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THE INFLUENCE OF TEMPERATURE UPON THE PYROLYSIS
OF AUSTRALIAN OIL SHALES

By

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INTRODUCTION

Oil shale is one of the most prospective sources for the production of synthetic liquid fuels. Most of the Australian oil shale deposits are located in Queensland with the total in-situ resources in excess of 4×10^{12} L (25 billion barrels) of shale oil. This is more than 12 times the current Australian recoverable petroleum resources. The CSIRO Division of Energy Chemistry is undertaking a comparative study of the processing characteristics of seven oil shales from Condor, Duaringa, Lowmead, Nagoorin, Nagoorin South, Rundle and Stuart deposits which represent more than 80% of the current Australian shale oil resource.

A "fines" retorting process - arbitrarily defined as a process which accepts a feed particle size of minus 12 mm - is being investigated. The process consists of the fluidized bed pyrolysis of raw shale, fluidized bed combustion of spent shale, and recirculation of solids (spent shale and shale ash) between the combustor and the pyrolyser to supply heat to the retorting step. This process utilizes all the mined shale and is self-sufficient in process heat.

A fluidized bed pyrolyser provides, first, good mixing of the solids (raw shale and hot recycled shale ash) and good heat transfer, and hence rapid heating of oil shale and a uniform pyrolysis temperature; second, short residence time of oil vapor in the hot zones to give low oil cracking; and third, an environment of low partial pressure of oil vapor to enhance oil evaporation. These conditions give improved oil yields. Fluidized bed pyrolysis (FBP) gave oil yields in excess of the Fischer Assay (FA) for US oil shales (1,2) and Australian oil shales (3,4). The latter studies, using steam as the fluidizing gas, indicated that the yield enhancement was due to the effect of gas sweeping and that heating faster than $12^{\circ}\text{C min}^{-1}$ had no additional effects on the oil yields from Rundle and Condor shales.

This paper presents results for the pyrolysis of Condor and Nagoorin oil shales in the temperature range 430 to 600°C using a laboratory-scale nitrogen fluidized bed pyrolyser. The Condor deposit (an in-situ shale oil resource of

1.3 x 10¹² L) is the largest Tertiary oil shale deposit in Australia and a potential candidate for the first new Australian shale oil production plant. The Nagoorin deposit is a carbonaceous oil shale which gives a high yield of oil of high aromatic content.

Small-scale fluidized beds severely dilute the product oil vapours with non-condensable fluidizing gases. Quantitative recovery of the diluted oil vapours presents problems with condensing the naphtha fractions and the formation of oil mists (1,3). A dichloromethane scrubber fitted with a series of shrouded turbine mixers was used to overcome these difficulties.

APPARATUS AND PROCEDURE

The pyrolyser, which had long solids and short (40.5 s) vapour residence times was designed to complete the kerogen decomposition and to minimize the oil loss due to the thermal cracking of oil vapor, and hence provided the ultimate yields and characteristics of the pyrolysis products. The final data will be used together with the data from pyrolysis kinetics (5) and oil cracking kinetics experiments to evaluate the performance of a large-scale continuous retort (6).

The FBP apparatus is shown in Figure 1. Metered high purity nitrogen was preheated to and controlled at the pyrolysis temperature in a coil of 9.5 mm o.d. tubing by an electric furnace before entering below a conical section at the base of the reactor vessel. The reactor was a stainless steel vessel (48 mm i.d. by 300 mm long) which was initially charged with 100 g of 0.5-1.0 mm roasted, acid-washed silica sand. The temperature of the fluidized bed was controlled to within $\pm 1^\circ\text{C}$ by an electric heater wound around the bed section. The reactor axial temperature had a uniform profile from the bottom of the bed to a height of 220 mm. Temperature at the top of the reactor was about 30°C lower than the bed temperature. Reactor wall temperatures were recorded at three heights to monitor for hot spots. A superficial velocity of 1.35 times the minimum fluidizing velocity was used.

Samples of dried oil shale (100 g, particle size 0.6-1.4 mm) were added to the bed at the rate of 0.22 g every five seconds via an air-operated feed valve which was actuated by a cycle timer. Spent shale was accumulated in the reactor and a further retorting period of two to ten minutes after the completion of shale feeding was used to simulate an infinite solid residence time. The pyrolysis gases were passed through an internal 10 mm o.d. cyclone to remove fines from the product. The fines were then recovered, weighed and combined with the spent shale for each run. The hot gases and vapors entered a turbine scrubber (80 mm i.d. by 400 mm long), containing 1.2 L of rectified dichloromethane, via a sparger. Oil vapors condensed and dissolved in the dichloromethane which was kept at between 2 and 5°C by evaporation. The dichloromethane was refluxed through a condenser (-60°C) into the scrubber. Oil mists formed within gas bubbles were scrubbed by three shrouded turbines connected in series; big bubbles were sheared into smaller ones and then recirculated through one turbine many times before being released to the next. Before being metered, the off-gas passed through a bed packed with glass wool which trapped about 1 to 2% of the oil yield.

The oil/dichloromethane solution was pressure-filtered to remove traces of spent shale which were then weighed and included in the material balance. Dichloromethane was separated from the oil by atmospheric and vacuum distillation. The atmospheric fractionation column concentrated the solution to about 40 wt % of dichloromethane in the oil to keep the temperature of the solution below 60°C. The vacuum distillation was performed in a closed-system rotary evaporator. The equilibrium vacuum of the system was determined by the condenser temperature (0°C). The oil yield was corrected for the

dichloromethane content in the oil (1 to 3%) and the naphtha content in the vacuum distillate (1 to 4% of whole oil) which were determined using gas chromatography.

The Condor brown shale was supplied by Southern Pacific Petroleum N.L. and Central Pacific Minerals N.L. from 152 mm diamond drill No. 43 cores (from 60.65 to 68.25 m depth). The Nagoorin shale was the bulk sample from Unit Cc. The samples used in this study were split from the 0.6-1.4 mm fractions freshly crushed of 200 kg batches. Before each experiment, the shale was dried in nitrogen at 105°C for at least seven hours to a moisture content below 2 wt%.

Fischer Assays were done in accordance with ASTM standard D-3904-80 except that the particle size was 0.6 to 1.4 mm and the pyrolysis gases were collected and analysed. Raw and spent shales were analysed for total carbon, hydrogen and carbonate carbon (Australian Standard, AS 1038 part 6), and for moisture (Australian Standard AS 1038 part 3). Total sulphur in the raw and spent shales was determined by the high temperature combustion method (7) and sulphur in the oils by the reduction method (7). Simulated distillation of the oils was done on a Varian 3400 gas chromatograph according to the ASTM D-2887 method.

RESULTS AND DISCUSSION

Raw shale.

Table 1 shows the analyses and Fischer Assay yields of the Condor and Nagoorin oil shales. Compared to the Condor shale the Nagoorin shale is much richer in organic carbon, but lower in the H/C atomic ratio of the kerogen and carbonate carbon; also it produces double the oil, five times the pyrolysis water, eight times carbon monoxide, and much more hydrocarbon gas and carbon dioxide. The balances of the inorganic carbon for the shales indicated that the Condor carbon dioxide was from carbonate carbon (siderite) whereas the Nagoorin carbon dioxide was from the decomposition of kerogen (carboxyl group).

Oil yields.

The results (ultimate yields, analyses of oil and spent shale, and recovery of organic carbon) for the FBP runs at various temperatures are given and compared with the FA data in Table 2 (Condor) and 3 (Nagoorin).

For Condor shale, the ultimate yield of the whole oil was constant in the range 450 to 525°C but decreased markedly from 525 to 600°C. The loss of the oil yield in the higher temperature range was caused mainly by thermal cracking in the oil vapor which correlated with the lower atomic H/C ratio, which for the 600°C oil was 1.49 compared to 1.60 for the 500°C oil. The cracking of oil vapor with a mean residence time of 0.5s at 600°C, estimated by the Burnham and Taylor equation (8), accounted for 71% of the oil yield loss.

Figure 2 shows the effect of pyrolysis temperature on the yields of oil fractions. The yields of naphtha (C₅ to 175°C) and kerosene (175 to 240°C) increased slightly with temperature. The yields of diesel (240 to 340°C) and gas oil (340 to 450°C) had maxima at about 550 and about 525°C, respectively. The yield of heavy gas oil (+450°C) decreased markedly with increase in temperature from 450 to 600°C. However, the reduction of temperature from 450 to 430°C reduced the yields of naphtha, kerosene, diesel and gas oil slightly, and the yield of heavy gas oil significantly. More than 50% of the oil yield loss at 430°C was accounted for by the loss of the heavy gas oil fraction which was believed to remain in the spent shale. This could be caused by the combination of the increased production and the decreased evaporation of the high boiling point oils at the lower temperature.

Figure 3 shows the influence of temperature upon the ultimate yields of the oils from the Nagoorin shale. The yield of the whole oil was constant (about 16.4 wt% dry basis) for temperatures from 450 to 550°C, except for 500°C where the yield reached the maximum of 17.1 wt%. Similar to the pyrolysis of the Condor shale, the yield of the whole Nagoorin oil decreased with temperatures from 550 to 600°C where the thermal cracking of oil vapor became significant. The general trend for the production of the oil fractions was also similar to that for the Condor shale, i.e. the yields of the low boiling point oil fractions (naphtha, kerosene and diesel) increased with temperature at the expense of the high boiling point gas oils.

The averages of the FBP oil yields at temperatures from 450 to 525°C for both the shales were about 10% greater than FAs. Table 4 compares the yields of naphtha, kerosene, diesel, gas oil and heavy gas oil from the FBPs and FAs. For both the shales, about 70% of the excess oils was heavy gas oil. This substantiates the claim that the increase in oil yield can be attributed mainly to enhanced evaporation of oil in a retort of low partial pressure of oil vapor (3).

Organic Carbon Conversion.

The organic carbon conversions to oils for both the shales were consistent with the oil yields (Tables 2 and 3). Compared to the FA results, the organic carbon conversions to oils increased at the expense of the conversions to spent shales. For the Condor shale, the organic carbon conversion to spent shale was independent of temperature (450 to 550°C), but for the Nagoorin shale, the conversion decreased with increase in temperature (450 to 600°C). This implied the continuing production of CO, CO₂ and hydrocarbon gases from the Nagoorin kerogen with temperature. When the shales were heated linearly at 3°C min⁻¹ to 850°C considerable amounts of carbon monoxide, carbon dioxide and methane from Nagoorin but not from Condor evolved at temperatures above 500°C, at which the production of oil ceased (9).

The Nagoorin spent shale had very high organic carbon content (about 50 wt%) which was more than ten times that of the Condor spent shale. Combustion of the Nagoorin spent shale will provide more than enough process heat for the retorting step; however, transferring the heat by recycling the hot shale ash would lead to a problem of balancing the recycled solids of suitable particle sizes.

Oil characteristics.

For both shales, the pyrolysis at the higher temperature gave oils of lower H/C atomic ratio. Figure 4 compares the short column gas chromatographs of the Nagoorin oils at 450 and 600°C. The 600°C oils had considerable more alkenes (peaks marked with 0 in Figure 4) and more light hydrocarbons (lower C₁₆/C₂₇ height ratios) than the 450°C oil. This was evident from the thermal cracking of the 600°C oil vapor.

Compared to the FA whole oils, the FBP whole oils from both the shales were more aromatic (lower H/C atomic ratio). The increase in the aromaticity of the FBP whole oils was attributed entirely to the presence of the additional gas oils and heavy gas oils (see Table 4). These heavy oils were highly aromatic (10).

As was expected, the Condor oil shale produced oils (from FA and FBP) of better quality (higher H/C atomic ratio, and lower contents of heteroatoms and density) than the Nagoorin carbonaceous shale. However, the Condor oil contained more heavy gas oil (especially the fraction boiling above 550°C), as is shown in Figure 5.

Carbonate Carbon.

By contrast with the shales from Green River formation, both shales contain small amounts of mineral carbonates (siderite). However, as is shown in Figure 6, the residual carbonate carbon in the Condor spent shale reduced sharply with increase in pyrolysis temperature, to 3% of the Condor shale carbonate carbon at 500°C. This implies that the heat of the decomposition of siderite has to be provided to the retorting step, hence the content of this mineral in the feed shale is vital to the retort heat balance.

SUMMARY

The pyrolysis of Condor and Nagoorin shales was studied in the temperature range 430 to 600°C in a nitrogen fluidized bed retort with long solid and short vapour residence times.

The oil yields were constant from 450 to 525°C (Condor) and from 450 to 550°C (Nagoorin), and both were about 10% in excess of Fischer Assay. The additional oils were mainly high boiling point fractions. The distribution of oil fractions, namely naphtha, kerosene, diesel, gas oil and heavy gas oil were significantly influenced by temperature. Generally, increase in temperature reduced the high boiling point fractions (gas oil and heavy gas oil) and increased the low boiling point fractions (naphtha, kerosene and diesel).

The yields and quality of the oils decreased with temperature from 525 to 600°C where the thermal cracking of the oil vapors (having 0.5 s residence time) became significant.

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LITERATURE CITED

1. M.J. Margolis, Proceedings of the 1981 Eastern Oil Shale Symposium, Lexington KY, 151 (1982).
2. A.M. Rubel and S.D. Carter, Preprints of Symposium on Characterization and Chemistry of Oil Shales, American Chemical Society, St. Louis, 202 (1984).
3. G.C. Wall, Proceedings of the First Australian Workshop on Oil Shale, Lucas Heights, 105 (1983).
4. G.C. Wall, Seventeenth Oil Shale Symposium Proceedings, Colorado School of Mines Press, 300 (1984).
5. G.C. Wall and N.V. Dung, Proceedings of the Second Australian Workshop on Oil Shale, Brisbane, 129 (1984).
6. N.V. Dung and G.C. Wall, *ibid*, 199.
7. P. Udaja, M.D. Chensee and T.A. Noble, *ibid*, 114, (1984).
8. A.K. Burnham and J.R. Taylor, Lawrence Livermore National Laboratory, Livermore, CA, UCID-18284 (1979).
9. A. Ekstrom, R.J. Hurst and C.H. Randall. American Chemical Society Symposium Series 230, 161 (1983).
10. J.A. Gray, C.J. Brady, J.R. Cunningham, J.R. Freeman and G.M. Wilson. Ind. Eng. Chem. Process Des. Dev., 22, 410 (1983).

TABLE 1
PROPERTIES OF RAW SHALES

SHALE	CONDOR		NAGOORIN	
	Mean	s.d.	Mean	s.d.
Moisture, % as received	6.61		22.20	
ANALYSIS, wt% dry basis (4 observations)				
Organic carbon	10.84	0.03	50.70	0.13
Inorganic carbon	0.82	0.01	0.09	0.01
Hydrogen (total)	1.82	0.02	4.77	0.03
Sulphur	0.65	0.01	1.34	0.02
(a)				
Kerogen atomic H/C	1.41		1.02	
Inorganic hydrogen (b)	0.55		0.46	
FISCHER ASSAY, wt% dry basis (4 observations)				
Oil (C ₅ +)	7.47	0.19	15.02	0.50
Water	0.97	0.03	6.28	0.33
Hydrogen	0.057	0.003	0.075	
Carbon monoxide	0.130	0.008	1.113	
Carbon dioxide	1.361	0.089	6.491	
Hydrogen sulphide	0.0	0.0	0.064	
Methane	0.163	0.009	0.900	
Ethane	0.132	0.007	0.442	
Propane	0.088	0.003	0.289	
n-Butane	0.063	0.003	0.126	
i-Butane	0.004	0.0	0.015	
Ethylene	0.042	0.003	0.131	
Propylene	0.080	0.006	0.213	
Butene	0.058	0.004	0.123	
Spent shale	89.06	0.09	68.78	0.48
TOTAL	99.68	0.14	100.06	0.43

(a) Data supplied by Southern Pacific Petroleum N.L. and Central Pacific Minerals N.L.

(b) Determined by the difference between the total hydrogen and the organic hydrogen which is calculated using the kerogen atomic H/C and the organic carbon of the shale.

TABLE 4
OIL YIELDS : FBP v.s. FISCHER ASSAY

OILS	CONDOR			NAGOORIN		
	FBP ^(a) (500°C)	FA ^(a)	Distribution of additional oil ^(b)	FBP ^(a) (500°C)	FA ^(a)	Distribution of additional oil ^(b)
Naphtha (C ₅ to 175°C)	9.9	9.6	3	6.2	7.5	-9
Kerosene (175 to 240°C)	10.7	10.6	1	12.8	13.9	-8
Diesel (240 to 340°C)	27.4	25.7	19	33.6	32.6	7
Gas oil (340 to 450°C)	33.4	32.8	7	39.2	33.8	39
Heavy gas oil (>450°C)	27.7	21.3	70	22.2	12.2	71
TOTAL	109.1	100.0	100	114.0	100.0	100

(a) % of the yield of FA whole oil

(b) $100 \times (\text{yield of FBP oil} - \text{yield of FA oil}) / (\text{yield of FBP whole oil} - \text{yield of FA whole oil})$

TABLE 2
RESULTS FROM CONDOR OIL SHALE

Temperature, °C	FA	FLUIDIZED BED PYROLYSIS							
		500	430	450	475	500	525	550	600
YIELDS, wt% dry basis									
Oil (C ₅ +)	mean	7.0	7.2	8.2	8.1	8.0	8.0	7.7	7.0
	s.d.	0.2	-	0.0	0.1	0.1	-	0.1	-
	number of tests	4	1	2	3	3	1	2	1
Spent shale	mean	89.1	88.9	87.2	85.5	84.9	84.6	84.3	84.6
	s.d.	0.1	-	0.1	0.5	0.2	0.0	0.2	-
	number of tests	4	1	4	3	11	2	2	1
ANALYSIS OF OIL									
Carbon, wt%	84.1	83.87	82.20	82.57	84.08	84.11	83.85	83.39	
Hydrogen, wt%	11.8	11.02	10.78	11.06	11.19	11.10	10.96	10.33	
Sulphur, wt%	0.44	0.44	0.44	0.43	0.45	0.44	0.45	0.45	
H/C atomic ratio	1.68	1.58	1.58	1.61	1.60	1.58	1.57	1.49	
Density, 60°C g/cm ³	0.84	0.89	0.89	0.88	0.88	0.91	0.87	0.90	
ANALYSIS OF SPENT SHALE wt% dry basis									
Organic carbon	4.62	4.60	4.26	4.37	4.35	4.24	4.29	4.57	
Inorganic carbon	0.45	0.63	0.48	0.13	0.02	0.01	0.00	0.00	
Hydrogen	0.69	0.79	0.46	0.53	0.41	0.09	0.23	0.13	
Sulphur	0.69	0.69	0.64	0.68	0.68	0.70	0.65	0.67	
RECOVERY OF ORGANIC CARBON, %									
Oil,	mean	58.0	55.8	62.5	61.2	62.1	61.7	59.1	54.3
	s.d.	1.0	-	0.2	1.7	1.0	-	0.5	-
Spent shale,	mean	38.0	37.1	34.2	34.1	34.0	33.1	33.3	35.7
	s.d.	1.5	-	1.4	1.7	1.1	0.1	0.3	-
Gas,	mean	5.2	-	-	-	-	-	-	-
	s.d.	0.3	-	-	-	-	-	-	-
Not accounted for	-1.2	7.1	3.3	4.7	3.9	5.2	7.6	10.0	

TABLE 3
RESULTS FROM NAGOORIN OIL SHALE

Temperature, °C	FA	FLUIDIZED BED PYROLYSIS							
		500	450	475	500	525	550	575	600
YIELDS, wt% dry basis									
Oil (C ₅ +)	mean	15.0	16.5	16.4	17.1	16.3	16.5	16.2	15.3
	s.d.	0.5	-	0.0	0.1	-	-	0.2	-
	number of tests	4	1	2	2	1	1	2	1
Spent shale,	mean	68.8	66.7	65.2	63.5	62.3	61.5	61.0	60.8
	s.d.	0.5	0.1	0.8	1.3	-	-	0.5	-
	number of tests	4	2	2	2	1	1	2	1
ANALYSIS OF OIL									
Carbon, wt%	82.60	81.94	81.79	81.00	81.51	81.78	81.70	81.28	
Hydrogen, wt%	10.52	9.83	9.77	9.50	9.85	9.50	9.61	9.34	
H/C atomic ratio	1.53	1.44	1.43	1.41	1.45	1.39	1.41	1.38	
Density, 60°C, g/cm ³	0.914	0.959	0.951	0.946	0.940	0.960	0.946	0.924	
ANALYSIS OF SPENT SHALE wt% dry basis									
Organic carbon	50.05	47.92	49.10	49.19	50.58	50.25	50.16	48.71	
Inorganic carbon	0.04	0.06	0.06	0.07	0.05	0.07	0.08	0.07	
Hydrogen	2.49	2.82	2.03	2.07	1.39	1.51	1.44	1.36	
Sulphur				1.48	1.50	1.30	1.20	1.42	
RECOVERY OF ORGANIC CARBON, %									
Oil,	mean	24.4	26.7	26.5	27.3	26.2	26.6	26.1	24.5
	s.d.	0.7	-	0.1	0.1	-	-	-	-
Spent shale,	mean	67.9	63.1	63.1	61.6	62.1	60.9	60.4	58.4
	s.d.	0.6	-	0.1	0.1	-	-	-	-
Gas,	mean	7.9	-	-	-	-	-	-	-
	s.d.	0.1	-	-	-	-	-	-	-
Not accounted for	-0.2	10.2	10.4	11.1	11.7	12.5	13.5	17.1	

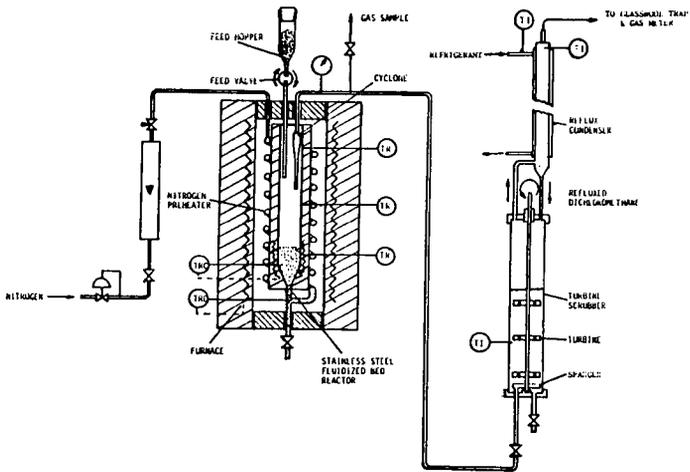


FIGURE 1. APPARATUS

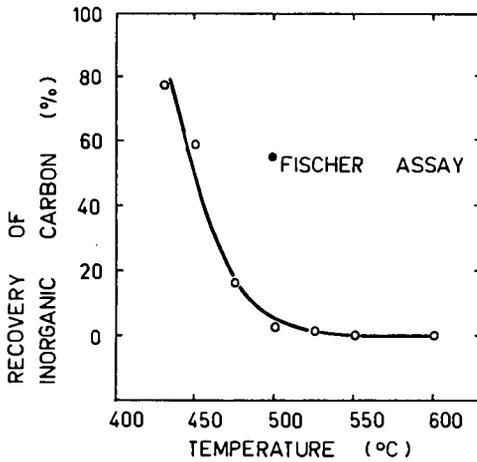


FIGURE 6. EFFECT OF TEMPERATURE ON RECOVERY OF INORGANIC CARBON IN CONDOR SPENT SHALE

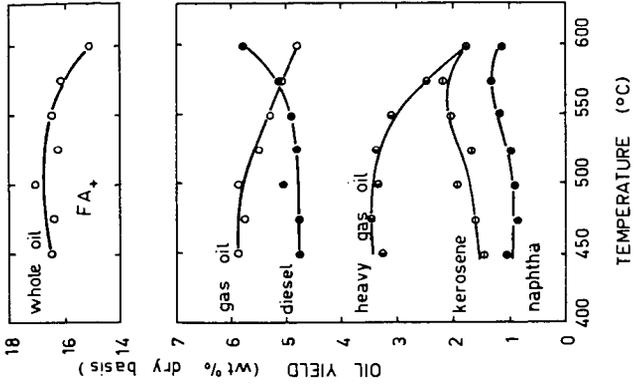


FIGURE 3. EFFECT OF TEMPERATURE ON YIELDS OF OILS FROM NAGORIN SHALE

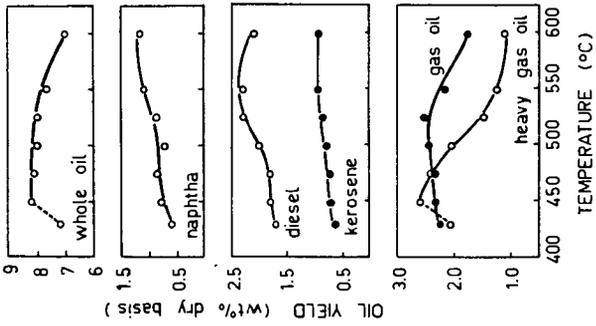


FIGURE 2. EFFECT OF TEMPERATURE ON YIELDS OF OILS FROM CONDOR SHALE

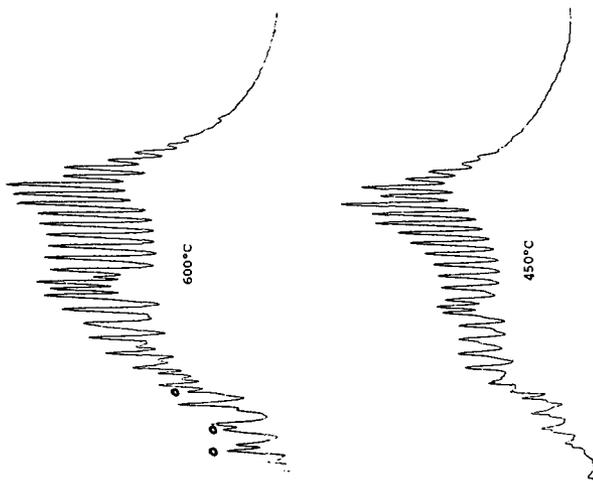


FIGURE 4. GAS CHROMATOGRAPHS OF NAGOORIN SHALE OILS AT 450 AND 600°C

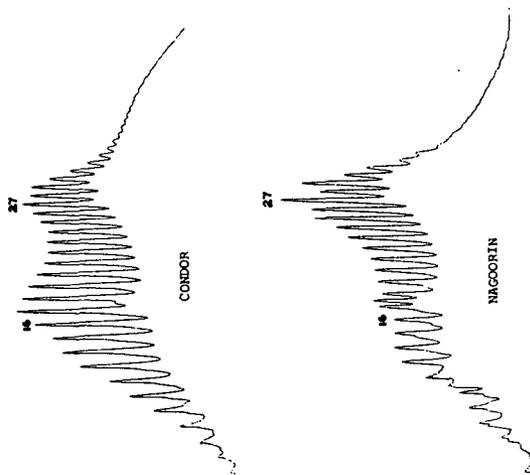


FIGURE 5. GAS CHROMATOGRAPHS OF CONDOR AND NAGOORIN SHALE OILS AT 450°C