

TABLE 4

<u>State</u>	<u>Capital\$</u>	<u>PWB\$</u>	<u>BCR</u>	<u>PWB\$/C\$</u>
1 - 0 0 0 0 -	\$0	\$0	0	0
2 - 0 0 3 0 -	\$435,000	\$292,000	1.44	0.67
3 - 1 0 0 0 -	\$465,000	\$934,000	2.32	2.01
4 - 0 0 0 4 -	\$634,000	\$275,000	1.28	0.43
5 - 1 0 3 0 -	\$899,000	\$1,226,000	1.89	1.36
6 - 0 0 3 4 -	\$1,068,000	\$567,000	1.35	0.53
7 - 1 0 0 4 -	\$1,098,000	\$1,209,000	1.72	1.10
8 - 1 0 3 4 -	\$1,533,000	\$1,501,000	1.64	0.98
9 - 0 2 0 0 -	\$2,883,000	\$2,018,000	1.46	0.70
10 - 0 2 3 0 -	\$3,318,000	\$2,311,000	1.46	0.70
11 - 1 2 0 0 -	\$3,348,000	\$2,953,000	1.58	0.88
12 - 0 2 0 4 -	\$3,517,000	\$2,293,000	1.43	0.65
13 - 1 2 3 0 -	\$3,783,000	\$3,245,000	1.56	0.86
14 - 0 2 3 4 -	\$3,952,000	\$2,585,000	1.43	0.65
15 - 1 2 0 4 -	\$3,982,000	\$3,227,000	1.53	0.81
16 - 1 2 3 4 -	\$4,416,000	\$3,519,000	1.52	0.80

Note: All \$ values are rounded to the nearest \$1,000.

ordered in ascending total capital involved. The first column indicates a row identifier, followed by four digits indicating the combination of proposals considered. Thus Row 5 includes doing proposals 1 and 3, requiring \$899,000 of capital and giving an overall B/C ratio of 1.89. The column labeled PWB\$ gives the present worth of added revenues minus added expenses for the combination being considered, over a 30 year period at a discount rate of 15 percent, and the last column ratios PWB\$ to Capital\$ to obtain the present worth of net benefits (profits) per dollar of capital invested.

For example, if the total capital available for this type of project is \$1.6 million, then Row 8 (do 1, 3 and 4) is feasible giving a B/C ratio of 1.64 (>1.2). If management has other places to use the \$1.6 million which will produce B/C ratios of 2.00, however, then only proposal 1 would be done for \$465,000 in capital giving a B/C ratio of 2.32 (>2.00). The remainder of \$1,600,000 - \$465,000 = \$1,135,000 would then be used for other groups of proposals

which have B/C ratios of 2.00 or more. Thus management can use Table 4 to make decisions, based on the economic criteria desired as applied to the group of proposals presented, so long as such proposals are not mutually exclusive.

REFERENCES

1. Robert L. Miller, James P. Roberts, G. K. Clement Jr.; (STRAAM Engineers, Inc.) Capital and Operating Cost Estimating System Handbook, Mining, Retorting and Upgrading of Oil Shale in Colorado, Utah and Wyoming. (Book) U.S.B.M. Contract No. J0265049
2. J. B. Fussell; How to Hand Calculate System Reliability and Safety Characteristics (Paper) IEEE Transactions on Reliability, Vol. R-24, No. 3, August, 1975

ISOTHERMAL FLUIDISED-BED PYROLYSIS OF AUSTRALIAN OIL SHALES IN
SUPERHEATED STEAM

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ABSTRACT

Samples of three Australian oil shales (Condor, Nagoorin, Rundle) were pyrolysed in steam at 450, 500 and 550°C in a bench-scale fluidised-bed reactor at atmospheric pressure; the yields and compositions of the oils and gases produced were compared with corresponding results from Fischer assays.

The maximum yield of oil occurred at 500°C for all three shales. The yields (expressed as percentages of the Fischer assay yield at 500°C max.) were: Rundle 110%; Condor 128%; Nagoorin 134%.

The yields of oil from the Rundle and Condor shales were almost identical with those obtained by fluidised-bed pyrolysis in steam at a heating rate of 12°C min⁻¹. This suggests that flash heating has no effect on the oil yields from these shales and that the yield enhancement is due entirely to the effect of the sweep gas. Reduced coking was identified as the primary reason for the increased oil yields but reduced cracking also appeared to be significant for the Nagoorin oil shale.

At 550°C, the three shales yielded less oil than at 500°C but the yield of pyrolysis gas increased considerably, suggesting that at this temperature oil cracking was significant.

INTRODUCTION

This study is the second in a program of research on the fluidised-bed pyrolysis of Australian oil shales. Our research was prompted by reports in the literature¹⁻⁶ that improved oil yields had been obtained in retorting studies on American oil shales by the use of high sweep gas velocities and/or high heating rates. We chose to use steam as the sweep gas primarily because it had the potential to simplify oil and gas recovery, but also to determine whether enhanced yields of hydrogen could be obtained from Australian oil shales, as was reported by Allred¹ for Colorado shale. In the first study⁷, we established that significant increases in oil yield were obtained when samples of three Australian oil shales were pyrolysed in static and fluidised beds, using steam at atmospheric pressure

as the sweep gas, and with the same heating conditions as the Fischer assay. The yields (expressed as percentages of Fischer assay yields) were Condor brown shale, 129%, Rundle, 107%, and Julia Creek, 114%. We concluded that the increased oil yields were due to reduced oil coking within the shale particles which resulted from enhanced oil evaporation under the influence of the steam sweep gas. We also confirmed that co-condensation of steam and oil provided a very efficient means of recovering the shale oil from the gas stream and, in addition, yielded a high quality pyrolysis gas which was free from inert diluents. However, there was no evidence that a chemical reaction between the steam and the oil shale yielded additional hydrogen.

In this second study, we determined the effects of the rapid heating of shale on the oil and gas yields by operating the steam fluidised-bed retort isothermally and compared the results with Fischer assays which use a relatively slow heating rate.

Three oil shales were used: (1) Condor shale from the brown shale unit; (2) Rundle shale from the Lower Ramsay Crossing slot cut, sample 08-046; and (3) Nagoorin carbonaceous shale from Auger hole NAH43, unit E. The first two shales were also used in the previous study. The Nagoorin oil shale was included in the present study as being representative of a completely different class of oil shale having a radically different pyrolysis behaviour.

APPARATUS AND PROCEDURE

A 20 kg sample of each shale was crushed and sieved; the 0.6 to 1.4 mm size fraction was then blended and split into 100 g samples for use in the Fischer assays and steam pyrolyses. The shale was not dried.

The steam fluidised-bed pyrolysis apparatus is shown in Figure 1. The reactor was a 48 mm i.d. by 300 mm long stainless steel vessel which was maintained at the selected pyrolysis temperature and controlled within $\pm 2^\circ\text{C}$ in an electrically heated tube furnace. Steam generated by flash-evaporating

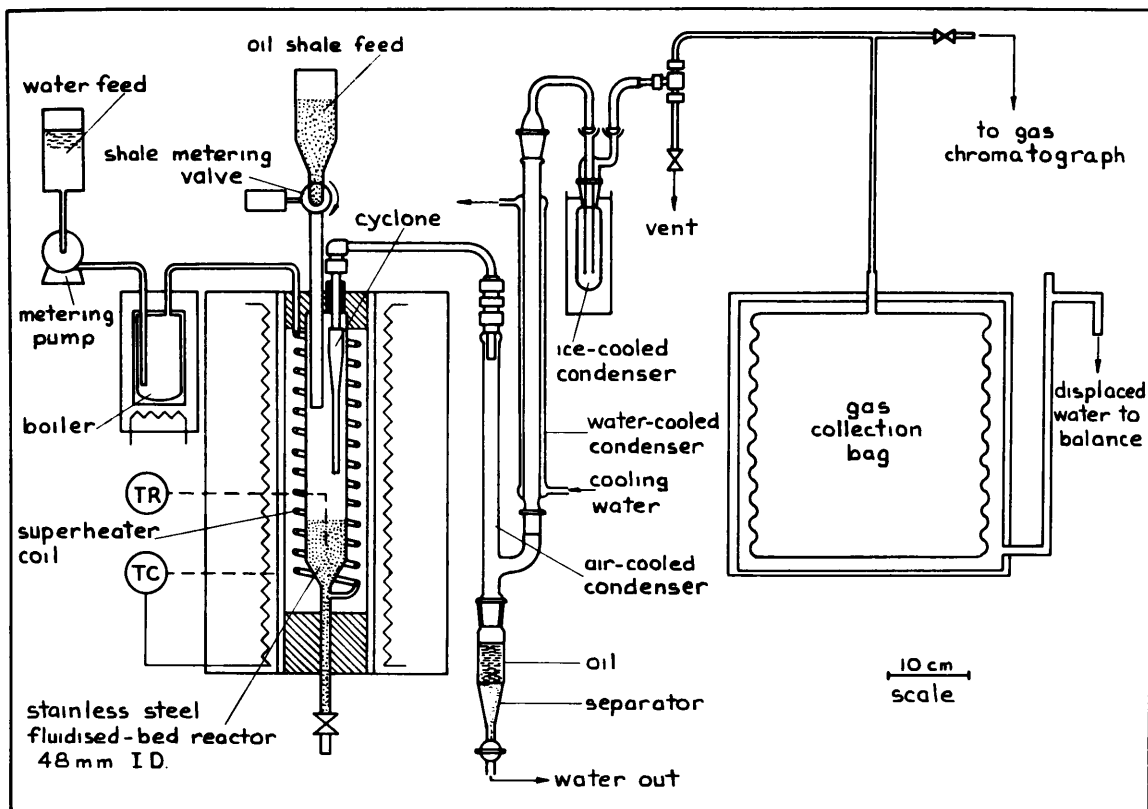


Figure 1. Apparatus

a metered supply of water was preheated to reactor temperature in a coil of 6 mm o.d. tubing and admitted to the reactor below a conical section at the base of the vessel. The steam flowrate gave a superficial velocity in the reactor of 0.6 m s^{-1} which was 1.3 times the minimum fluidising velocity. Inspection of the bed under operating conditions and tests in a glass replica of the reactor showed that uniform fluidisation was achieved.

Each run was started with a charge of 50 g of 0.6 to 1.4 mm acid-washed silica sand in the bed. The sample of oil shale (100 g) was then added to the bed at the rate of 0.3 g every five seconds via a pneumatically operated metering valve which was controlled by a cycle-timer.

Before leaving the reactor, the pyrolysis gases passed through an internal 10 mm o.d. cyclone which effectively removed all dust from the product; the dust was recovered and weighed at the end of each run. After leaving the reactor, the product gases first passed through an air-cooled glass condenser which removed the heavy oil fractions and prevented fouling of the water-cooled condenser. The rest of the oil and all of the steam were then co-condensed

in the water-cooled reflux condenser and the oil and water collected and separated in the vessel below the condenser. Water was continuously removed and collected for analysis. Good oil/water separation was generally achieved in spite of the relatively high densities of some of the oils.

An ice-cooled condenser was used to remove residual oil from the pyrolysis gases leaving the primary condensers; the efficiency of co-condensation of oil and steam is illustrated by the fact that the amount of oil collected in the ice-cooled condenser was never more than 100 mg and the pyrolysis gas was free from oil mist.

Pyrolysis gases were collected in a plastic bag located inside a water-filled Perspex box, and the gas volume was measured by weighing the water displaced from the box. At the end of each run, the gas was sampled and analysed by gas chromatography.

Once all the oil shale sample had been fed into the reactor, the steam flow was maintained until gas evolution ceased (generally < 5 minutes); the apparatus was then purged with nitrogen for ten minutes and the oil and spent shale were recovered for weighing and analysis.

TABLE 1. SUMMARY OF RESULTS FROM NAGOORIN OIL SHALE

	Fischer Assay		Steam Pyrolysis		Steam Pyrolysis		Steam Pyrolysis	
Number of runs	3		3		3		3	
Temperature deg C	500		450		500		550	
YIELDS g/100 g of Shale	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Oil	6.83	0.186	6.97	0.076	7.17	0.214	6.79	0.586
Oil in cond. water	0.00	0.000	1.19	0.038	1.43	0.067	1.34	0.039
Water *	11.74	0.342	11.74	0.000	11.74	0.000	11.74	0.000
Hydrogen	0.05	0.002	0.02	0.001	0.06	0.000	0.13	0.004
Carbon monoxide	0.99	0.012	0.84	0.009	1.30	0.008	1.82	0.034
Carbon dioxide	6.99	0.157	5.90	0.044	6.89	0.025	7.49	0.034
Hydrogen sulphide	0.07	0.010	0.32	0.007	0.52	0.013	0.64	0.038
Methane	0.57	0.020	0.21	0.004	0.47	0.005	0.71	0.010
Ethane	0.23	0.006	0.10	0.001	0.16	0.011	0.18	0.003
Propane	0.10	0.003	0.05	0.001	0.09	0.000	0.09	0.002
n-butane	0.06	0.003	0.04	0.002	0.05	0.001	0.06	0.002
i-butane	0.01	0.001	0.05	0.001	0.04	0.002	0.03	0.005
Ethylene	0.07	0.002	0.06	0.001	0.11	0.001	0.17	0.005
Propylene	0.11	0.002	0.08	0.001	0.12	0.000	0.16	0.002
Butenes	0.07	0.001	0.06	0.003	0.08	0.000	0.11	0.003
Pentane	0.13	0.012	0.13	0.014	0.15	0.003	0.19	0.009
Hexane	0.11	0.019	0.22	0.038	0.24	0.008	0.29	0.016
Heptane	0.06	0.019	0.43	0.009	0.56	0.018	0.62	0.130
Spent shale	71.09	0.324	71.43	0.155	67.37	0.335	64.29	0.168
TOTAL	99.27	0.265	99.86	0.133	98.55	0.245	96.35	0.511
TOTAL Oil (Oil+C5to7)	7.13	0.163	8.95	0.078	9.55	0.2267	9.23	0.639
ANALYSES % as recovered								
Fresh Shale								
Organic carbon	41.63	0.00	41.63	0.00	41.63	0.00	41.63	0.00
Inorganic carbon	0.14	0.00	0.14	0.00	0.14	0.00	0.14	0.00
Spent Shale								
Organic carbon	46.02	0.11	44.04	2.64	43.12	0.86	44.99	3.39
Inorganic carbon	0.12	0.02	0.12	0.02	0.15	0.03	0.16	0.03
Oil								
Organic carbon	80.62	1.34	81.72	0.03	81.48	0.18	82.27	0.63
Hydrogen	9.53	0.73	9.06	0.28	9.19	0.32	9.33	0.14
CARBON BALANCES								
Organic,								
Fresh shale	41.63	0.00	41.63	0.00	41.63	0.00	41.63	0.00
Spent shale	32.71	0.21	31.50	1.89	29.05	0.65	28.97	2.13
Oil	5.75	0.19	7.31	0.07	7.78	0.17	7.59	0.55
Hydrocarbon gas & CO	1.38	0.03	0.90	0.01	1.46	0.01	1.98	0.03
Carbon dioxide	1.85	0.04	1.55	0.01	1.84	0.01	2.00	0.01
TOTAL in products	41.69	0.18	41.26	1.84	40.12	0.49	40.54	1.95
Inorganic,								
Fresh shale	0.14	0.00	0.14	0.00	0.14	0.00	0.14	0.00
Spent shale	0.08	0.01	0.08	0.01	0.10	0.01	0.10	0.02
Carbon dioxide	0.06	0.01	0.06	0.01	0.04	0.01	0.04	0.01
TOTAL in products	0.14	0.01	0.14	0.01	0.14	0.01	0.14	0.01
TOTAL carbon recovered	41.83	0.13	41.40	1.85	40.26	0.48	40.69	1.95
% carbon recovered	100.15	0.32	99.11	4.42	96.39	1.14	97.40	4.68
Oil density 60°C g/cm ³	0.932	0.004	1.002	0.005	0.980	0.016	1.004	0.018
Oil H:C atomic ratio	1.49	0.04	1.35	0.07	1.35	0.05	1.35	0.01

*The water yield from steam pyrolysis was assumed to be equal to the yield from Fischer assay.

TABLE 2. SUMMARY OF RESULTS FROM RUNDLE OIL SHALE

	Fischer Assay		Steam Pyrolysis		Steam Pyrolysis		Steam Pyrolysis	
Number of runs Temperature deg C	3 500		3 450		4 500		3 550	
YIELDS g/100 g of Shale	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Oil	11.05	0.078	11.12	0.015	11.17	0.155	10.00	0.112
Oil in cond. water	0.00	0.000	0.59	0.024	0.60	0.000	0.67	0.030
Water *	3.40	0.320	3.40	0.000	3.40	0.000	3.40	0.000
Hydrogen	0.04	0.001	0.02	0.001	0.03	0.003	0.08	0.003
Carbon monoxide	0.19	0.003	0.18	0.005	0.22	0.010	0.30	0.025
Carbon dioxide	2.06	0.033	2.24	0.031	2.47	0.076	3.11	0.050
Hydrogen sulphide	0.04	0.002	0.23	0.002	0.38	0.025	0.59	0.005
Methane	0.20	0.004	0.08	0.002	0.15	0.011	0.26	0.018
Ethane	0.18	0.004	0.07	0.002	0.13	0.006	0.17	0.005
Propane	0.13	0.003	0.06	0.001	0.09	0.004	0.11	0.002
n-butane	0.09	0.001	0.05	0.002	0.08	0.003	0.09	0.004
i-butane	0.01	0.000	0.00	0.000	0.00	0.001	0.00	0.001
Ethylene	0.06	0.002	0.03	0.001	0.07	0.007	0.19	0.017
Propylene	0.12	0.002	0.07	0.002	0.11	0.007	0.19	0.008
Butenes	0.08	0.001	0.07	0.002	0.10	0.006	0.16	0.009
Pentane	0.18	0.003	0.17	0.007	0.24	0.018	0.30	0.018
Hexane	0.13	0.007	0.20	0.004	0.27	0.029	0.34	0.035
Heptane	0.05	0.002	0.24	0.017	0.26	0.045	0.31	0.066
Spent shale	81.14	0.131	79.43	0.161	78.69	0.287	77.11	0.388
TOTAL	99.15	0.213	98.26	0.192	98.46	0.241	97.38	0.408
TOTAL Oil (Oil+C5to7)	11.41	0.09	12.32	0.03	12.53	0.10	11.62	0.04
ANALYSES % as recovered								
Fresh Shale								
Organic carbon	15.13	0.00	15.13	0.00	15.13	0.00	15.13	0.00
Inorganic carbon	0.74	0.00	0.74	0.00	0.74	0.00	0.74	0.00
Spent Shale								
Organic carbon	5.58	0.11	4.47	0.28	3.80	0.20	3.81	0.10
Inorganic carbon	0.55	0.02	0.52	0.02	0.44	0.03	0.26	0.02
Oil								
Organic carbon	83.88	0.46	83.63	0.19	83.84	0.40	84.19	0.32
Hydrogen	11.34	0.36	11.15	0.15	11.17	0.07	10.70	0.20
CARBON BALANCES								
Organic,								
Fresh shale	15.13	0.00	15.13	0.00	15.13	0.00	15.13	0.00
Spent shale	4.53	0.10	3.55	0.22	2.99	0.15	2.94	0.07
Oil	9.57	0.02	10.30	0.04	10.51	0.12	9.78	0.05
Hydrocarbon gas & CO	0.79	0.01	0.44	0.01	0.69	0.04	1.09	0.06
Carbon dioxide	0.26	0.01	0.28	0.01	0.29	0.01	0.31	0.01
TOTAL in products	15.15	0.09	14.57	0.26	14.47	0.16	14.12	0.06
Inorganic,								
Fresh shale	0.74	0.00	0.74	0.00	0.74	0.00	0.74	0.00
Spent shale	0.44	0.01	0.41	0.02	0.35	0.03	0.20	0.01
Carbon dioxide	0.30	0.01	0.33	0.01	0.39	0.02	0.54	0.01
TOTAL in products	0.74	0.01	0.74	0.01	0.74	0.01	0.74	0.02
TOTAL carbon recovered	15.90	0.09	15.31	0.28	15.21	0.16	14.86	0.06
% carbon recovered	100.16	0.58	96.46	1.74	95.81	1.03	93.64	0.39
Oil density 60°C g/cm ³	0.854	0.004	0.912	0.005	0.909	0.005	0.917	0.001
Oil H:C atomic ratio	1.62	0.05	1.60	0.02	1.60	0.01	1.53	0.03

* The water yield from steam pyrolysis was assumed to be equal to the yield from Fischer assay.

TABLE 3. SUMMARY OF RESULTS FROM CONDOR OIL SHALE

	Fischer Assay		Steam Pyrolysis		Steam Pyrolysis		Steam Pyrolysis	
Number of runs	3		3		3		2	
Temperature deg C	500		450		500		550	
YIELDS g/100 g of Shale	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Oil	5.93	0.268	7.05	0.160	6.85	0.095	6.07	0.424
Oil in cond. water	0.00	0.000	0.42	0.056	0.46	0.077	0.30	0.003
Water *	6.93	0.204	6.93	0.000	6.93	0.000	6.93	0.000
Hydrogen	0.06	0.002	0.04	0.004	0.07	0.001	0.10	0.004
Carbon monoxide	0.08	0.001	0.09	0.001	0.11	0.003	0.16	0.004
Carbon dioxide	2.47	0.049	2.60	0.047	2.71	0.022	2.83	0.049
Hydrogen sulphide	0.00	0.000	0.12	0.019	0.26	0.004	0.39	0.014
Methane	0.15	0.004	0.07	0.007	0.13	0.001	0.21	0.006
Ethane	0.12	0.002	0.06	0.006	0.09	0.001	0.12	0.003
Propane	0.08	0.002	0.04	0.005	0.06	0.002	0.07	0.003
n-butane	0.05	0.001	0.03	0.003	0.05	0.001	0.06	0.001
i-butane	0.00	0.000	0.00	0.000	0.00	0.001	0.00	0.000
Ethylene	0.04	0.001	0.02	0.003	0.05	0.001	0.14	0.009
Propylene	0.07	0.002	0.04	0.006	0.07	0.001	0.12	0.005
Butenes	0.05	0.001	0.03	0.004	0.06	0.001	0.10	0.004
Pentane	0.10	0.011	0.09	0.011	0.14	0.004	0.20	0.001
Hexane	0.08	0.022	0.12	0.020	0.18	0.009	0.26	0.009
Heptane	0.03	0.014	0.17	0.006	0.27	0.029	0.35	0.008
Spent shale	83.58	0.126	82.25	0.592	81.78	0.179	81.06	0.325
TOTAL	99.83	0.22	100.16	0.47	100.27	0.19	99.48	0.82
TOTAL Oil (Oil+C5to7)	6.15	0.28	7.84	0.22	7.89	0.13	7.18	0.42
ANALYSES % as recovered								
Fresh Shale								
Organic carbon	9.81	0.00	9.81	0.00	9.81	0.00	9.81	0.00
Inorganic carbon	0.69	0.00	0.69	0.00	0.69	0.00	0.69	0.00
Spent Shale								
Organic carbon	4.81	0.04	3.61	0.13	3.41	0.18	3.68	0.02
Inorganic carbon	0.01	0.01	0.03	0.02	0.02	0.02	0.03	0.02
Oil								
Organic carbon	84.54	0.27	80.87	0.98	83.86	2.27	84.73	0.47
Hydrogen	11.67	0.12	10.86	0.53	10.83	0.45	10.50	0.39
CARBON BALANCES								
Organic,								
Fresh shale	9.81	0.00	9.81	0.00	9.81	0.00	9.81	0.00
Spent shale	4.02	0.04	2.97	0.11	2.78	0.15	2.99	0.03
Oil	5.20	0.23	6.34	0.24	6.62	0.34	6.08	0.39
Hydrocarbon gas & CO	0.49	0.01	0.27	0.03	0.47	0.13	0.74	0.03
Carbon dioxide	0.00	0.00	0.05	0.00	0.06	0.00	0.10	0.00
TOTAL in products	9.70	0.22	9.64	0.21	9.93	0.32	9.92	0.45
Inorganic,								
Fresh shale	0.69	0.00	0.69	0.00	0.69	0.00	0.69	0.00
Spent shale	0.01	0.00	0.03	0.02	0.01	0.02	0.02	0.01
Carbon dioxide	0.67	0.01	0.66	0.01	0.68	0.03	0.67	0.01
TOTAL in products	0.68	0.01	0.69	0.02	0.69	0.01	0.69	0.00
TOTAL carbon recovered	10.39	0.23	10.33	0.21	10.62	0.33	10.61	0.45
% carbon recovered	98.94	2.16	98.34	2.02	101.16	3.15	101.03	4.31
Cil density 60°C g/cm ³	0.823	0.003	0.924	0.011	0.930	0.006	0.930	0.010
Oil H:C atomic ratio	1.66	0.01	1.61	0.10	1.55	0.0404	1.49	0.05

* The water yield from steam pyrolysis was assumed to be equal to the yield from Fischer assay.

The steam pyrolysis experiments were generally repeated three times for each set of conditions. Pyrolyses were done at 450, 500 and 550°C. The Fischer assays were carried out in accordance with ASTM standard D-3904-80, except that the particle size was as stated above and the pyrolysis gas was collected and analysed. Three assays were done on each shale.

RESULTS

Summaries of the results for the Nagoorin, Rundle and Condor oil shales are given in Tables 1, 2 and 3 respectively. These tables show, for each set of process conditions, the means and standard deviations of all of the product yields, the analyses and recoveries of organic and inorganic carbon in the products and the oil densities and hydrogen/carbon ratios.

Oil Yields and Conversion of Organic Carbon to Oil

The yields of oil from fluidised-bed steam pyrolysis are compared with Fischer assay yields in Table 4, and the fraction of the organic carbon recovered in the steam pyrolysis oils is compared with the recovery in the Fischer assays in Table 5. Except for Condor oil shale pyrolysis at 450°C, there is good agreement between the two estimates of yield enhancement. This discrepancy was traced to water contamination (about 4%) of the three oil samples from the Condor 450°C experiments which resulted in an overestimate of the oil yields and to a low estimate of the inorganic carbon content.

TABLE 4. OIL YIELDS

Oil Shale	Fischer Assay Yield, Mass %	Steam Pyrolysis Yield, % of Fischer Assay Yield		
		450°C	500°C	550°C
Nagoorin	7.13	126	134	129
Rundle	11.41	108	110	102
Condor	6.15	127	128	117

TABLE 5. FRACTION OF ORGANIC CARBON RECOVERED IN OIL

Oil Shale	Fischer Assay, % RSOC* recovered in oil	Steam Pyrolysis RSOC* in Oil, % of Fischer Assay Recovery		
		450°C	500°C	550°C
Nagoorin	13.8	128	136	132
Rundle	63.3	108	110	102
Condor	53.0	122	127	117

* Raw Shale Organic Carbon

From these results it is clear that steam pyrolysis results in enhanced oil yields over the temperature range 450 to 550°C and that the yield enhancement is at a maximum at 500°C for all three shales. The yields of oil at 500°C from the Rundle (110%) and Condor (128%) shales were almost identical with those obtained in the first study⁷ of the fluidised-bed pyrolysis of these two shales in steam under Fischer assay heating conditions, namely 107 and 129% respectively. These results indicate that flash heating produces no additional oil yield from these two shales beyond that resulting from the effect of the steam sweep gas.

Distribution of Organic Carbon in Pyrolysis Products

The distribution of organic carbon between oil, gas and spent shale is shown in Table 6. The carbon mass balances were satisfactory other than for Rundle shale at 550°C where only 93.3% of the raw shale organic carbon was accounted for in the products. To allow comparison of the split of carbon between the pyrolysis products, these results are shown in Figure 2 with the total organic carbon recovery normalised to 100%. For all three shales, it is apparent that steam pyrolysis at 450 and 500°C volatilised organic carbon from the shale with increasing efficiency compared with retorting under Fischer assay conditions. At 550°C, the fractions of organic carbon remaining in the spent shales were essentially the same as at 500°C.

TABLE 6. DISTRIBUTION OF ORGANIC CARBON IN PYROLYSIS PRODUCTS

Oil Shale	Product	Fischer Assay	% of Raw Shale Organic Carbon		
			Steam Pyrolysis		
			450°C	500°C	550°C
NAGOORIN	Spent Shale	78.6	75.7	69.8	69.6
	Gas	7.8	5.9	7.9	9.6
	Oil	13.8	17.6	18.7	18.2
	TOTAL	100.2	99.2	96.4	97.4
RUNDLE	Spent Shale	29.9	23.5	19.8	19.4
	Gas	7.0	4.8	6.4	9.3
	Oil	63.3	68.1	69.5	64.6
	TOTAL	100.2	96.4	95.7	93.3
CONDOR	Spent Shale	41.0	30.3	28.3	30.5
	Gas	5.0	3.3	5.4	8.6
	Oil	53.0	64.6	67.5	62.0
	TOTAL	99.0	98.2	101.2	101.1

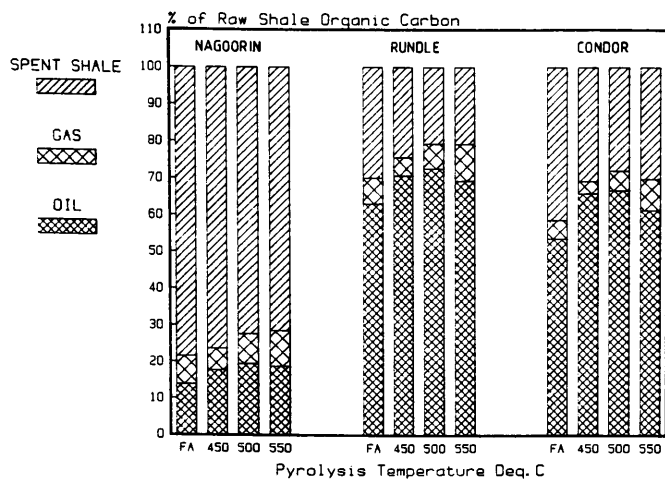


Figure 2. Distribution of Carbon in Products
(Normalised to 100%)

The distribution of organic carbon between oil and gas is shown in Table 7 and Figure 3. The fraction of the volatilised carbon appearing as oil decreased with increase in the steam pyrolysis temperature. Steam pyrolysis of Rundle and Condor shales at 500°C yielded more evolved carbon as oil than the Fischer assay, but at 550°C the oil fraction fell below that of the Fischer assay. In the case of Nagoorin shale, the enhancement of the oil fraction in steam pyrolysis was more marked, and was still significant at 550°C.

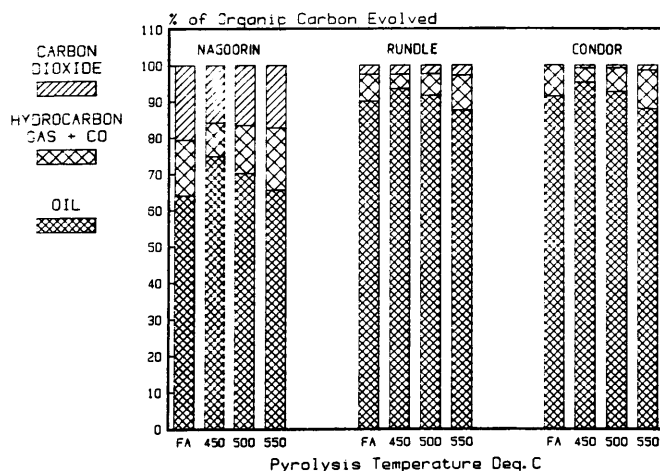


Figure 3. Distribution of Carbon in Volatile Products

Potential oil yield can be lost either by decomposition of part of the oil to coke within the shale particles or by the cracking of evolved oil vapours to produce gas. Cracking may also result in

the re-deposition of carbon on the spent shale and the hot retort surfaces.

Our results suggest that the enhanced oil yields obtained from fluidised-bed steam pyrolysis were due primarily to the reduced coking of oil within the shale. At 500°C, the yield enhancements attributable to reduced vapour phase cracking in the steam pyrolysis of Condor and Rundle shales were less than two per cent. For Nagoorin shale, cracking appeared to play a more significant but still secondary role; at 500°C, about two thirds of the 34% increase in yield appears to have resulted from reduced coking and one third from reduced cracking. At 550°C, the fall in oil yields from the three shales appears to have been due to increased cracking.

TABLE 7. DISTRIBUTION OF ORGANIC CARBON IN VOLATILE PRODUCTS

Oil Shale	Product	Fischer Assay	Steam Pyrolysis		
			450°C	500°C	550°C
NAGOORIN	Oil	64.1	74.9	70.2	65.6
	Carbon Dioxide	20.6	15.9	16.6	17.3
	Hydrocarbon gas & CO	15.3	9.2	13.2	17.1
RUNBLE	Oil	90.0	93.5	91.6	87.5
	Carbon Dioxide	2.5	2.5	2.4	2.8
	Hydrocarbon gas & CO	7.5	4.0	6.0	9.7
CONDOR	Oil	91.4	95.2	92.6	87.9
	Carbon Dioxide	0.0	0.8	0.8	1.4
	Hydrocarbon gas & CO	8.6	4.0	6.6	10.7

Pyrolysis Gas Yields

Variations in the composition of the pyrolysis gases are shown as a function of steam pyrolysis temperature in Figures 4, 5 and 6. The yields of these gases are compared with the Fischer assay yields as the mass of gas per unit mass of organic carbon evolved.

At 500°C, the yields of hydrogen were equal to or slightly less and those of carbon monoxide slightly higher than the Fischer assay yields. This is in sharp contrast to the results on Colorado shale reported as evidence for chemical reaction between steam and oil shale by Allred¹ who found that steam pyrolysis yielded 65% more hydrogen and about half as much carbon monoxide as the Fischer assay. Clearly, our results do not confirm that the steam was chemically active.

The results shown in Figures 4 to 6 give further evidence for vapour phase cracking at 550°C. Oil cracking in the vapour phase produces high alkene/alkane ratios⁸ and it is apparent that this ratio increases markedly between 500°C and 550°C for all three shales.

DISCUSSION AND CONCLUSIONS

The results of this study indicate that the fluidised-bed pyrolysis of Nagoorin, Rundle and Condor shales at temperatures between 450° and 550° C produces higher oil yields than Fischer assay and that the primary source of yield enhancement is reduced oil coking. Since there is no evidence of chemical action by the steam, and since the oil yields are almost identical with those obtained from fluidised-bed pyrolysis at a much lower heating rate ($12^{\circ}\text{C min}^{-1}$), it appears that the improved yields result from enhanced evaporation of oil from the shale because of the low partial pressures of oil vapours in the fluidised-bed retort and the consequent effect on the competition between evaporation and coking.

These differences in oil yield enhancement may be due, in part, to the different aromaticities of the shales, for coking is generally believed to predominate in oils derived from aromatic components of the kerogen⁹. All the steam pyrolysis oils were denser and had lower hydrogen to carbon ratios than the Fischer assay oils produced from the same shale, which suggests that the additional oil was at least partly aromatic. The largest yield increase was obtained from the Nagoorin shale which is also the most aromatic of the three shales¹⁰. However, the difference in aromaticities of the Rundle and Condor shales is small, hence the large difference in yield enhancement between these two shales cannot be related to aromaticity. Indeed, it may be related to the effect of oil shale grade on organic carbon conversion efficiency reported by Gannon et al.¹¹ who found, in Fischer assays of Stuart oil shale, that the fraction of organic carbon recovered increased as the grade of the oil shale increased, reaching an asymptotic limit at high grades. Similar effects were observed with Rundle and Condor oil shales¹⁰. They speculated that this effect may be the result of enhanced coking and/or cracking when the ratio of minerals to kerogen is high, i.e. when the grade of the oil shale is low.

Since the grade of our Condor sample was much lower than the Rundle sample (6.15 mass % Fischer assay oil yield v. 11.41%), the potential for improving the oil yield by reducing coking may have been higher in the Condor shale. It is worth noting that steam pyrolysis at 500° C increased the organic carbon recovery in the oil from the Condor shale

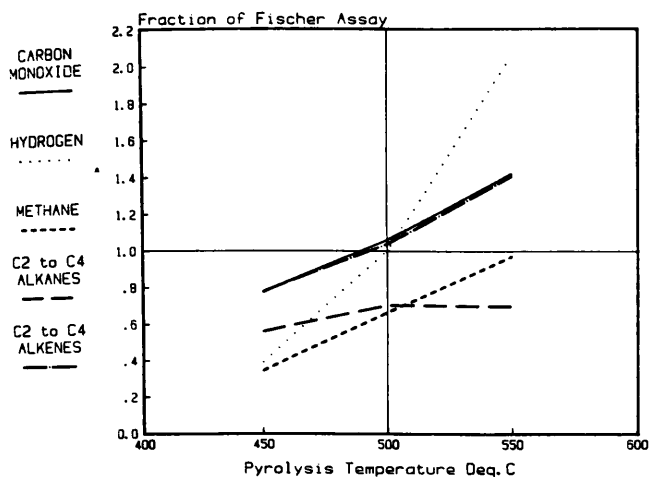


Figure 4. Nagoorin Pyrolysis Gas Yields (Per Unit Mass Organic Carbon Evolved)

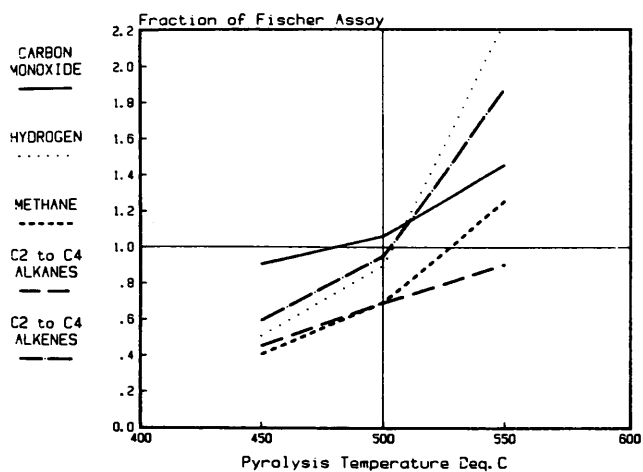


Figure 5. Rundle Pyrolysis Gas Yields (Per Unit Mass Organic Carbon Evolved)

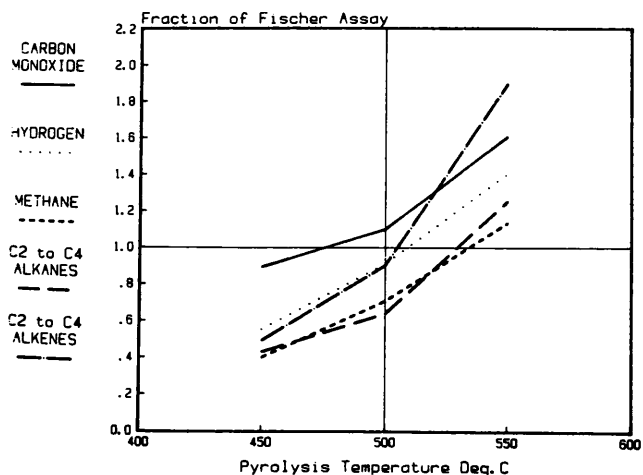


Figure 6. Condor Pyrolysis Gas Yields (Per Unit Mass Organic Carbon Evolved)

from 53.0% (Fischer assay) to 67.5%, and the recovery from the Rundle shale increased from 63.3% to 69.5%; i.e. the maximum efficiency of recovery was about the same for the two shales.

The increases in oil yield losses attributable to cracking when the temperature of the fluidised-bed reactor was increased from 500°C to 550°C ranged from 4.5% for the Rundle shale to 6.6% for the Nagoorin shale. This is much higher than the cracking loss observed by Bissell et al.¹² for Colorado oil shale. The vapour residence time in our fluidised-bed retort was 0.5 seconds; from the results of Bissell et al. we calculated that at this residence time the increased cracking likely to occur between 500°C and 550°C would be less than 1% for oil vapours from Colorado oil shale. Our results suggest that it is especially important to avoid high temperature gradients which could overheat the oil vapours in a retorting system for these shales.

Finally, the advantages of using steam as a fluidising gas are emphasised. As in our previous study, we were impressed with the efficiency of steam-oil co-condensation in quantitatively recovering the oil and producing a pyrolysis gas free from inert diluents. We are now involved in a fluidised-bed pyrolysis study using nitrogen as the fluidising gas and have found that a far more complex oil recovery system is required to recover all of the oil.

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