations between integrated intensity (1600-1800 cm^{-1}) and oxygen content can also be obtained for naturally weathered samples. Figure 8 shows partial spectra for a series of eastern Canadian coal samples taken a various distance from the seam face. The extent of oxidation decreases from top to bottom. An excellent correlation between integrated intensity and directly determined oxygen is obtained for these samples (Table II). Thus it appears that carbonyl oxygen, reflected by the integrated intensity between 1600-1800 cm^{-1}, is directly proportional to the total oxygen functionality introduced during weathering. The demonstration of this for naturally weathered coals indicates a similarity between such oxidation and that occurring in the laboratory at 105°.

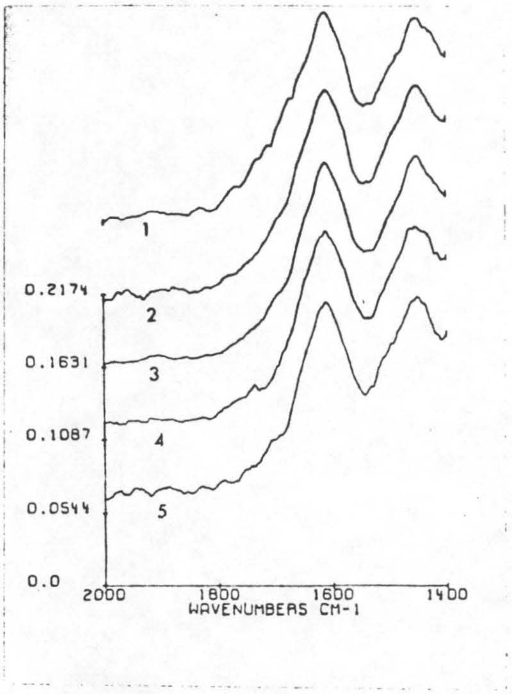


FIGURE 8. Partial FT-IR Spectra for naturally weathered samples. Weathering decreases from 1 to 5.

Correlations can also be developed between integrated carbonyl intensity and time of oxidation (at 105°). Table III shows some results for a medium-volatile biuminous coal from western Canada.

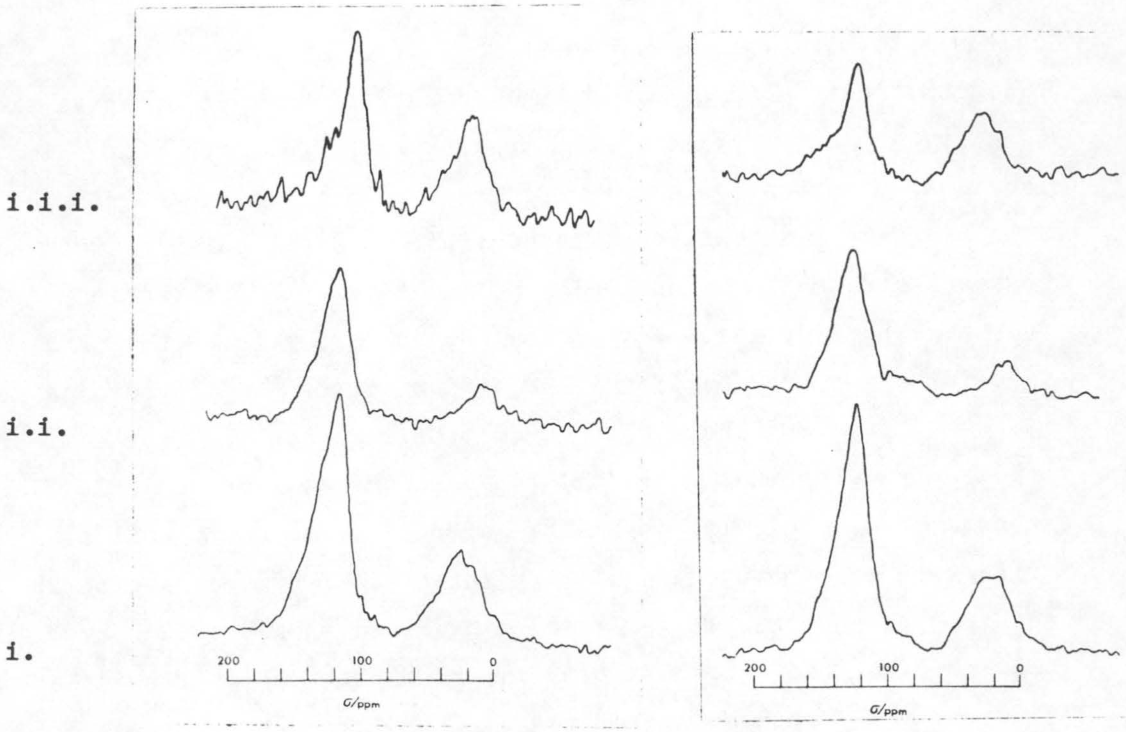
The usefulness of such correlations between infrared spectral parameters and oxidation on a practical level is evident. The rapid assessment of degree of weathering for bituminous coals is possible in a relatively simple and reproducible manner. However, the exact interpretation of infrared data in terms of oxidation mechanism remains a controversial issue (6, 7).

^{13}C nmr Studies of Weathered Coals

Recent advances, both technical and theoretical, have made it possible to obtain high resolution ^{13}C nmr spectra of solid samples. The application of these techniques to pure compounds appears to be relatively straightforward although there are still some doubts as to whether the nmr experiment is actually "seeing" all the carbons in a fossil fuel sample. A recent publication examining the question of the determination of carbon centre types in both model compounds and solid fossil fuel materials supports the quantitative use of ^{13}C nmr with cross polarization and magic angle spinning (8).

The small compositional changes that accompany mild oxidation of coal samples are rather difficult to follow by ^{13}C nmr techniques (9).Aromaticity changes alone are not sufficiently informative since this quantity may not vary much more than experimental error for oxidation levels of practical interest. Of greater interest is the dipolar dephasingexperiment where it is possible to distinguish between carbons possessing a rapid nuclear relation mechanism (i.e. attached to hydrogen) and those that do not. In particular, for aromatic carbons a discrimination between protonated and non-protonated carbons is possible.

Figure 9 shows the ^{13}C nmr (CP/MAS) spectra of the fresh and oxidized samples whose chemical composition is given in Table I. The spectra using a dipolar dephasing interval of 40 us as well as the difference spectra are given. The integrals corresponding to these spectra are shown in Table IV. The oxidized sample (192 hrs. @ 105°) has had its dilatation reduced to a nil value although melting is still observed. The change in aromaticity from fresh to oxidized coal is slight and could be considered within experimental error as could be the change in atomic H/C accompanying oxidation. The dipolar dephasing results give some clue as to what is happening. It can be seen that the ratio of non-protonated to protonated aromatic carbons changes from an initial value of 1.2 in the fresh coal to 1.8 in the oxidized sample, a substantial change even though the aromaticities change only slightly. This result is consistent with the formation of carbon-carbon single bonds between aromatic centres.



a. b.

FIGURE 9. ^{13}C nmr spectra (CP/MAS) of fresh a. and oxidized b. DEVCO coal. In each case is given i. the full spectrum, i.i. the spectrum with a dipolar dephasing interval of 40 μs, and i.i.i. the difference spectrum. Spectra were obtained on a Bruker CXP180/90 spectrometer with a cross-polarization time of 1 ms.

Oxidation of this coal at 105° also introduces phenolic –OH groups. This is clearly seen unambiguously from the ^{13}C nmr spectra of the samples methylated with $^{13}CH_3I$ using the Liotta procedure(6). Figure 10 shows that the amount of phenolic –OH is significantly increased after oxidation. Surprisingly enough Liotta has not detected the formation of phenolic –OH groups in the oxidation of Illinois #6, a coal somewhat different from the one studied here.

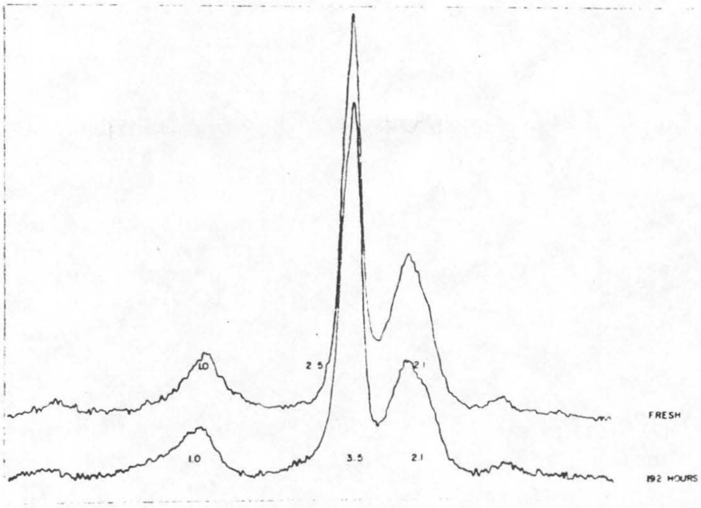


FIGURE 10. ^{13}C nmr spectra (CP/MAS) of fresh and oxidized DEVCO coal methylated with 90% $^{13}CH_3I$ using the Liotta procedure (6). Integrated intensities are given relative to the aromatic resonance. Spectra were obtained on a Bruker CXP 180 spectrometer (cross-polarization time 1 ms).

Overview

The results of our own work on coal oxidation indicate a complexity of chemical reactions which may or may not be acting independently. Carbonyl groups, in the form of carboxyl and possibly ketonic or quinone functions, are introduced during the low-temperature oxidation of a bituminous coal. Phenolic -OH groups are also introduced in significant amounts at the same time. No evidence was found for the formation of ether cross links although this has recently been considered elsewhere(6). Some of the nmr evidence (^{13}C nmr, CP-MAS, with dipolar dephasing) is consistent with the formation of carbon-carbon bonds between aromatic centres.

The intriguing problem with coal oxidation is how to explain, in mechanistic terms, the alteration of technological properties: loss of coking, reduction of liquefaction yields, increased formation of unburnt carbon in fly-ash etc. The traditional view invokes the formation of structural cross-links (in particular, ether cross-links) as the cause of the alteration of technical properties. While this is a sufficient condition the evidence to date points to a more complex situation requiring much more detailed work on a wide range of coals.

TABLE I

DEVCO Harbour 26, High-Volatile A Bituminous Coal

Proximate Analysis (wt.%)

	Fresh Coal	Oxidized (192 hrs @ 105°)
Moisture	0.86	0.66
Ash	1.27	1.11
Volatile Matter	33.58	32.34
Fixed Carbon	64.29	65.89
Ultimate Analysis (wt.%, dry)		
Carbon	84.89	83.08
Hydrogen	5.37	5.35
Sulphur	0.70	0.65
Nitrogen	2.19	1.89
Oxygen (by diff.)	4.72	7.26
Oxygen (detd.)	5.50	8.32
Atomic H/C	0.75	0.77
Formula	$C_{100}H_{7.5}O_{4.9}N_{2.2}S_{0.3}$	$C_{100}H_{7.7}O_{7.5}N_{1.9}S_{0.3}$
Dilatometric Properties (Ruhr Dilatometer)		
Softening Point, θ_S(°C)	339	362
Contraction, C(%)	24	13
Temp. Max Cont. θ_C (°C)	398	474
Dilatation (%)	293	nil
Temp. Max. Dil. (°C)	463	-
Plasticity Index, $P.I.=C/(\theta_C-\theta_S)$	0.41	0.20
Petrographic Analysis (Vol. %)		
Vitrinite	82.7	
Exinite	3.8	
Micrinite	4.2	
Semi-fusinite	6.5	
Fusinite	2.8	

R_0,max 1.07

TABLE II

CORRELATION BETWEEN INTEGRATED INTENSITY OF PAIFT SPECTRA FROM 1600-1800 CM-1 WITH OXYGEN CONTENT, BITUMINOUS COAL SAMPLES AT VARIOUS DEPTHS

Sample #	Intensity (relative)	Oxygen % (direct analysis)
1	1.0000	6.22
2	1.0940	6.79
3	1.1175	7.01
4	1.2440	7.54
5	1.4152	8.34

Intensity = 0.25 + 0.199*(Oxygen %)
r = 0.9956

Sample 5 nearest sample to coal face; sample 1 farthest.

Changing oxygen content predicts 99% of the changes in intensity.

TABLE III

WESTERN CANADIAN BITUMINOUS COAL
RELATIONSHIP BETWEEN INTEGRATED CARBONYL INTENSITY AND TIME OF OXIDATION

TIME (hrs)	CARBONYL INTENSITY (RELATIVE)	
	OBSERVED	CALCULATED
0	1.00	1.04
48	1.15	1.10
120	1.18	1.21
336	1.55	1.54

RELATIVE CARBONYL INTENSITY = 1.04 + 0.00154 x (TIME OF OXIDATION)
correlation coefficient r=0.988

TABLE IV

DIPOLAR DEPHASING - INTEGRATED INTENSITIES (Fig. 9)
DEVCO COAL

		FRESH	
		AR	AL
a. T_{DD} = 0		68.2	31.8
b. T_{DD} = 40 μs		36.9	12.0
	Ratio b/c	1.18/1	1/1.65
c. Diff		31.3	19.8

OXIDIZED (192 hrs. @ 105°C)

a. T_{DD} = 0		69.6	30.4
b. T_{DD} = 40 μs		44.7	9.9
	Ratio b/c	1.80/1	1/2.07
c. Diff		24.9	20.5

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