^{1}H NMR EVIDENCE TO SUPPORT THE HOST/GUEST MODEL OF BROWN COALS

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ABSTRACT

Many groups have proposed a two-component molecular structure for brown coals. This hypothesis has been investigated by in situ ^{1}H NMR measurements during heating (to 875 K) of a suite of Australian and New Zealand brown coals, a set of Morwell brown coal lithotypes, and extracts and extract residues of some of these coals. The variation in the behaviour of the coals during heating and pyrolysis, although significant, was not particularly sensitive to lithotype ranking but showed a strong correlation with atomic H/C ratio. The extracts were found to be fully mobilized in the temperature range 470-700 K whereas the residues essentially remained rigid molecular lattices throughout the heating and pyrolysis. This behaviour was independent of the lithotype and H/C ratio of the source coal. The much higher H/C ratios of the extracts compared to the residue materials allow these observations to be explained (to a first approximation) in terms of the host/guest hypothesis whereby the coals are composed of extract (guest) and residue (host) materials in differing proportions.

INTRODUCTION

Morphological variation in brown coal seams has led to 'lithotype' classification schemes. The classification for Victorian brown coals is based on the colour of the dried, weathered coal and ranges from 'pale' to 'dark' in five steps. A number of studies (1-4) have sought to establish relationships between lithotype and the composition, structure and properties of the coals. Although these studies have established that major chemical (2) and physical (3) differences do exist between the extreme pale and dark lithotypes within a given seam, it has not been demonstrated that basic coal properties are significantly ranked by the lithotype classification.

Palaeobotanical analysis of a lithotype suite (5) has led to the suggestion that the principal factor in producing lithotype variation was the prevailing depth of the water table during deposition and has shown that the content of woody material and the extent of gelification decreases along the sequence from dark to pale lithotype. Maceral analysis of this lithotype suite (from the LY1276 core, Latrobe Valley, Victoria) showed that the principal differences in the maceral composition were in the distribution of huminite, which was much greater in the three lighter lithotypes, and in the liptinite content, which was significant only for the lighter lithotypes (5).

NMR and infrared spectroscopic analysis of the same lithotype suite and a set of light lithotypes giving a depth profile of the same core revealed that the main chemical variations between lithotypes were higher aromatic and lower carbonyl/carboxyl contents in the darker lithotypes, but correlation of these criteria with lithotype ranking was poor (6). By contrast, other studies (7,8) have shown that dark lithotypes have greater polar functionality, including carbonyl/carboxyl content, than the corresponding pale lithotypes. Moreover, Hatswell et al. (4), who studied the liquefaction properties of a range of lithotypes (also from the LY1276 core) with similar elemental compositions (to remove any effect of H/C), found no variation with lithotype. It would therefore appear that correlations between lithotype classification and maceral analysis or chemical properties are poor.

Several groups (1-3, 9) have considered brown coal structure at the molecular level and have suggested that brown coals have a two-component molecular structure. Hatcher's proposal (1), based mainly on ^{13}C cross-polarization magic angle spinning

NMR and infrared studies of peats and a range of other materials at different stages of coalification, is that coals are derived from a mixture of highly aliphatic sapropelic material of aquatic origin on the one hand and vascular plant-derived lignin residues on the other.

Lynch and Webster (3), in a preliminary study of the pyrolysis behaviour of brown coal lithotypes, found a correlation between the thermal behaviour and H/C ratio of the coals and also noted a close identity between the proportion of the hydrogen mobilized during heating and that lost by volatilization below 800 K. It was argued that these observations were consistent with Hatcher's two-component structural model.

Redlich et al. (9) separated a suite of brown coals with a wide range of H/C values into two fractions by heating the dried coal under nitrogen in the presence of decalin at 593 K for 1 h and, after cooling, extraction with dichloromethane. These apolar, non-hydrogenating conditions were thought to be sufficiently mild to avoid major decomposition of the coal and, essentially, to result in the extraction of physically bound aliphatic materials, although even at temperatures as low as 600 K some decarboxylation did occur. The decalin used in the dichloromethane extraction process could not be easily separated from the total extract, therefore the pentane-insoluble or 'asphaltene' part of the extract was studied. This treatment excluded the decalin together with the less polar species from the extract. The pentane insolubles accounted for 1/3 of the total extract. In all cases, the properties of the extracts and residues were found to be mostly independent of the source coal. The residue fraction, or 'host', was described as a phenolic, macromolecular material, probably lignin-derived, while the 'guest' (the dichloromethane-soluble fraction) was always predominantly aliphatic (f_a ~0.3) (9). This lack of variation led to the conclusion that the differences in brown coal properties depend to a first approximation on the ratio of these fractions present in the coal.

Verheyen et al. (6), as part of their study, separated lithotype specimens into alkali soluble 'humic acids' and insoluble 'kerogen'. The 'humic acids' accounted for ~20% of the dark to ~50% of the pale lithotypes, the actual quantities depending on the severity of the treatment. However, in contrast to the fractions separated by the method of Redlich et al. (9), which yielded similar proportions of extract and residue, the properties of both the 'humic acid' and 'kerogen' fractions varied with lithotype and the H/C of the source coals.

The preliminary study by Lynch and Webster (3) using the proton nuclear magnetic resonance (^{1}H NMR) thermal analysis (PMRTA) technique (10), which supported the host/guest model, is extended here to a wider selection of brown coals (Table 1) including some New Zealand coals and the lithotype set from the LY1276 core studied by Hatswell et al. (4). The residues and pentane-insoluble extracts of some of the coals prepared by the method of Redlich et al. (9) were also examined.

EXPERIMENTAL

Whole coal samples were predried at 378 K under nitrogen. Samples of ~200 mg were pyrolysed in open glass tubes, under flowing nitrogen, at a heating rate of 4 K/min to temperatures of 875 K in an NMR furnace-probe (11). Solid echo measurements of the proton NMR transverse relaxation signal, I(t), were made on the specimens at regular intervals during pyrolysis. The intensity of the signals was empirically corrected to account for the temperature sensitivity of the NMR measurement. (See Lynch et al. (10) for a more detailed description of the techniques used.)

Residues and extract specimens were supplied in a predried state and measured under the same conditions as the whole coals. Yields of residue obtained (wt% basis) are given in Table 1, together with elemental compositions and lithotype classifications for the brown coals and lithotypes.

TABLE 1. DATA FOR BROWN COAL SUITE

Sample		H/C	C[a]	O[a]	Lith[b].	Resid. (wt%)	%mm	Coal M_{400} (kHz^2)	Coal M_{600} (kHz^2)	Resid. M_{600} (kHz^2)
Victorian and New Zealand coals										
1	Bacchus Marsh	1.22	70.5	20.6	1	50	62	24.5	9.5	24.8
2	Roxburgh (NZ)	1.11	69.8	23.0	-	60	55	19.5	11.6	25.4
3	R5	1.08	70.9	21.8	1	59	58	21.7	10.2	24.7
4	H1317	0.99	71.4	22.0	1	67	48	26.1	13.8	25.2
5	Idaburn (NZ)	0.95	68.4	25.5	-	72	39	19.5	15.7	25.6
6	Newvale (NZ)	0.91	67.6	26.6	-	77	28	24.7	19.7	26.4
7	R30	0.89	69.5	24.5	4	80	26	24.8	20.3	25.9
8	H1317	0.85	70.6	24.4	5	-	21	26.8	22.9	-
9	LY1276/Morwell	0.79	68.4	26.2	5	88	15	25.4	24.2	26.1
Lithotype suite										
a	LY1276/Morwell	0.83	66.8	27.0	1	-	33	23.0	18.0	-
b	LY1276/Morwell	0.78	66.1	28.0	2	-	27	25.0	19.6	-
c	LY1276/Morwell	0.80	66.5	27.2	3	-	23	25.2	20.8	-
d	LY1276/Morwell	0.81	66.2	26.6	4	-	23	25.7	20.5	-
e	LY1276/Morwell	0.75	67.0	27.2	5	-	23	24.2	21.3	-

[a]Expressed as wt% on a dry, mineral matter and inorganic ion free basis.
[b]Lithotype ranking 1 = pale, 5 = dark.

RESULTS

Figure 1 shows stacked plots of the ^1H NMR transverse relaxation signals obtained during PMRTA of a Bacchus Marsh brown coal and its extract and residue specimens. Analysis of such data provides parameters that semi-quantitatively describe aspects of the composition and molecular dynamics of the specimens during heating. Thus, (i) the initial intensity, I(0), of the transverse relaxation signal (taken as the peak of the solid echo, Fig. 1) gives an estimate of the residual hydrogen content of the specimen; (ii) in general each of the ^1H NMR signals can be resolved into a slowly relaxing exponential component fitted at longer times (the 'mobile' component), and a rapidly relaxing Gaussian-like residual signal(the 'rigid' component). Because resolution of these components is somewhat subjective and sensitive to the details of the curve fitting procedure used, care was taken to use a consistent procedure to analyse all the data. The initial intensities of the fitted components are taken as measures of the fraction of hydrogen in 'mobile' and 'rigid' (on a time scale of ~ 10^{-5} s) molecular structures of the specimen; (iii) each recorded NMR signal, I(t), is characterized by an empirical second moment, M_{2T}, of a truncated (at 10 kHz) frequency absorption spectrum obtained by its Fourier transformation (10). For a rigid organic solid the magnitude of M_{2T}, which is an intensive property, is directly related to the average short range (~1 nm) proximity of hydrogen atoms to each other. However, importantly, the contribution of a particular molecular unit within a structure to this quantity rapidly decreases with the onset of its molecular mobility so that M_{2T} is inversely related to the average molecular mobility of the structure.

The temperature dependences of the residual hydrogen content and the percentage of the initial hydrogen content that is defined as mobile are plotted in Fig. 2a for the high H/C Bacchus Marsh pale lithotype coal and its extract and residue specimens. The corresponding pyrograms for the empirical second moment are compared in Fig. 2b. The residual hydrogen content pyrograms define the region of main pyrolytic decomposition and loss of volatiles, and the second moment and remaining

mobile hydrogen pyrograms reflect changes in the molecular mobility of the specimens. Data for the LY1276 lithotype suite are presented in Fig. 3 and results for the suite of brown coals are shown in Fig. 4. The second moment pyrograms for residues of samples 1-7 and 9 and pentane-insoluble extracts of samples 1,3 and 4 are compared in Fig. 5.

The M_{2T} values at 400 K (M_{400}) and at 600 K (M_{600}) and %mm (the greatest remaining mobile hydrogen value achieved during the pyrolysis, which occurs at about 600 K for all the brown coals) are secondary parameters derived from the pyrograms. The values of M_{600} and %mm for the coals and M_{600} for the residues are plotted against H/C in Fig. 6, and in Fig. 7 %mm for the coals is plotted against the yield of residue.

DISCUSSION

The Bacchus Marsh, R5 and H1317 (sample 4, pale lithotype) brown coals gave high enough yields of extract to allow PMRTA of their extracts. PMRTA data for the Bacchus Marsh coal, which had the highest H/C and extract yield of the brown coals, its 'asphaltene' extract and its residue material are compared in Figs 1 and 2. Although their M_{2T} values (Fig. 2b) indicate that these materials are not totally rigid molecular lattices on the time scale of 10^{-5} s at room temperature, the absence of a significant slowly relaxing exponential signal shows that none of these materials contains highly mobilized components. The similarity of the three M_{2T} values at room temperature (Fig. 2b) is unexpected. The common value of 30 kHz^2 is typical of a rigid aromatic lattice (e.g. bituminous coal) but much lower than that for a rigid aliphatic lattice. This indicates a degree of molecular mobility within the aliphatic structures to give lower M_{2T} values which are fortuitously similar to the value for the (presumed) rigid aromatic structures in the coals.

The extract became fully mobilized on heating above 460 K whereas the residue acquired a maximum of only 15% mobile structure near 600 K. The whole coal specimen also passed through a well defined maximum of 60% mobile structure near 600 K. In each case it can be seen that as heating proceeded beyond 600 K there is a parallel between 'devolatilization', indicated by the decline in residual hydrogen, and the rapid loss of the mobile component of the remaining sample (Fig. 2a). The pyrograms in Fig. 2 clearly distinguish the different thermal behaviour of the Bacchus Marsh coal, residue and extract specimens and qualitatively display the intermediate or composite nature of the whole coal.

There is considerable variation in the thermal properties of the individual brown coals (samples 1-9) as shown in Fig. 4. These coals exhibit a strong correlation between the yield of residue and hydrogen content but none with carbon content (Table 1), therefore the residue and extract materials must have vastly different hydrogen contents but similar carbon contents. A weaker but significant positive correlation between the yield of residue and oxygen content suggests that the residue would be more oxygen-rich than the extract.

In the light of the two-component hypothesis, the great difference between the H/C values of extract (1.4) and residue (0.6) materials from this suite of coals (9) suggests a strong correlation between thermal properties and H/C ratio of the brown coals. This is seen to be the case at higher temperatures (Figs 4 and 6). In particular the maximum extent of mobilization, as indicated (inversely) by M_{600} and (directly) by %mm, increased with increasing H/C of the coals (Fig. 6). However below 500 K the coals showed some individual variations which were not H/C dependent.

The fact that the PMRTA parameters near 600 K correlate strongly with H/C whereas below 500 K they do not is probably the result of variations in the interactions between the extract and residue in the source coals. The low molecular weight molecules may not be uniformly dispersed and may range from those that are

intimately interacting with the 'host' so that their thermal properties are those of a sorbed phase to those that are clustered and behave similarly to the bulk extract. Therefore the observed variations of M_{400} (Table 1) may reflect variations in the dispersion of the 'guest' molecules in the coals. Alternatively there is some evidence that the extracts from coals that show relatively lower M_{400} values are richer in straight-chain aliphatic materials (P. Redlich, unpublished data). Both these physical and chemical distinctions would be lost at higher temperatures where the 'guest' molecules are fully mobilized.

In contrast, the second moment pyrograms of the residues from these coals (Fig. 5) show that the residues all behaved similarly and acquired little molecular mobility during the pyrolysis. This close similarity is consistent with the host/guest hypothesis and is in agreement with earlier work (9) which showed that the properties of the 'host' varied little between the brown coals. It is possible that the minor degree of structural mobility acquired by the residue specimens was a consequence of their incomplete extraction and/or the retention of some of the extraction solvent. The latter possibility is supported by the noticeably earlier loss of (hydrogen) volatiles by the residue than by the coal or extract (Fig. 2a).

The temperature variation of the NMR signals of the extracts (e.g. Fig. 1c) and the second moment values calculated from them (Fig. 5) show that the extracts remain fully mobilized in the temperature range 470-700 K. At higher temperatures, the rapid increase in M_{2T} values reflects the rapid loss of volatiles and indicates that the material left after volatile evolution, containing 10% of the original specimen hydrogen (Fig. 2a), is a rigid coke at its temperature of formation.

Variations are apparent in the M_{2T} pyrograms (Fig. 5) of these extracts. For example, H1317 coal extract (from sample 4) softened at a higher temperature than the extracts of the other two coals. In addition, a secondary M_{2T} maximum at 630 K was observed for this extract, which suggests that rapid crosslinking reactions may have been occurring, leading to a reduction in structural mobility with increase in temperature/time.

Redlich et al. (9) have emphasised the direct linear relationship between the yield of extract and H/C ratio in support of the host/guest model for brown coals. They have also demonstrated that hydroliquefaction reactivity is closely correlated to atomic H/C (9) and Brookes et al. (12) have shown strong linear correlations between the intensity of infrared aliphatic C-H stretching bands and the H/C content of these coals. The good linear relationships between the maximum extent of thermally activated molecular mobility (%mm) and yield of extract residue on the one hand and H/C ratio on the other (Figs 6 and 7) are further strong support for this two-component model of brown coal structure. The identification of the extractable material as the component that is thermally mobilized in the whole coal structure, suggested by the PMRTA results, also supports the contention that the method of extraction used by Redlich et al. (9) does not chemically degrade the coal structure to any great extent.

Comparison of the PMRTA pyrograms (Fig. 3) of the five LY1276 lithotypes, which were chosen to give as wide a lithotype range as possible with minimum variation in elemental analysis (4), establishes that the thermal behaviour within this lithotype set was very similar and hence relatively insensitive to lithotype ranking.

CONCLUSIONS

1. The thermal behaviour under pyrolysis conditions of a suite of brown coals and their extracts and residues, as revealed by PMRTA, lends further support to the host/guest model of these coals. Although the residues and extracts showed very different thermal behaviour, the results within each group were similar and independent of the H/C value of the source coals. On the other hand the thermal behaviour of the coals varied significantly and there was a strong positive

correlation between the maximum extent of molecular mobilization during heating and both H/C and extract yield. The much higher H/C ratio of the extract compared to the residue material allows these observations to be explained in terms of the host/guest hypothesis whereby the coals are composed of extract and residue materials in differing proportions.

2. The thermal behaviour of brown coals of similar H/C is insensitive to lithotype.

3. Hydrogen content or atomic H/C ratio gives a much better correlation with PMRTA parameters at temperatures above 500 K than lithotype.

4. The molecular structure of the residues was largely immobile and hence relatively unreactive during heating to ~ 875 K. The pentane-insoluble 'asphaltene' extract softened at ~380 K and devolatilized rapidly above 700 K leaving some rigid coke residue.

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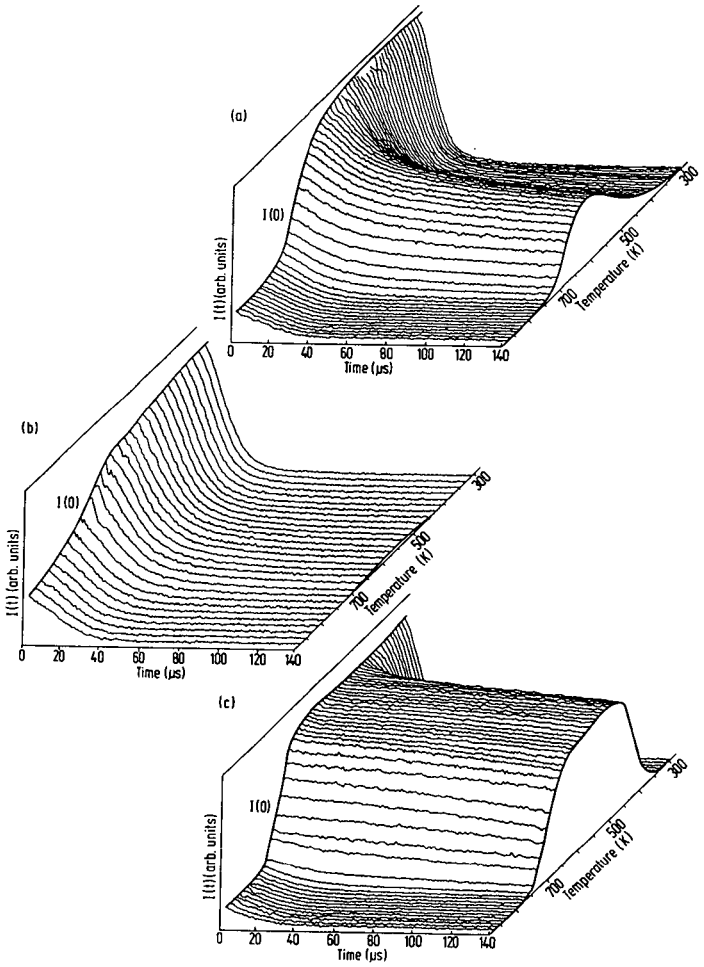

Figure 1. Stacked plots of signals obtained from ^{1}H NMR thermal analysis of (a) a Bacchus Marsh brown coal, (b) the residue after treatment at 593 K with decalin, followed by room temperature extraction with dichloromethane (9) and (c) the dichloromethane-soluble, pentane-insoluble fraction of the 593 K extract (9). The signals have been interpolated to 10 K intervals.

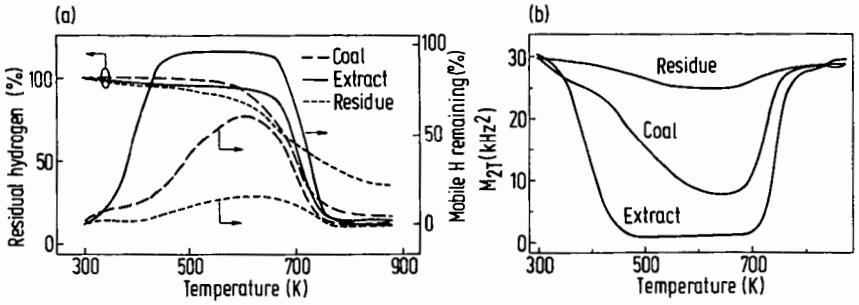

Figure 2. Plots of (a) residual hydrogen content and remaining mobile hydrogen content and (b) M_{2T} (10 kHz truncation) for a Bacchus Marsh coal, its residue and its extract during pyrolysis at 4 K/min.

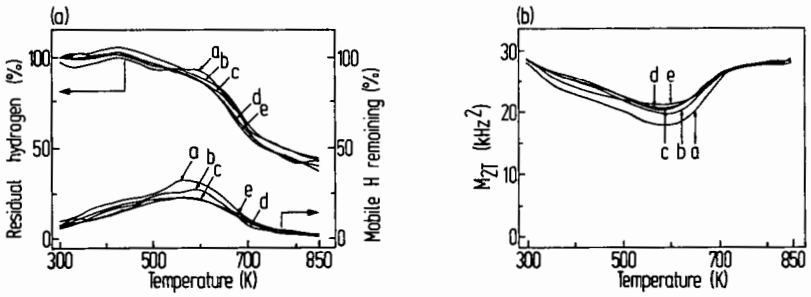

Figure 3. Plots of (a) the residual hydrogen content and remaining mobile hydrogen pyrograms and (b) the M_{2T} pyrogram for the LY1276 suite.

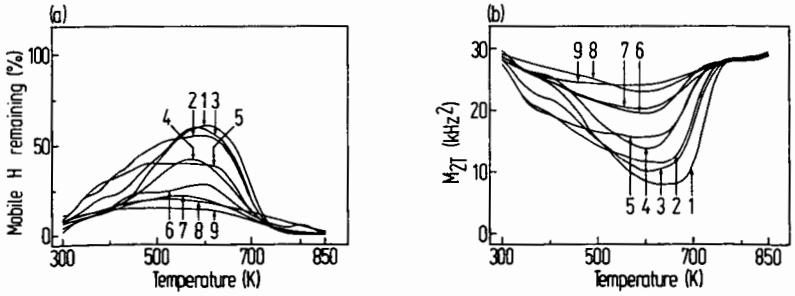

Figure 4. Plots of (a) the remaining mobile hydrogen pyrogram and (b) the M_{2T} pyrogram for the brown coals (samples 1-9).

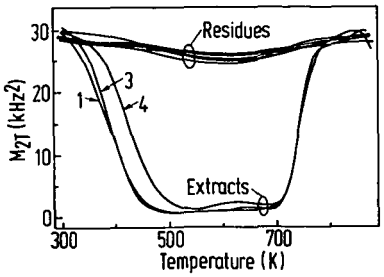

Figure 5. M_{2T} pyrograms for the residues of samples 1-7 and 9 after extraction, and the extracts of samples 1, 3 and 4.

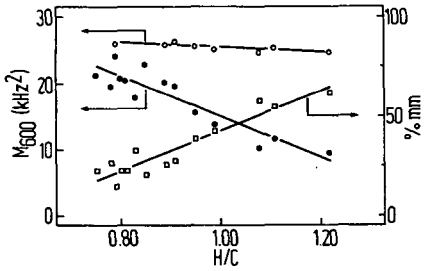

Figure 6. Variation with H/C of the extent of maximum mobility (%mm, □) and M_{2T} at 600 K (M_{600}, ●) for all samples, and M_{2T} for the residues at 600 K (o).

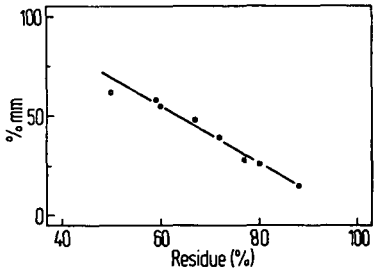

Figure 7. Plot of the extent of maximum mobility (%mm) vs yield of residue after treatment at 593 K and extraction with dichloromethane.