

Simulated sub-surface release of coal-sourced hydrocarbons

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In the global cycling of carbon, coal formation and the subsequent generation of hydrocarbons to form oils has become more significant as coals are increasingly recognised as potential source rocks for oil accumulation (Powell and Boreham, 1994). Generation mechanisms of hydrocarbons are by no means clear nor are the transport mechanisms. Ground water studies of bore water samples from the Latrobe Valley, SE. Australia undertaken in our laboratory suggest that generation of hydrocarbons from coal seams is presently occurring. Hence, we have used hydrous pyrolysis over a temperature profile to study the release of products from Victorian Brown Coal and this paper reports results using the Pale lithotype as ROM coal because of its known high H/C ratio.

The environment of deposition can be expected to be a major parameter in determining the nature of the brown coal found in the five recognised lithotypes occurring in the Latrobe Valley deposits. In this study the coal sample was of the Pale lithotype taken from Core LY 1276 from the Flynn Field. Both angiosperm and gymnosperm sources of organic matter have contributed to the lithotypes and organic geochemical studies (Li and Johns, 1991) utilising triterpenes suggest that angiosperm contributions exceed those of gymnosperms in the Pale lithotype and the hopane content reflects an active bacterial reworking. The work of Holdgate *et al.*, (1995) suggests that the Pale lithotype would arise from an environment of low pH following deposition of the Dark lithotype. In such a case the microbial community structure would change and in particular this would limit the bacterial species utilising the organic substrates. The organic solvent extracts of the lithotypes are lean in content and for the Pale lithotype is surprisingly restricted in the component distribution (Li and Johns, 1991). The pattern is, however, deceptive and hydrous pyrolysis which is considered to be a useful technique in understanding subsurface release (maturation) of hydrocarbons from source rocks reveals a much wider range of components and as expected is sensitive to the temperature used. Our study has covered a profile of reaction temperatures (200°, 250°, 275°, 300°, 325° and 350°C) in order to observe changes in the composition of components released and to observe

the potential for further hydrocarbon generation from the residues.

Table 1 summarises much of the quantitative data from this study. Over the temperature profile of the hydrous pyrolyses the Total Extract rises from 7.4 % to a maximum of 14.9 %. Whilst the extractable yield remains in a narrow band over the temperature profile but the amounts released can double that obtained from the ROM coal. The n-alkane maximum slowly shifts from nC₂₉ to nC₁₇ whilst the CPI value remains in the range of 1.23 to 1.49. There is no evidence for cracking of higher molecular weight alkanes (characteristic of higher plants) given the CPI values, rather the shift to the lower maximum is due to an increasing proportion of nC₁₇ in the alkane fraction. The Aliphatic fraction increases its proportion of the Total Extract up to 325°C (> 3 × the yield from ROM coal) emphasising the interpretative weakness of the Total Extract patterns of these coals when used in coal structure studies. nC₁₇ is often taken as indicative of a marine source input and recent work from microfossil analyses point to marine incursions to interbedded clays corresponding to the Pale lithotype horizons.

Although Total Extracts can be considered as gross parameters measuring bitumen release it is relatively insensitive to temperature changes; this is not the case for parameters such as the component classes of the Extract. These might be considered as measures of 'quality' of the hydrocarbons released. This view is reflected in the changes induced over the temperature profile of component classes comprising the Total Extract and shown in Table 1. The Asphaltene and Aliphatic Fractions are good examples of sensitivity to temperature. The ratios of light alkanes to heavy alkanes (L/H) strongly change suggesting that different components of the coal macromolecules release their constituent molecules over a temperature (energy) range. The data also suggest that the generation of hydrocarbons occurs over a more extended temperature range with a brown coal unlike a shale kerogen when release of bitumen occurs within a narrow oil window. This probably reflects the stronger catalytic effect of mineral matter on hydrocarbon generation from kerogen in source rocks, but the data reported here

TABLE 1. Analyses of extracts and residues from hydrous pyrolyses of the Morwell Pale Lithotype over a temperature profile

Total Extracts and Component Fractions (as percentages)						
Temperature (°C)	ROM#	250	275	300	325	350
Total Extract	7.4	11.7	14.9	13.2	14.2	12.4
Aliphatics	7.7	11.0	12.3	14.2	25.5	18.2
Aromatics	17.5	32.0	32.5	37.8	32.4	41.3
NSO	30.7	35.9	39.8	37.7	37.6	38.2
Asphaltenes	44.1	21.0	15.5	10.3	4.6	2.3
Residual Pressure*		50	100	10	130	200
H/C Ratios of Residues	1.16	0.86	0.83	0.77	0.64	0.6
Selective Ratios from GC Analyses of Aliphatic Fractions						
CPI		1.5	1.2	1.2	1.3	1.4
L/H Alkanes**		0.14	0.18	0.24	0.49	0.94
Pr / Ph	3.2	16.4	11.5	3.4	2.9	
C _n (max)	C29	C29	C29	C29	C25	C17

*= in psi; **L/H = Light / Heavy; #ROM = Run of Mine Coal

show that coal itself can be a catalytic surface for hydrocarbon release from bitumen.

Insights from coal maceral studies would suggest that some are more prone to hydrocarbon release than others and the work by Stout (1994) points to the differences which can be observed between micro-lithotypes in more mature coals. It is not surprising, therefore, that we have observed a temperature bias in the abundance of individual components released on hydrous pyrolysis. This is most marked when the thermal release of pristenes, pristane and phytane are compared. It is characteristic of Victorian brown coal that the quantity of phytane observed in extracts or generated by dry pyrolysis is minimal. This is also the case for hydrous pyrolysis, and the pristane/phytane ratio in the Aliphatic Fraction maximises at 250°C decreasing steadily after that as both isoprenes decrease in absolute concentrations.

The Residues after hydrous pyrolysis release significant amounts of the pristene isomers (-1 and -2) on Py/GC analysis but again, insignificant amounts of phytane. The temperature profile plot shows that pristene-1 is released in good relative abundance from the Residue of 250°C hydrous pyrolysis (6 %) reducing by a factor of 2 at 300°C to somewhat less than that of phytane from the 325°C Residue. Pristene-2 follows a similar release pattern whilst pristane fluctuates around the 2% abundance level until 350°C when it also drops to 0.5% (with phytane at ~0.25%). This behaviour suggests that pristane and phytane are derived from different sources. Tocopherols and Archaeobacterial cell

membranes are sources of pristane (Peters and Moldowan, 1993) which should be considered particularly in the Pale and Light lithotypes.

Gas/Liquid ratios calculated from Py/GC of the Residues show surprisingly consistent values over the temperature profile of the hydrous pyrolyses (averaging ~4 at 550°C and ~9 at 700°C). 700°C generates much more gas than liquid in keeping with our understanding of gas generation from shale source rocks which have experienced high geothermal histories. Table 1 reports the residual gas pressures measured after hydrous pyrolysis at the given temperatures. These pressures increase significantly with temperature and analyses show the gases to comprise CO, CO₂ and CH₄.

The GC patterns of the Aromatic Fractions isolated from the Total Extracts released on hydrous pyrolysis exhibit a general similarity unlike the Aliphatic Fractions. Light microscopy of the Residues show major changes have occurred in the coal structure by 200°C although our data commence only at 250°C. By 350°C, however, carbonisation is apparent and yields of products are then reduced. The Aromatic Fraction which consists predominantly of smaller molecules is consistently a significant component of the generated hydrocarbons indicating a catalytic degradation on the coal surfaces by the heat treatment of the bitumen released.

In most respects the data suggest that coal can react similarly to kerogen in source rocks given appropriate geothermal histories and is thus a player in the cycling of carbon in the geosphere.