

AERIAL OXIDATION OF MACERAL ISOLATES FROM AN AUSTRALIAN BITUMINOUS COAL

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ABSTRACT

A comparative study of the relative reactivities of Run-of-the-Mine (ROM) Blair Athol coal and constituent maceral lithotypes, fusain and vitrain to laboratory oxidation conditions at 100°C is reported using a surface reflectance FTIR technique (DRIFT). The DRIFT spectra of pure maceral isolates established the aliphatic content to be in the order of exinite >> vitrinite > inertinite. The difference spectra of the maceral lithotypes fusain and vitrain show the ready loss of aliphatic groups in the former as an early oxidation step. Oxygen uptake by vitrain is initially slow compared with ROM and fusain coals. Carbonyl formation is a primary reaction in the earliest stages for all coal samples studied, and on more extended oxidation, leads to a range of oxygen functionalities including a shift of carbonyl absorptions to higher wavenumbers consistent with anhydride and lactone formation.

INTRODUCTION

Atmospheric oxidation or weathering of coal can result in the deterioration of many of its technologically important properties thereby significantly altering the utilization potential of coal. We are engaged in a longer term study of the chemistry of Blair Athol coal and the chemical effects of weathering has been one topic of major interest (1). Blair Athol coal from Queensland has an ASTM classification of high volatile bituminous C and is typical of many Gondwanaland coals in that it has a high inertinite maceral content. The porous nature, high moisture holding capacity, and very good steaming coal properties place Blair Athol towards one end of the range of Australian inertinite-rich coals.

The main seam of Blair Athol is best described as a durain coal but within the deposit samples of the maceral lithotypes fusain and vitrain occur, and this has allowed a chemical study to be undertaken of the effect of prolonged oxidation of each maceral lithotype and a comparison with Run-of-the-Mine coal (ROM) to be made. More recently we have been able to separate Blair Athol coal by the Density Gradient Separation technique (2,3) into high purity maceral isolates of exinite, vitrinite and inertinite. Their study, primarily by infrared spectroscopy, has further refined our understanding of the chemically reactive centres involved in coal oxidation and the relative reactivities of the macerals.

EXPERIMENTAL

The coal used was from the Blair Athol coal-field located in Queensland, Australia and was received as -40mm pieces in sealed containers. The naturally occurring maceral lithotypes were chosen with the assistance of the mine geologist and identification was based on their physical appearance (4). The 'pure' maceral isolates were obtained from a sample of ROM coal with the assistance of G.R. Dyrkacz and C.A.A. Bloomquist at the Argonne National Laboratories (U.S.A.) according to their published Density Gradient Centrifugation (DGC) procedure (2,3).

The naturally occurring maceral concentrates and a sample of ROM coal were oxidized at 100°C under a continuous flow of moist air (3 ml sec⁻¹) in a modified Kugel oven. A run was also performed under a nitrogen atmosphere. Samples were taken at regular intervals and stored in nitrogen flushed vials to prevent further oxidation before analysis.

Diffuse Reflectance FTIR (DRIFT) Spectra were obtained on a Nicolet 60SX FTIR equipped with a nitrogen cooled, high sensitivity mercury : cadmium : tellurium detector. Each sample resulted in a single sided interferogram of 4096 data points which provided a resolution of 4 cm⁻¹. 500 scans per sample were obtained.

RESULTS AND DISCUSSION

The naturally occurring maceral lithotypes were readily distinguished by their physical appearance. The vitrain sample was black, of very bright lustre and brittle. The fusain sample was black in colour and very soft and friable. Its physical structure appeared to be more porous and open and usually had a higher water content than the other samples investigated. The high proportion of this maceral lithotype in Blair Athol coal would appear to be the cause of the high water content of the 'as mined' coal (typically ~16%).

TABLE 1. Elemental and Petrographic Analyses of Blair Athol Coals

Elemental Analyses	C	H	N (DAF)	S	O*	Ash	H/C (atomic)	O/C
Run of Mine (ROM)	82.55	4.72	1.88	0.26	10.59	6.5	0.658	0.102
Vitrain	80.97	4.92	1.79	0.48	11.84	4.4	0.724	0.084
Fusain	80.27	4.06	1.78	1.30	12.59	9.4	0.602	0.118

* By difference

Petrographic Analyses

	Exinite	Vitrinite (wt %, mmf)	Inertinite
Run of the Mine	4.1	28.4	67.5
Vitrain	8.2	78.9	12.9
Fusain	3.1	15.7	81.2

Table 1 reports the elemental and petrographic analysis of the samples. Although these samples are petrographically and physically quite different, this is less obvious from their elemental analysis with the main difference being the hydrogen content of the samples. A variation in sulphur content is also seen.

Vitrain has the highest H/C value of the samples studied while fusain has a relatively low H/C value. The ROM and durain coal samples have similar H/C values and these lie between those for fusain and vitrain. These observations are strikingly reinforced by the DRIFT spectra of the C-H region (Fig. 1) which reveals that the aliphatic content of the maceral isolates is exinite >> vitrinite > inertinite.

Figure 1 reports for the first time DRIFT spectra of Gondwanaland coal maceral isolates of very high purity (98.5% and better). In addition to its high aliphatic component, the other distinguishing feature of the exinite fraction is the strong C=O absorption centred at ~1700 cm⁻¹ which has also been reported for Northern Hemisphere exinites (5,6). The broad 1100-1300 cm⁻¹ stretch which can be assigned to C-O type stretches together with the strong carbonyl peak and apparent lack of a

strong -OH band ($3200-3600\text{ cm}^{-1}$) suggest esters (especially alkyl esters in this case) may strongly contribute to the exinite fraction. The carbonyl absorption is much less marked in the spectra of the other two macerals. The DRIFT spectra suggest a strong aromatic contribution to both the vitrinite and inertinite. Pyrolysis-GC/MS also indicates that the vitrinite sample contains more phenolic material than either of the other two macerals. The unusually high, inherent water content of Blair Athol coal can be associated with the hydrophilic properties of these hydroxyl-containing residues as revealed by the release of the phenolic components on pyrolysis. Water is considered to be a factor in the weathering of coal.

Figure 2 gives further insights to the type of C-H bonding in the macerals, the changes in which are noticeable during coal oxidation. Fourier Self Deconvolution (FSD) has been used to enhance the resolution of the aliphatic region and give more specific structural information (7). The aliphatic symmetric and asymmetric bands resolve into asym. $-\text{CH}_2$ and asym. $-\text{CH}_3$ (2920 and 2960 cm^{-1} respectively) and sym. $-\text{CH}_2$ and sym. $-\text{CH}_3$ stretches (2853 and 2870 cm^{-1} respectively). The deconvoluted exinite spectra show extremely strong methylene stretches (2853 and 2920 cm^{-1}) relative to methyl stretches (2870 and 2960 cm^{-1}). This suggests a strong contribution of long chain aliphatic material to this maceral and is consistent with the release of $n\text{-C}_{10}$ to $n\text{-C}_{27}$ hydrocarbons by thermal distillation from ROM coal (8). By comparison, the deconvoluted vitrinite and inertinite spectra suggest a greater methyl contribution to their aliphatic component. The technique, however, was not successful in further improving the resolution of the carbonyl region due to complications with moisture variations.

Oxidation in a stock-pile is initially a surface phenomenon and we have used the DRIFT technique to observe sites of oxygen incorporation as revealed by IR. The oxidation profiles reported here are after oxidation at 100°C for convenience of study, although similar changes do occur at lower temperatures (i.e., 50°C) but observable only after extended periods of time.

Figure 3 shows the variation in atomic O/C ratio with time of oxidation for the natural maceral concentrates and the ROM coal. The ROM coal treated at 100°C but in nitrogen, showed only a small increase in O/C. Although a small amount of adventitious oxygen may have reacted with the coal, the increase in O/C is more likely due to the loss of volatile hydrocarbons through the thermal disruption of the coal (8). The ROM coal treated at 100°C in a constant air flow showed an increase in O/C value from 0.102 to 0.200 over a period of 20 days. The O/C increase is initially rapid but after 2 days the rate of increase slows. Although fusain has a higher initial O/C value (c.a., 0.118) it also shows a rapid initial increase. After 20 days the Fusain sample reached an O/C value of (0.248). The Vitrain sample, however, displayed a contrasting behaviour. From a relatively low O/C value of 0.084 it showed a slow initial increase in O/C over the first two days at 100°C , followed by a strong increase in O/C so that after 20 days it reaches an O/C value of 0.22.

It is evident that there is a difference in the mechanism or rate of oxygen reaction between the ROM coal and fusain sample when compared with the vitrain sample. This difference is undoubtedly due to the differences in the chemical composition of the coal maceral lithotypes and reflects the structural differences seen in the DRIFT spectra of the pure macerals (Fig. 1).

The structural changes occurring during the 100°C oxidation of the coal samples are seen in the DRIFT spectra of the $4000-800\text{ cm}^{-1}$ region (Fig. 4). The loss of aliphatic material indicated by the decrease in the aliphatic stretches ($2800-3000\text{ cm}^{-1}$) with oxidation is common to all the coal samples examined but is especially severe for the fusain sample which is 81% Inertinite. Fusain, although having little aliphatic material initially, is almost devoid of aliphatic material after 10 days oxidation.

Accompanying this decrease in aliphatic material is an increase in the C=O regions (centred at 1700 cm^{-1}). The formation of this peak begins early in all samples but for the fusain sample is resolved after 1 day of oxidation. Although the C=O peak is complex and consists of many overlapping bands it can be resolved into at least three major bands at 1840, 1770 and 1715 cm^{-1} . The 1840 cm^{-1} peak appears after prolonged oxidation and has been assigned to anhydrides (9). The appearance of this peak was not observed for the coal oxidized under nitrogen and hence is a genuine oxidation product. Careful examination of the spectra also reveals that the vitrain sample shows the greatest increase in the carbonyl region. This increase together with the greater aliphatic content of vitrain is consistent with benzylic sites as possible centres of oxidative attack. This is also supported by the observation that the pyrolytic yield of alkylated aromatics (including phenols) decreases more rapidly relative to their non-alkylated analogues as determined by Py-GC/MS.

The difference spectra (Fig. 4d) are useful in illustrating the changes in functionality consequent upon oxidation. The strong positive absorptions in the carbonyl region confirms earlier observations but further analysis reveals that the nature of the carbonyl groups formed changes in the latter stages of oxidation. For both the fusain and the vitrain samples a shift to higher wavenumber is seen for the carbonyl peaks in the latter stages of oxidation (i.e., 20-10 days). While fusain shows an early and continual loss of aliphatic material, vitrain shows little if any loss during the early stages (1-0 days). Fusain also displays a strong increase in the C-O region ($1100\text{-}1300\text{ cm}^{-1}$) in the latter stages of oxidation but which is not so significant as for the vitrain sample.

These observations are consistent with views that multiple pathways of oxidation are operative. The chemical nature of the coal and hence its maceral composition appears to influence the nature of the oxidative processes occurring. However, the resolving limits of IR spectroscopy allow us to observe only the broader effects. Even so the data suggest the insertion of oxygen into carbon centres that yield a variety of carbonyl containing structures. Some of these will be precursors for more complex products such as anhydrides. The data suggest that esters including lactones rather than carboxylic acid centres are formed. Small changes are also seen in the hydroxyl region. These changes are consistent with the initial formation of peroxides (10) which are known to show instability at 100°C and can be expected to lead to carbonyl as well as hydroxyl functionalities.

Figures 3 and 4 demonstrate clear differences of reactivity to oxidation between ROM coal and its constituent maceral lithotypes fusain and vitrain. The differences between ROM and fusain coals do not seem explicable in terms of Inertinite content only, suggesting that the physical properties of the fusain play a significant role. Since coal measures are by no means homogenous in their maceral composition, the data presented exemplify the predictive value of knowing relative chemical reactivities of constituent macerals, which could then be applied to minimizing handling problems where autooxidation can cause difficulties.

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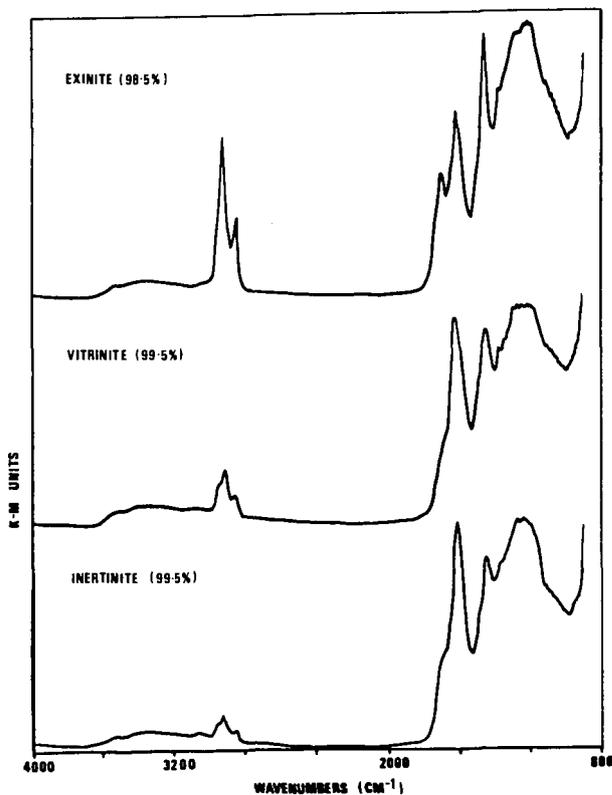


Figure 1. IR spectra (4000 - 800 cm^{-1}) of Blair Athol DGC pure maceral isolates.

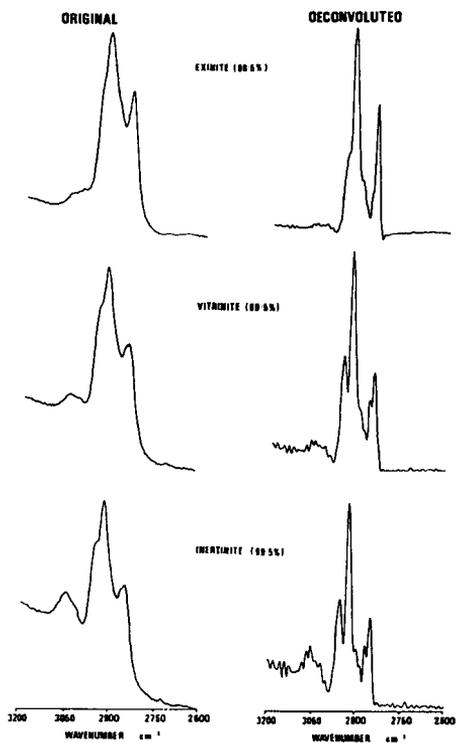


Figure 2. Original and deconvoluted DRIFT spectra (3200 - 2600 cm^{-1}) of the Blair Athol DGC pure mineral isolates.

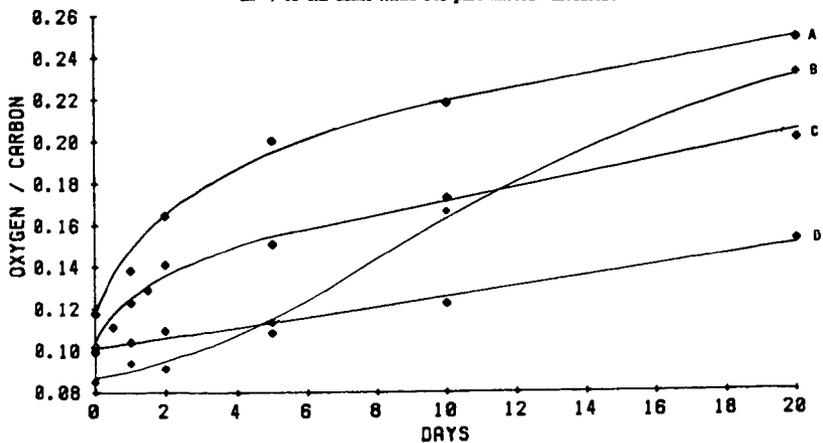


Figure 3. Variation in atomic O/C ratio with increased oxidation at 100 C.

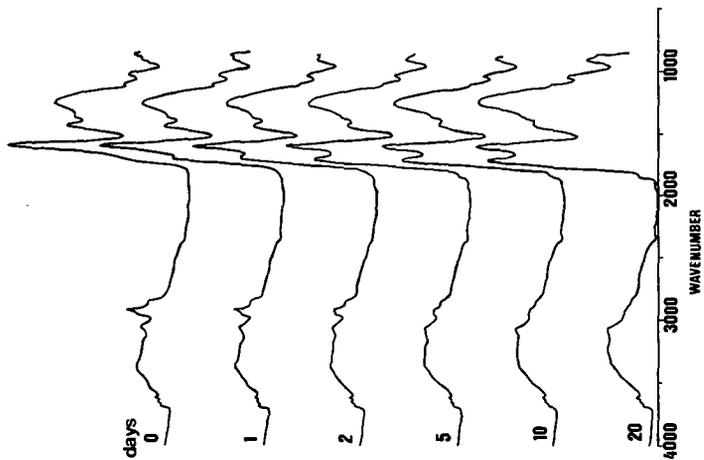


Figure 4(b). 4000 - 800 cm^{-1} DRIFT spectra of unoxidized (0 days) and progressively oxidized fusicin.

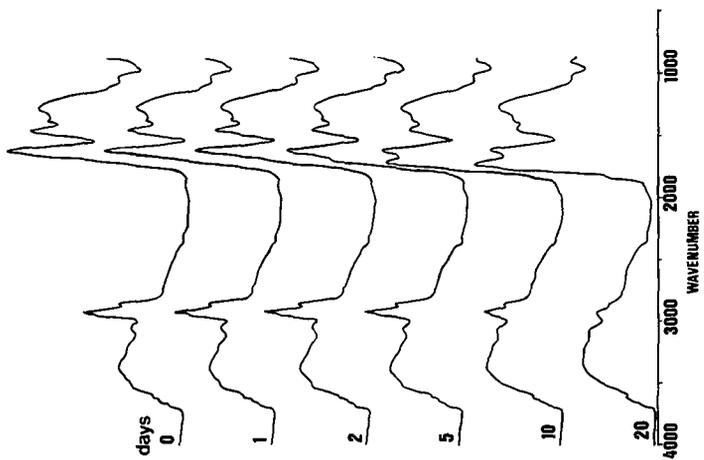


Figure 4(a). 4000 - 800 cm^{-1} DRIFT spectra of unoxidized (0 days) and progressively oxidized vitrain.

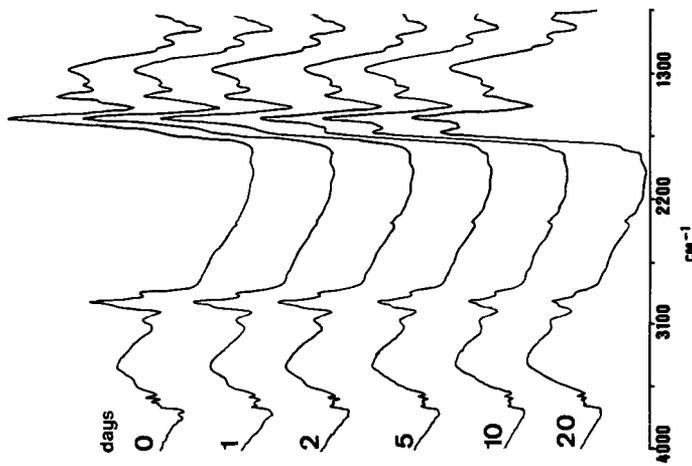


Figure 4(c). 4000 - 800 cm^{-1} DRIFT spectra of unoxidized (0 days) and progressively oxidized RCM coal

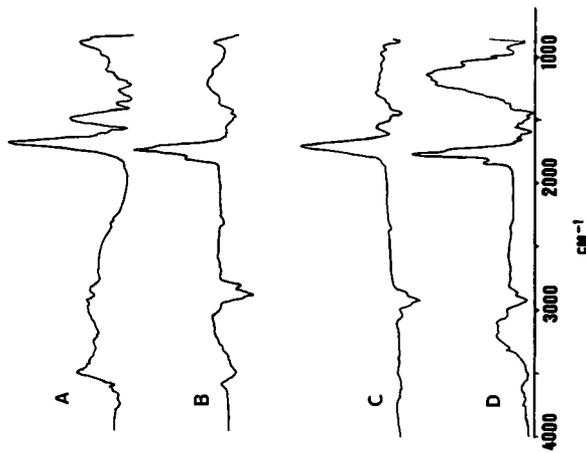


Figure 4(d). DRIFT subtraction spectra of: (A) oxidized (1 day) - unoxidized vitrain, (B) 20 day - 10 day oxidized vitrain, (C) oxidized (1 day) - unoxidized fusain, (D) 20 day - 10 day oxidized fusain.