THE RETORTING OF SELECTED AUSTRALIAN OIL SHALES UNDER HIGH PRESSURE HYDROGEN AND NITROGEN

By

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INTRODUCTION

There is increasing interest in the effects of gas pressure on the retorting properties of oil shales, both as a means of increasing the oil yield and as an aid to developing a better understanding of the chemical processes involved in oil shale retorting. In the presence of hydrogen at pressures up to 7 MPa, significant increases in oil yield have been reported for some shales(1-5), and the technique forms the basis of the HYTORT process under development in the USA(6,7). Although the small increase in oil yield observed(8) when Green River shale was retorted under 2.7 MPa hydrogen was accompanied by a slight increase in the aromaticity(8-10), the changes in the composition of the oils produced from shales, which under higher hydrogen pressures gave very much greater oil yields (up to 500%), have not been reported.

The present work was undertaken to investigate the effects of hydrogen and nitrogen pressure at 6 MPa on the yields and composition of the oils produced from three Australian oil shales. These included Rundle as representative of the Tertiary shales of lacustrine origin found in Queensland, and Nagoorin as typical of the highly aromatic and organic rich shales of mixed lamosite/lignite origin(11). The extent of the Mt Coolon deposit, located approximately 200 km west of the city of Mackay in Queensland is at present unknown. The shale was formed in the early Miocene, is unusually rich in parts, and is probably best regarded as an immature torbanite(12).

EXPERIMENTAL

Samples of the shales were crushed and sieved to -2.8 +1.4 mm. Retorting was carried out at various pressures in a fixed bed reactor using a heating rate of 6°C/minute to 550°C followed by a 30 minute soak period. The gas flow rates were adjusted to give a constant residence time of 30 seconds at all pressures. This required very high gas flow rates at the higher operating pressures. The oils (condensed at ~10°C) were analysed by gas chromatography/mass spectrometry (GC/MS: JEOL DX300) and nuclear magnetic resonance (NMR: JEOL GX400) techniques. Solution ^{13}C spectra were determined in the presence of chromium relaxation reagents with an inverse gated decoupling and a recycle time of five seconds. Proton spectra were recorded with a recycle time of 20 seconds.

RESULTS AND DISCUSSION

(a) Properties of Shales

Table 1 illustrates the diversity of the shales used in this study with respect to their organic carbon content, atomic H/C ratio, aromaticity and retorting properties. Of particular interest are the very poor conversions of organic carbon in the shale to oil obtained under normal (Fischer Assay) retorting for the Mt Coolon and Nagoorin shales, indicating that for these shales conventional retorting procedures are not particularly effective.

(b) Effect of Pressure on Oil Yields

For all three shales, increasing nitrogen pressure resulted in only minor decreases in oil yields (Figure 1) and organic carbon conversions (Figure 2). Increasing hydrogen pressure had no effect on the oil yield from the aliphatic Rundle shale, although a reduction in the organic carbon remaining in the char was observed, presumably reflecting the conversion of the carbonaceous residue to methane, as has been previously observed for Green River shale(8).

However, increases of 150 and 350% of Fischer Assay oil yields were observed for the Mt Coolon and Nagoorin shales, equivalent to oil yields of 390 and 290 L t^{-1} respectively, assuming an oil density of 0.9 g cm^{-3}. These large increases are matched by corresponding decreases in the organic carbon remaining in the char (Figure 2) which, in the case of Nagoorin decreased from 58 to 24% at 6 MPa hydrogen. Increased hydrogen pressure resulted in only small changes in the conversion of organic carbon to gaseous products.

As shown in Figure 3, the oil yields determined for three Australian(13) aromatic shales retorted in 6 MPa hydrogen compared favourably with similar results(3) for a variety of other shales. Data on the importance of the total oil yield on the economics of HYTORT type processes do not appear to have been published, but it appears that the three Australian shales are particularly suited to retorting in high pressure hydrogen.

(c) Effect of Pressure on Oil Composition

Although increased oil yields are obviously important, the composition of the oil is equally significant from the viewpoint of the subsequent hydrotreatment and refining of the crude product.

Increasing nitrogen pressure had no effect on the ^{1}H and ^{13}C aromaticities of the whole shale oils (Figure 4), but large changes were observed with increasing hydrogen pressure, particularly for the Mt Coolon and Nagoorin shales. For example, the Nagoorin oil formed in 6 MPa hydrogen had carbon and proton aromaticities of 68 and 29% respectively. The data indicate that for the Mt Coolon and Nagoorin shales a substantial part of the additional oil formed in the presence of hydrogen is aromatic.

Examination of the whole oils by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) showed (Figure 5) that phenol, the cresols and dimethyl/ethyl phenols were prominent components of the oils retorted under high pressure hydrogen from the Mt Coolon and Nagoorin shales. These compounds also completely dominate the ^{13}C NMR spectra of these oils in the aromatic region but were absent in the oils retorted from the Rundle shale in both nitrogen and hydrogen.

Nitrogen had virtually no effect on the yield of any of the various molecular groups determined by proton NMR spectroscopy (Figure 6), as was expected from the absence of any corresponding effect on the total oil yield However, large increases in the proportions of particularly polycyclic aromatics were observed for the Mt Coolon and Nagoorin shales retorted in the presence of hydrogen. Very much smaller increases in the relative proportions of these compounds were observed in oils retorted from the aliphatic Rundle shale.

Taken together, the results obtained for the Nagoorin and Mt Coolon oils retorted under hydrogen suggest that these are not normal shale oils, but more closely resemble coal-derived liquids, no doubt reflecting the partial lignitic origin of these shales. The results also indicate that for these shales in the

absence of hydrogen, a major coke forming process involves the decomposition of aromatic compounds, particularly phenols.

An unusual aspect of these results is the lack of any effects of shale composition and retorting conditions on the alkene yields. Proton NMR measurements showed that 3.2% of the protons in the Rundle oil were present as alkenes, 2.8% in Nagoorin oil and 2.4% in Mt Coolon oil. Similarly, the alkene content of Green River shale oil has been reported as 3.1%(8). Furthermore, the total alkene yield and the ratio of internal/terminal alkenes were not significantly affected by the presence of high pressure hydrogen or nitrogen. Similar results have been reported for Green River shale(8).

A possible source of alkenes is the disproportionation of alkane-free radicals produced in turn from the primary decomposition of the kerogen(14). However, it is not at all clear why quite different kerogens should give almost identical yields of alkenes. Further, it is difficult to accept that a hydrogen pressure of 6 MPa does not reduce the above disproportionation reaction, and even hydrogenate the newly formed alkenes.

(d) Model for Kerogen Decomposition

Published models for the decomposition of kerogen(8-10) are based on work with Green River shale which is highly aliphatic, produces an oil of low aromaticity with a yield and composition which are only marginally affected by hydrogen pressure, and which thus generally resembles the shale from the Rundle deposit. Our work has shown that the aromatic Mt Coolon and Nagoorin shales can be retorted under conditions which give oils containing large amounts of phenols and polycyclic aromatics and thus resemble coal pyrolysis liquids. For these shales, the reactions of the dominant aromatic components of the kerogen are at least equally as, and possibly even more important than those of the aliphatic components, whose behaviour dominates the retorting chemistry of shales from Rundle or Green River. For these aromatic shales, the following retorting model is proposed:

(i) The organic matter in these shales is composed of material of algal (predominantly aliphatic) and lignitic (predominantly aromatic) origin. Varying amounts of wax and material derived from leaf cuticles may also be present and, for the Mt Coolon shale, these may be major components(12).

(ii) The aliphatic components of the organic matter decompose to give largely aliphatic products. As shown by the work of Regtop et al.,(15) some of the aliphatic oil may be converted to aromatics by reactions catalysed by the spent shale surfaces. The contribution of such reactions to the total aromatic yield must however be small because of the very short residence times.

(iii) The aromatic components of the shale organic matter decompose to aromatic and reactive products which, under normal retorting conditions, rapidly decompose to give coke and gas. Under certain circumstances, e.g. high pressure hydrogen or very short residence times, these compounds survive and appear in the oil as phenols and other aromatic compounds. The decomposition of these compounds during normal retorting serves as a preliminary clean-up of the oil, at the expense of the organic carbon conversion.

(iv) The coke formed during pyrolysis of the aromatic shales can undergo further aromatisation reactions, as is shown by the loss of hydrogen

and methane at temperatures significantly higher than those normally required for retorting(16).

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TABLE 1
PROPERTIES OF OIL SHALE

PROPERTY[a]	RUNDLE	MT COOLON	NAGOORIN
ANALYSIS			
Weight loss on drying (%)	10	50	25
Inorganic carbon (%)	0.89	-	0.14
Organic carbon (%)	13.9	45.9	44.8
Hydrogen (%)	2.1	4.3	3.1
Nitrogen (%)	0.4	0.4	2.1
Sulphur (%)	0.6	3.1	1.5
H/C ratio	1.84	1.12	0.81
^{13}C Aromaticity	0.20	0.33	0.48
RETORTING			
Fischer Assay (wt % dry shale)	11.0	24.6	7.6
Organic carbon in char (%)	14.8	45.2	41.6
Conversion of organic carbon to oil (%)	50	35	10

[a] Based on dry shale.

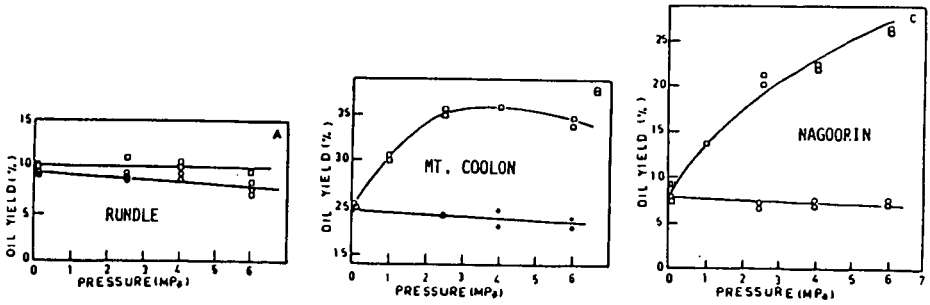

FIGURE 1. Effect of pressure on oil yields
o nitrogen, □ hydrogen

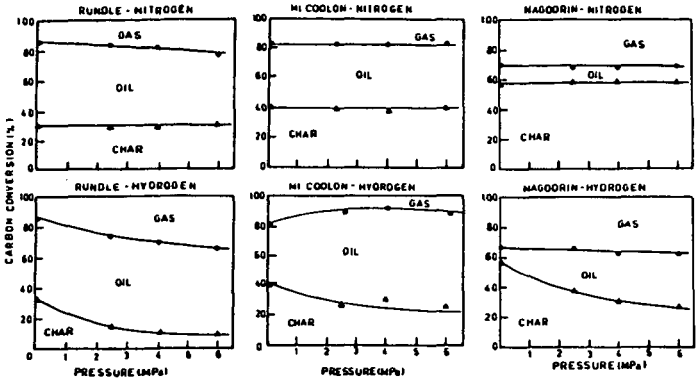

FIGURE 2. Effect of pressure on organic carbon distributions

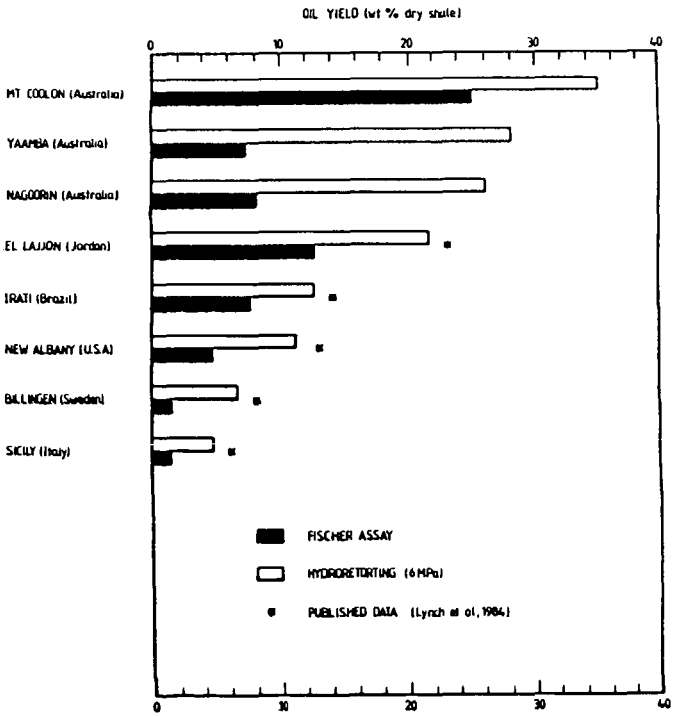

FIGURE 3. Comparison of the effects of hydrogen pressure on oil yields.

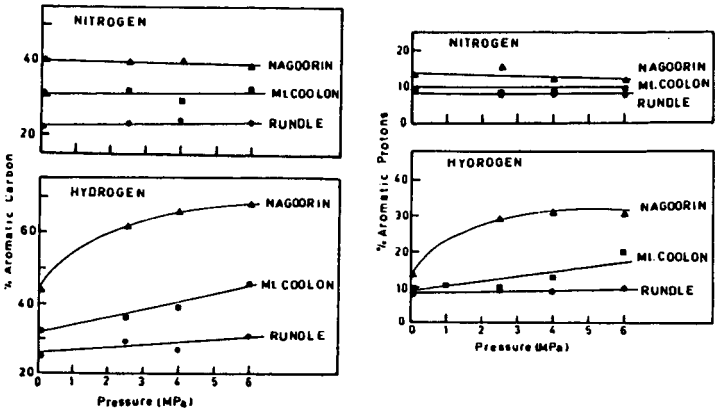

FIGURE 4 Effect of retorting pressure on carbon and proton aromaticities.

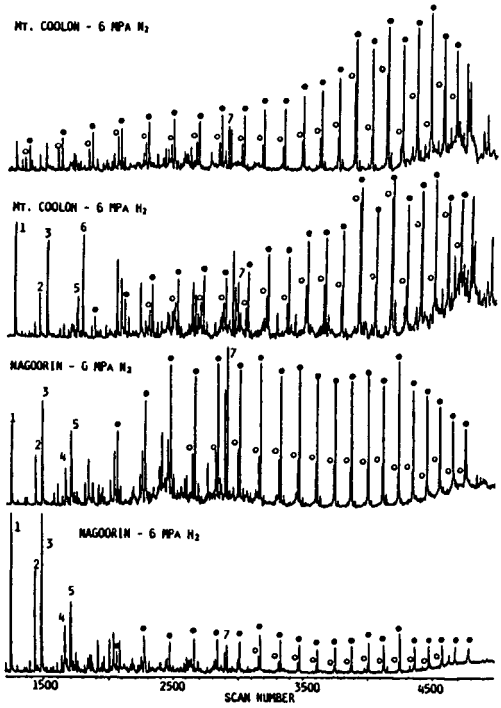

FIGURE 5. Total ion chromatograms of whole oils retorted in hydrogen and nitrogen.

1 phenol
2 o-cresol
3 m&p cresol
4 & 5 dimethyl and ethyl phenols
6 napthalene
7 pristenes

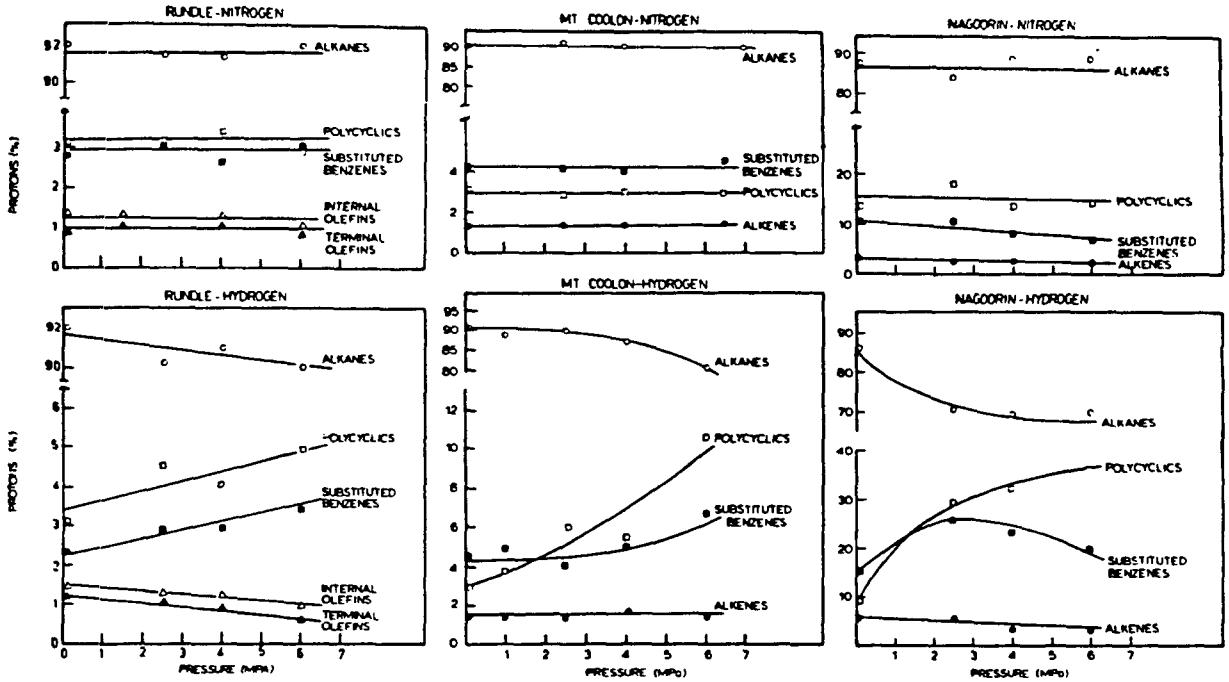

FIGURE 6. Effects of retorting pressure on the proton distributions in the shale oils.