Reactivity and structure of two coals containing significant methoxy group concentrations

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Two coals (Beulah, PSOC-1483, and a Thai coal, TH23) of unusually high reactivity with hydrogen and tetralin were shown to contain significant methoxy group contents. The fate of the methoxy groups when these coals were reacted under N_2 at 320°C (with and without added decalin) and with H_2–tetralin and H_2–SnO_2 at 405°C was studied. The reactions of TH23 coal gave unexpectedly high water yields. Reactions of model compounds containing methoxy groups under similar conditions also gave high water yields. Proton magnetic resonance thermal analysis (PMRTA) confirmed that TH23 host and guest coal components are structurally distinct from those of Loy Yang (Victoria) run-of-mine coal.

Previous work by the authors has led to the characterization of coals by their relative reactivity in reactions with H_2–tetralin at 405°C[1,2]. Good correlations between total conversion or oil yield and the H/C atomic ratio of the coal were observed. Other workers have also reported correlations of coal H/C atomic ratio with product yields for a range of reactions, e.g. hydrogenation[3,4] and pyrolysis[5]. The previous work[1,2] was based on the reactions of 44 coals from Australia and the rest of the world. As part of a collaborative project on the production of fluid fuels supported by the New Energy and Industrial Technology Development Organisation of Japan (NEDO), some additional coals were obtained and characterized for hydroliquefaction potential by the authors' usual procedure[1,6,7]. Two of the newly acquired coals, Beulah (PSOC-1483) from the upper Beulah seam, North Dakota, USA, and Ban-Pu3 from the Ban-Pu mine, Li, Lamphun, northern Thailand (designated TH23), showed higher reactivity than that predicted by the reactivity–H/C atomic ratio correlations (*Figure 1*).

This paper describes attempts to characterize some of the structural features of the coals which are responsible for this heightened reactivity. Comparisons are made with a typical Victorian brown coal, Loy Yang run-of-mine (LYROM).

Model compounds have frequently been used in attempts to reproduce the reactivity patterns of structural features in coals[8-10]. This paper also describes the reactions of some simple aromatic methoxy compounds,

since one of the structural features responsible for the enhanced reactivity was shown to be the presence of aromatic methoxy groups in the coals (see below).

EXPERIMENTAL

Materials

The coals were ground to $< 250 \mu m$ and acid-washed according to previously described procedures[6].

2-Methoxyphenol (guaiacol), methoxybenzene (anisole) and 4-methylanisole were freshly distilled before use as model compounds.

Reaction conditions

Reactions of the acid-washed coals, host components[1,11] and model compounds were conducted in 70 ml rocking autoclaves for 1 h under the following conditions: (1) 3 g of dry coal, 6 MPa initial hydrogen pressure, with tetralin at a 3 : 1 solvent:coal ratio at 405°C; (2) 9 g of dry coal, 10 MPa initial hydrogen pressure with no solvent, but in the presence of 1 mol kg^{-1} dry coal of stannic oxide, at 405°C; (3) 3 g of dry coal, 6 MPa initial nitrogen pressure with decalin at a 2 : 1 solvent coal ratio at 320°C; (4) as (3) but in the absence of solvent.

Full details of the experiments have been reported elsewhere[1]. It should be noted that water yields were measured by Lundin distillation using dichloromethane. The products were separated into oils, asphaltenes
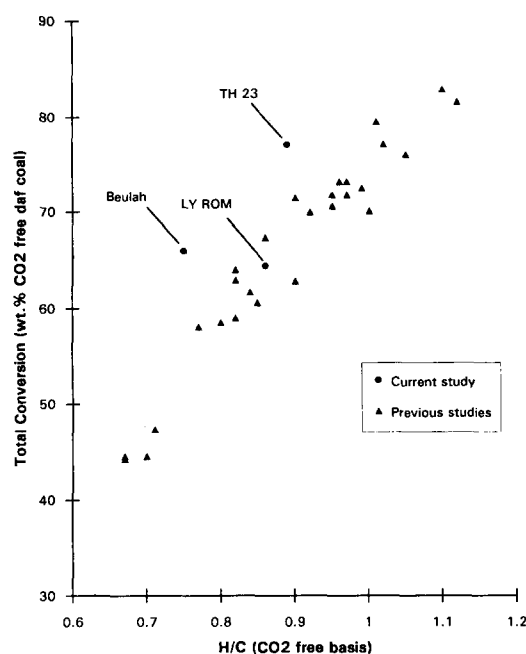
Figure 1 Relation between total conversion and H/C atomic ratio of a range of coals. See ref. 11 for an explanation of the use of quantities on a CO_2-free basis

and residues by a solvent separation scheme based on 60–70°C b.p. petroleum (Shell X4) and dichloromethane[1].

Spectroscopic analysis

Solution proton n.m.r. spectra were recorded using a spectrometer operating at 300 MHz with a pulse width of 3.0 μs. Samples were dissolved in $CDCl_3$ and tetramethylsilane was used as an internal standard. Selected spectra were analysed with a D_2O exchange so that phenols and alcohols would not mask other protons associated with carbons. Solid-state ^{13}C n.m.r. spectra were recorded using a spectrometer with a CP–MAS double air bearing accessory, 7 mm polished zirconia rotors with Kel-F caps. Samples were spun at a rate of 4–5 kHz for CP–MAS. The magic angle was set using a ^{79}Br signal. The following conditions were used to obtain spectra: contact time 1.5 μs, pi pulse for Hartmann–Hahn condition 6 μs, hexamethylbenzene as an internal standard, data processing using FELIX (Biosym) software, with Gaussian/Lorentzian or pure Gaussian windows, and zero filling.

PMRTA (proton magnetic resonance thermal analysis). The coals were dried at 105°C overnight under nitrogen before being subjected to the standard PMRTA test (measuring the n.m.r. signals from the sample every minute while heating it at $4 \, K \, min^{-1}$ under nitrogen to 600°C).

The n.m.r. signals are characterized by their $M_{2T}16$ value[12], which provides an estimate of the extent and degree to which the sample is fused. The $M_{2T}16$ value ranges from 0 for fully fused samples such as liquids to > 50 for completely unfused materials such as dry coals at room temperature. In a typical pyrolysis of brown coal, the $M_{2T}16$ value first decreases with increasing temperature, as the liptinite or 'guest' in the brown coal begins to fuse, reaches a minimum near 350°C, and finally increases again as the coal devolatilizes, leaving a rigid char. For brown coals, the minimum $M_{2T}16$ value reached during the pyrolysis decreases with increasing liptinite or guest content[13,14].

Gas chromatography

Gas–liquid chromatography was carried out with a flame ionization detector, a 25 m SGE BP-5 capillary column and temperature programming from 30 to 300°C at $4 \, K \, min^{-1}$ after an initial 2 min at 30°C. Product distribution was determined by the use of an integration package. Analysis of the reaction gases was performed using a gas chromatograph utilizing both flame ionization and thermal conductivity detectors.

RESULTS AND DISCUSSION

Coal analysis and reactivity

The elemental analyses of the coals are given in *Table 1*, where the similar H/C atomic ratios of LYROM (0.86) and TH23 (0.89) can be seen. TH23 had a higher fraction of aromatic carbon (f_a) than the value of 0.55 predicted from its H/C ratio[6], and Beulah a lower f_a than the value of 0.66 so predicted. The coals were reacted under the standard conditions described previously[1] and the product distribution is shown in *Table 2*. The conversions for these coals are compared in *Figure 1* with those for all other coals studied by the authors. Both Beulah and TH23 coals can be seen to be significantly more reactive, with conversions of 63 and 75 wt% respectively (on a CO_2-free basis), than would be predicted on the basis of the reactivity correlation shown by all the other coals, i.e. 55 and 68 wt% respectively. Each reaction was

Table 1 Elemental composition of the acid-washed coals[a]

| Coal | H/C atomic ratio[b] | Elemental analysis (wt% daf) | | | | | f_a[b] | Ash (wt% db) |
		C	H	N	S	O[c]		
Beulah[d]	0.75	70.1	4.24	1.2	0.8	23.7	0.60	4.4
LYROM[e]	0.86	70.7	4.91	0.7	0.5	23.2	0.51	0.5
TH23[f]	0.89	68.2	4.88	0.6	0.6	25.7	0.63	2.4

[a] Analyses performed by Herman Research Laboratory, Mulgrave, Victoria
[b] CO_2-free basis[11]
[c] By difference
[d] Pennsylvania State University Coal Bank No. PSOC-1483
[e] Loy Yang (Victoria, Australia) run-of-mine
[f] Ban Pu Mine, Li, Lamphun, northern Thailand

Table 2 Product distributions from the 405°C reactions[a]

			Product yields (wt% daf coal)			
Coal	Total conversion[b]	Asphaltenes	H_2O	CO_2	HC gas	Oil[c]
Beulah	63	24	10	9.0	2.0	21
LYROM	61	22	8	8.3	2.0	24
TH23	75	28	11	9.3	2.4	26

[a] 3 g coal, 9 g tetralin and 6 MPa hydrogen (cold) heated at 405°C for 1 h in a 70 ml reactor
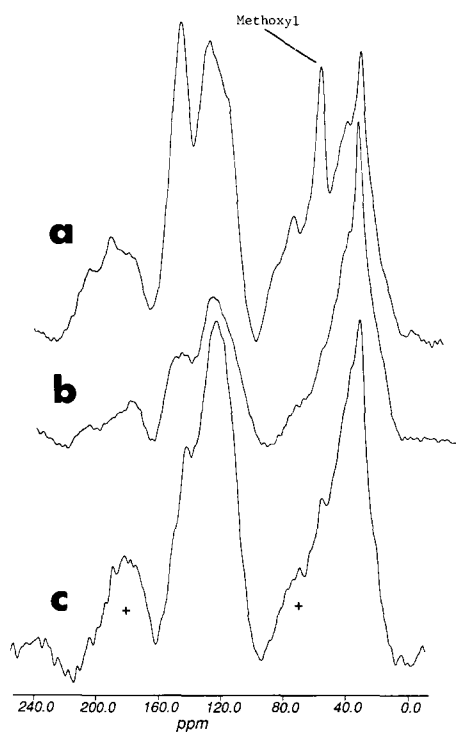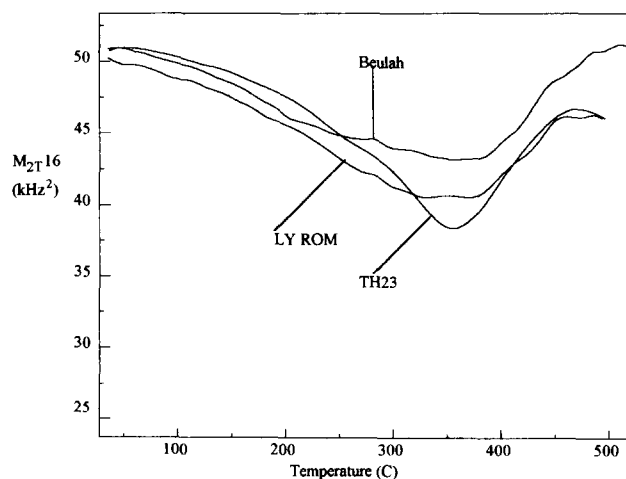[b] CO_2-free basis[11]
[c] By difference

repeated three times; the results varied by <3%. The product distributions (*Table 2*) show that for both coals the water yield was abnormally high, 2–3 wt% above that for LYROM. For TH23 the asphaltene yield, 28 wt%, was higher than the 22 ± 2 wt% given by other low-rank coals[1], whereas the oil yield was that predicted by the correlation with H/C atomic ratio for all the other coals. In contrast, for Beulah the asphaltene yield was normal, 24 wt%[1], but the oil yield, 21 wt%, was higher than the 18 wt% predicted by the H/C correlation[1]. A high yield of water (5.3 wt%) was also obtained when TH23 was heated at 320°C in decalin under nitrogen. Under these conditions LYROM gave significantly less water (2.0 wt%).

Spectroscopic characterization of the coals

In an effort to establish the cause of the enhanced reactivity, the coals were examined by a range of spectroscopic techniques. The solid-state [13]C n.m.r. of the coals showed, near 55 ppm (*Figure 2*), a strong signal for methoxy carbons in TH23 and a significant signal for Beulah. Hatcher *et al.*[15] showed that methoxy groups

were lost only in the second stage of coalification, so that geologically young coals contain appreciable concentrations of methoxy groups. The loss of methoxy groups as wood structure breaks down and gelifies during coalification was studied in detail by Wilson *et al.*[16]. Other workers have reported relatively high concentrations of methoxy groups in Victorian coalified wood[17], New Zealand Southland lignites[18], Hungarian soft brown coals[19] and Ulster lignite[20] and a moderate concentration in Beulah Zap lignite[21], but methoxy signals of the intensity shown by TH23 and Beulah have not been observed in the solid-state [13]C n.m.r. spectra of any of the large number of coals previously studied by the present authors[2,6]. Further evidence for the presence of methoxy groups in these two coals was seen in the FT-i.r. spectra. Strong peaks at 1450 and 1050 cm^{-1}, characteristic of methoxy groups[22], were seen for TH23, weaker ones for Beulah, and none for LYROM. Stray *et al.*[23], studying reactions of lignin under similar conditions to those of this work, also measured high water yields (5–7 wt% at 300°C, 20–23 wt% at 405°C), though in other respects (lower asphaltene yields, relatively high conversions at temperatures as low as 250°C) lignin liquefaction differed from that of any brown coal studied.

PMRTA spectra were recorded for TH23, LYROM and Beulah. The plot of $M_{2T}16$ versus temperature (*Figure 3*) shows a curve for LYROM which is characteristic of a wide range of brown coals[14]. In contrast, the curve for TH23 shows that molecular mobilization in this coal occurs at unusually high temperatures, indicating that its fusible material is more resistant to thermal

Figure 2 Solid-state [13]C n.m.r. spectra of (a) TH23, (b) LYROM, (c) Beulah coals. +, Position of aromatic spinning side bands

Figure 3 $M_{2T}16$ values plotted against temperature for TH23, Beulah and LYROM (PMRTA)
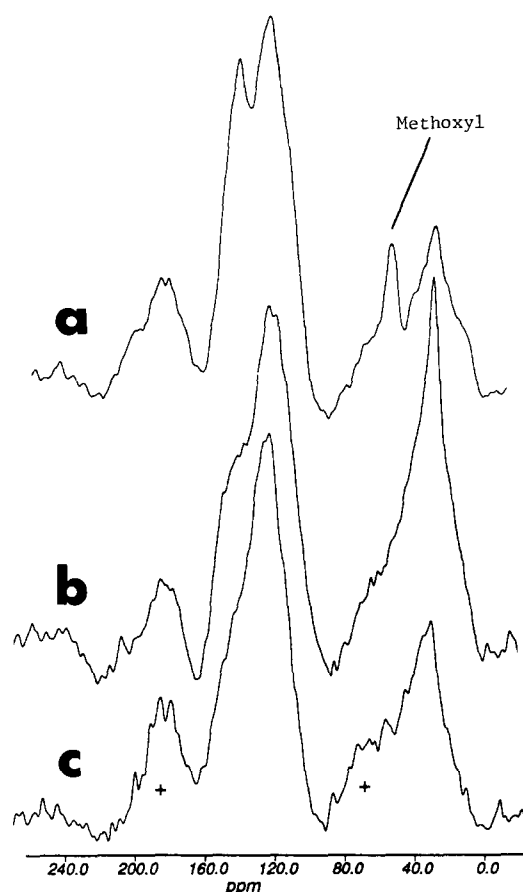
Figure 4 Solid-state ^{13}C n.m.r. spectra of (a) TH23 host, (b) LYROM host, (c) Beulah host. +, Position of aromatic spinning side bands

destabilization, which suggests that it has unusual structural features. The curve for Beulah however is similar to those recorded for other brown coals of similar H/C atomic ratio[14].
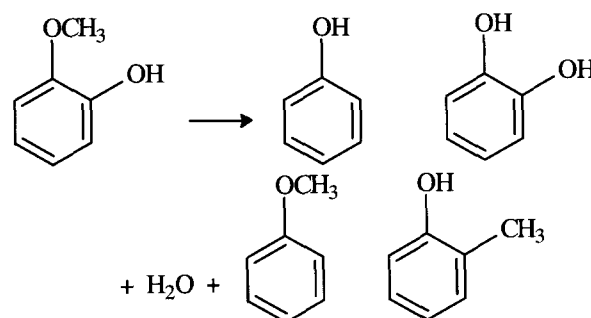
Product characterization

The products from reactions of the coals at 320°C were divided into dichloromethane-soluble matter ('guest') and insolubles ('host')[11]. Both the host and guest fractions from TH23 contained methoxy groups as shown by solid-state ^{13}C n.m.r. (host) (*Figure 4*) and solution ^{1}H n.m.r. (guest). Reactions of Beulah coal gave only a small amount of guest, as would be expected from its low H/C atomic ratio (0.75)[1,11], and ^{1}H n.m.r. showed a small but significant signal for methoxy protons (3.8 ppm). Comparison of the solid-state ^{13}C n.m.r. of Beulah host with that of LYROM host suggested that there was a small concentration of methoxyl groups in Beulah host (*Figure 4*). G.c.-m.s. of the guest oil from TH23 and Beulah coals confirmed the presence of methoxy-containing compounds; among those specifically identified were 2-methoxyphenol (guaiacol), methylguaiacol, various alkylated guaiacols and traces of anisole. No methoxy-containing compounds were identified by g.c.-m.s. of LYROM guest oil.

The gas chromatograms of the 405°C oils from Beulah and TH23 were similar in all respects to those expected for brown coals of the same H/C atomic ratio; no signals corresponding to methoxyl groups were observed, either in the g.c.-m.s. or in the ^{1}H n.m.r. spectra.

Reactions of model compounds

Attempts were made to discover the origin of the relatively high water yields from the reactions of TH23 coal at 320 and 405°C. Since a range of guaiacols and other methoxy-containing aromatics had been found in the oil from reaction at 320°C, reactions of guaiacol were conducted to establish whether this was a source of water in these reactions.

Guaiacol was first reacted with hydrogen in the presence of SnO_2 without solvent at 405°C for 1 h. A large volume of water was produced, greater than that estimated to be formed by the reaction of SnO_2 with hydrogen. The reaction gave almost 100% conversion of guaiacol and a large number of products were formed. The main products were phenol and catechol (1,2-benzenediol), with lesser amounts of simple substituted benzene molecules (see *Scheme*) and some high-molecular-weight products, probably due to polymerization.

Scheme Products from the reaction of guaiacol with SnO_2 and H_2 at 405°C, no solvent

Reaction of guaiacol at 405°C with tetralin and hydrogen produced catechol as the major product (52 wt%), which could be obtained pure by a single recrystallization, and several minor products such as phenol and anisole. A substantial water yield was obtained, accounting for $\sim 40\%$ of the oxygen in guaiacol. This suggested that the guaiacol-type compounds could be the source of the additional water. However, attempted reactions of guaiacol at 320°C under a variety of conditions gave little conversion and only a trace of water. The results are in agreement with the presence of guaiacols in the 320°C oils and demonstrate that these compounds could be the source of the additional water from 405°C reactions.

The 320°C oil did not contain significant quantities of anisole and its alkylated analogues. Previous work[24] has shown that anisole is more reactive than guaiacol under similar reaction conditions. Reactions of 4-methylanisole were therefore carried out at 320°C with H_2-decalin and H_2-tetralin. No water was formed in these reactions, but, surprisingly, small but significant quantities (~ 20 wt%) of products arising from oxygenation of the decalin or tetralin, e.g. 3,4-dihydro-1(2H)-naphthalenone, were observed.

Vassallo[25] used ^{13}C labelling to study the fate of methoxy groups in hydrogen-tetralin liquefaction of coal at 400°C. The methoxy groups were introduced by methylation with ^{13}C-labelled methyl iodide. By ^{13}C n.m.r. he showed that nearly all the methoxy groups disappeared during the reaction, in agreement with the results of this work, and furthermore showed by product analysis that at least some of the methoxy groups were converted to methane.

The product distribution and predominant reaction mechanisms for methoxy groups depend on the atmosphere, temperature and catalyst used. For the clay-catalysed pyrolysis (150–200°C) of synthetic lignins with ^{13}C-labelled methoxy groups, Botto[26] found that cresols were a major product rather than a minor one as in hydrogenation reactions of guaiacol (see above), and there was evidence of demethoxylation by aromatic C–O bond scission to form methanol. Thus the study of mechanisms using models must attempt to reproduce the conditions of the coal reactions being studied as closely as possible.

ACKNOWLEDGEMENTS

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