

CONCLUSION

The stability of coal liquids, as measured by their viscosity, is adversely affected by oxygen, temperature and asphaltene content. The mechanism of ageing of coal liquids appears to be complicated and the role of oxygen in the ageing process is not fully understood. At room temperature oxygen had a considerable effect on the viscosity of both the TSP and the oil but no noticeable change in the products could be detected by spectroscopic methods. Further work to elucidate the role that oxygen plays in the ageing of coal liquids is required. The fact that coal liquids age under a nitrogen atmosphere may indicate that hydrogen bonding increases with time and this may explain why asphaltenes cause an acceleration in the ageing rate. Asphaltenes are known to readily take part in hydrogen bonding.⁹

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Anomalous coking properties of the Wolgan Seam, NSW Australia

Stephen Creaney, David E. Pearson* and Leland G. Marconi

Institute of Sedimentary and Petroleum Geology, 3303 — 33rd Street N.W., Calgary, Alberta Canada

**Ministry of Energy, Mines and Petroleum Resources, Douglas Building, Victoria, British Columbia, Canada*

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During petrographic analysis of coals submitted to the British Columbia Ministry of Energy, Mines and Petroleum Resources three samples from Australia were analysed. Samples of the Wolgan Seam from the Sydney Basin in New South Wales showed variability in coking properties which could not reasonably be explained in terms of the broad similarity of their petrography (observed in white light). Detailed and grouped maceral analyses and reflectance data for the three samples are listed in Table 1 and the coking test data are shown in Table 2.

There is an increase in fluidity from sample PW9A → PW15 → PW16 for which the exinite content cannot be solely responsible because it shows an almost progressive decrease from PW9A → PW16. Also, the total vitrinite content is approximately the same for samples PW9A and PW15 even though their fluidities show a marked difference. The detailed petrography, however, reveals a reduction in vitrinite A (telinite + telocollinite), with a progressive increase in vitrinite B (desmocollinite + gelocollinite) from PW9A (42.8 wt %) → PW15 (55.0 wt %) → PW16 (65.4 wt %).

Observation in ultra-violet light revealed that some of the vitrinite B also fluoresced with a dark orange/brown colour. The samples were subsequently point counted in ultraviolet light and the results are shown

Table 1 Wolgan coal project NSW — detailed petrography (vol %)

	PW9A	PW15	PW16
Vitrinite A	28.8	14.0	16.0
Vitrinite B	42.8	55.0	65.4
Semi-Fusinite	5.9	8.8	4.8
Fusinite	6.1	6.8	4.2
Resinite	1.2	0.8	0.6
Cutinite	0.8	0.8	0.9
Undifferentiated Exinite	1.4	8.8	4.8
Sporinite	9.3	3.3	1.5
Micrinite	0.8	0.8	1.2
Macrinite	—	0.5	0.9
Semi-macrinite	2.8	—	—
	99.9	99.6	100.3
<i>Maceral Group Analysis</i>			
Vitrinite	71.6	69.0	81.4
Exinite	12.7	13.7	7.8
Semi-inert	8.7	8.8	4.8
Inert	6.9	8.1	6.3
	99.9	99.6	100.3
<i>Ro values (mean maximum)</i>			
Vitrinite A	0.79	0.79	0.82
Vitrinite B	0.74	0.72	0.73

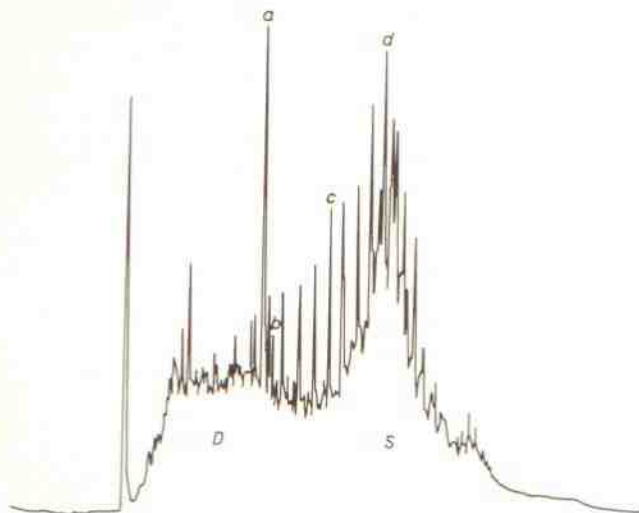


Figure 1 Gas chromatographic trace of saturated hydrocarbons from sample PW15 (Wolgan coal). a, pristane; b, phytane; c, nC₂₂; d, nC₂₆; D, diterpane 'hump'; S, sterane and triterpane 'hump'

Table 2 Coking test data

1 Maximum Fluidity		PW 9A	2335 ddpm ^a
		PW 15	13 100 ddpm
		PW 16	36 000 ddpm
2 Stability Factor			
Theoretical factor indicated by the Composition Balance Index and the Strength Index as calculated from petrographic data.			
		DI ₁₅ ^{30b}	80
Actual factor obtained by the Japanese Steel Mills in 1973 tests on drum samples			
		DI ₁₅ ³⁰	87.6–90.6

^a Dial divisions per min

^b Japanese Industrial Standard coke stability factor

in Table 3. The exinite contents, assessed during ultra-violet illumination, show reasonable agreement with those assessed in white light. A major proportion of the vitrinite B in all samples was found to be fluorescent: 70.1% in PW9A, 93.8% in PW15 and 77.7% in PW16.

Fluorescent vitrinite precursors are common in low-rank coals (peats and lignites)¹ but this property usually disappears with increasing coalification. However, Teichmüller² describes fluorescent vitrinites in high-volatile coals from Illinois, the Saar district, Upper Bavaria, Roumania, Pakistan and Hokkaido. The rank of these coals varies from a mean oil reflectance of 0.50% to 1.15% (high-volatile bituminous) and their fluorescent properties were associated with increased hydrogen content, increased volatile matter, low water content and weak reflectance relative to non-fluorescent vitrinite. Teichmüller² suggested that this fluorescence is produced by a 'sweating out' of 'petroleum-like' mobile organic products from liptinites and vitrinites with a subsequent absorption into the vitrinite pore structure. This suggestion is supported by the Wolgan coal although the fluorescence is almost entirely confined to vitrinite B, which in turn is always associated with the bulk of the exinites. Thus much of the petroleum-like compounds in this coal must be

derived from the vitrinite B bands and associated exinites.

In an attempt to distinguish chemically the material responsible for this fluorescence, the three coal samples were extracted with 87:13 chloroform/methanol and the soluble material was analysed by gas chromatography. The overall results of this analysis are listed in Table 4 and a typical gas chromatographic trace is shown in Figure 1. The total extract yields of 72 to 109 mg g⁻¹ org C are high for coals of this rank. Durand *et al.*³ quote extract yields of 10 to 20 mg g⁻¹ org C for coals in the rank range of 0.77–1.22% vitrinite reflectance. It is interesting to note that the increasing yield of extract, from PW9A→15→16 correlates with the progressive increase of vitrinite B content and fluidity of these coals (see Figure 2). However, the yields of total hydrocarbons are low for coals of this rank³ implying that much of the extractable material is not strictly 'oil-like' but is more asphaltic and resinous.

Table 3 Ultra-violet point count data (vol %)

	PW9A	PW15	PW16
Non fluorescent organic	56.4	32.0	42.0
Fluorescent vitrinite	30.0	51.6	50.8
Exinite	13.6	16.4	7.2
	100.0	100.0	100.0

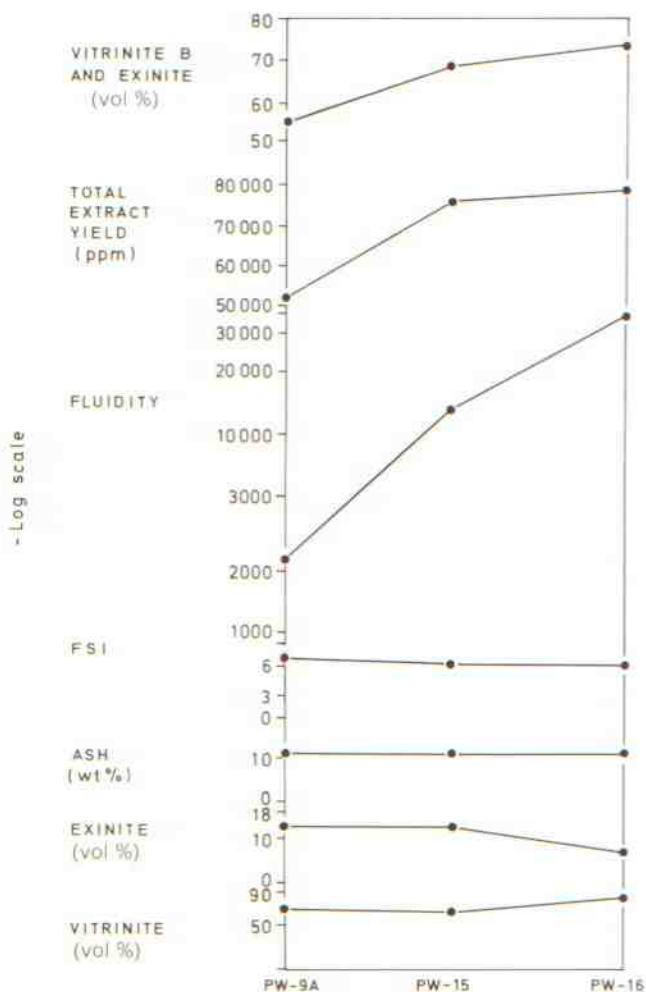


Figure 2 Variation in properties of Wolgan coal samples. FSI, Free Swelling Index

Table 4. Results of analysis by gas chromatography

	PW9A	PW15	PW16
Wt rock (g)	4.0762	2.7374	2.3621
Wt % Org C	71.6	73.2	72.1
Total Extract			
wt (mg)	211.2	203.0	185.6
mg g ⁻¹ Org C	72.4	101.3	109.0
ppm	51810	74160	78570
Asphaltenes			
wt (mg)	140.0	137.5	133.7
wt % total extract	66.3	67.7	72.1
mg g ⁻¹ Org C	48.0	68.6	78.6
Saturates			
wt (mg)	13.5	4.8	3.8
wt % total extract	6.4	2.4	3.5
mg g ⁻¹ Org C	4.6	2.4	3.8
ppm of rock	3310	1750	1610
Aromatics			
wt (mg)	27.2	22.3	20.6
wt % total extract	12.8	11.0	11.1
mg g ⁻¹ Org C	9.3	11.1	12.1
ppm of rock	6670	8150	8720
Resins			
wt (mg)	17.6	17.3	20.5
wt % total extract	8.3	8.5	11.0
mg g ⁻¹ Org C	6.0	8.6	12.0

The distribution of saturated hydrocarbons, as indicated in Figure 1, is atypical of coals, which are usually dominated by a high content of normal alkanes. The Wolgan coals have a very high content of naphthenic hydrocarbons and the distribution of the unresolved 'humps' indicates a high content of diterpenoid derivatives with steranes and triterpanes. The overall absence of an odd-even predominance, the content of pristane and the high pristane to phytane ratio are all consistent with the rank of these coals.

Brown *et al.*⁴ have shown that vitrinite B has a higher-volatile-matter yield than vitrinite A from the same sample and also has a higher hydrogen content. They have also suggested that this compositional

difference will have a marked effect on coking properties. Vitrinite B is probably broadly analogous to the 'reactive vitrinite' of Benedict *et al.*⁵ which they have shown, experimentally, to be more reactive than vitrinite A (which may or may not include pseudovitrinite) during coking.

The fluorescence exhibited by vitrinite B is indicative of an enrichment in asphaltenes and resinous material, which will cause further enhancement of coking properties. The enrichment takes place almost exclusively in the vitrinite B and is probably related to local diffusion from both the included exinite and from the vitrinite B itself. This diffusion or exudation is probably dependent on the degree of coalification, and in the case of Wolgan coal correlates with the position of maximum oil generation described by Teichmüller and Ottenjann⁶. The fluorescence of the vitrinite B of Wolgan coals perhaps indicates a more 'bituminous' nature in the original vitrinite B precursor, since this property is not present in all coals of similar age and rank in Australia.

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On the 'polymeric nature' of petroleum asphaltenes*

James G. Speight and Speros E. Moschopedis

Alberta Research Council, 11315-87th Avenue, Edmonton, Alberta, Canada T6G 2C2

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A recent report in this journal describing the results of a study of the chemical depolymerization of petroleum asphaltenes¹ bears such a close resemblance to work carried out in our laboratories that we think it pertinent to take this opportunity to report our data.

Thus, reaction of the pentane-insoluble asphaltenes from Athabasca bitumen with a toluene-*p*-sulphonic acid/phenol mix (which will cleave aliphatic-aromatic carbon-carbon bonds as found in diphenylethane) for 24 h at approximately 180°C yields a product (110 wt % yield) that was only sparingly soluble in benzene,

toluene, chloroform or acetone and which had a molecular weight in pyridine of 1170 compared to a molecular weight of 2650 for the original asphaltenes in this same solvent.

The infrared spectrum of this reaction product exhibited absorptions (increased intensity relative to the original asphaltenes) in the region 3100 to 3550 cm⁻¹ (assigned to hydrogen-bonded hydroxyl groups; Reference 2), at 1000 cm⁻¹, 1030 cm⁻¹ and 1100 cm⁻¹ (assigned to sulphur-oxygen functions) as well as at 675 cm⁻¹ (assigned to carbon-sulphur bonding). In addition, absorption bands at 740 cm⁻¹ and in the 800-900 cm⁻¹ region indicates the occurrence of

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