

FLUIDISED-BED RETORTING OF AUSTRALIAN OIL SHALES

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ABSTRACT

The pyrolysis characteristics of oil shales from eight deposits in Queensland, Australia, were compared using material balance modified Fischer Assays (FA) and a bench-scale fluidised-bed pyrolyser (BFP). A process variable study was also conducted on Condor and Stuart oil shales using the BFP. Under both FA and steam pyrolysis conditions, a shale having high kerogen hydrogen-to-carbon ratio (H/C) produced high organic carbon conversion to oil and high oil H/Cs. Compared to the FA oil yield, steam pyrolysis produced 15+4% more oil for all shales except Duaringa which yielded a 33% increase. However, steam pyrolysis oils had lower H/Cs and higher sulfur and nitrogen contents than the FA oils. For Condor and Stuart samples, temperatures from 450 to 525 C had little effect on the yields and chemical characteristics of the oils. However, a temperature above 525 C significantly reduced oil yields and increased hydrocarbon gas yields. In the presence of shale ash, oil yields from both nitrogen and steam pyrolysis decreased significantly as the ash-to-shale ratio increased.

INTRODUCTION

The CSIRO Division of Fuel Technology (formerly Division of Energy Chemistry) has a major research program aimed at the efficient processing of Tertiary oil shales from the Condor, Duaringa, Lowmead, Nagoorin, Nagoorin South, Rundle, Stuart and Yaamba deposits in Queensland, Australia. These deposits represent a total in-situ resource of more than 20 billion barrels (3×10^{12} L), that is, over ten times the current

Australian recoverable petroleum resources. Two projects completed to date have studied the processing characteristics of these Australian oil shales (1984-85)¹, and compared reactor types for the processing of these oil shales (1986-87)². A third project is investigating the integrated processing of the oil shales. This paper presents the major results from a study comparing pyrolysis characteristics in a bench-scale fluidised-bed pyrolyser (BFP) with nitrogen or steam as the sweep gas, and material balance modified Fischer Assays (FA) results.

EXPERIMENTAL

Nine oil shale samples from the Queensland deposits were studied. The elemental analyses of these samples are given in Table 1; their detailed descriptions have been given elsewhere^{1,2}.

The 48 mm diameter semi-continuous BFP, with nitrogen as the sweep gas, and the experimental procedure have been described elsewhere³. A description⁴ of the BFP with steam as sweep gas and its ancillary units; and a procedure⁵ to ensure complete oil/water separation and accurate determination of oil yield have also been given elsewhere. The pyrolyser, which was initially charged with 80 g of sand or sand/shale ash mixture, provided conditions under which shale was rapidly heated and isothermally pyrolysed to completion (solids residence time > 30 minutes) with a short residence time (0.5 s) for the oil vapour.

RESULTS AND DISCUSSION

Comparison of oil shales

Table 1 compares the results for all oil shale samples retorted under FA and steam BFP conditions. Mass balances for FA's on all oil shales were outstanding, being better than 99.5 % in all cases except for Yaamba where the balances were only slightly lower at 98.8 %. In the steam BFP runs, the yield of retort water was not determined, so the mass balances could not be closed. For both types of retorting, the organic carbon balances were good.

The shales gave FA oil yields of between 5.3 and 15.7 wt% on a dry

TABLE 1. COMPARATIVE PYROLYSIS CHARACTERISTICS OF NINE AUSTRALIAN OIL SHALES.

SHALE NAME	CONDOR CDD43		CONDOR 7090		D'ARINGA		LOWMEAD		NACORIN		NACORIN SOUTH		RUNDLE		STUART		YAAMBA	
	FA	SBFP	FA	SBFP	FA	SBFP	FA	SBFP	FA	SBFP	FA	SBFP	FA	SBFP	FA	SBFP	FA	SBFP
KEROGEN ATOMIC H/C	1.44	1.41	1.57	1.10	0.86	1.33	1.51	1.49	NA									
ANALYSIS OF RAW SHALE (%wt db)																		
Organic carbon	10.81	10.64	10.13	20.96	20.10	12.07	12.5	12.72	20.35	20.69	23.59	23.50	20.35	20.69	23.59	23.50	23.59	23.50
Inorganic carbon	0.72	0.75	0.07	0.29	0.28	0.77	1.15	1.11	0.46	0.47	2.36	2.37	0.46	0.47	2.36	2.37	2.36	2.37
Hydrogen	1.87	1.77	1.91	2.54	2.88	2.06	2.13	2.12	3.09	3.10	3.02	3.05	3.09	3.10	3.02	3.05	3.02	3.05
Sulfur	0.62	0.65	0.91	0.65	0.63	1.14	1.28	1.22	1.44	1.43	2.22	2.37	1.44	1.43	2.22	2.37	2.22	2.37
Nitrogen	0.74	0.74	0.42	0.72	0.70	0.43	0.33	0.38	0.56	0.65	0.89	0.88	0.56	0.65	0.89	0.88	0.89	0.88
YIELDS, g/100 g dry shale																		
Oil C5+	7.01	7.94	5.32	8.35	9.60	6.78	9.06	10.41	14.36	16.93	11.48	13.65	14.36	16.93	11.48	13.65	11.48	13.65
C2-C4 Alkanes	0.29	0.19	0.26	0.43	0.32	0.37	0.41	0.26	0.52	0.27	0.52	0.40	0.52	0.27	0.52	0.40	0.52	0.40
C2-C4 Alkenes	0.18	0.17	0.18	0.24	0.41	0.23	0.27	0.40	0.35	0.31	0.37	0.57	0.40	0.35	0.31	0.37	0.57	0.57
Methane	0.18	0.16	0.15	0.36	0.52	0.88	0.84	0.25	0.30	0.23	0.39	0.47	0.30	0.23	0.39	0.47	0.39	0.47
Hydrogen	0.07	0.13	0.02	0.06	0.16	0.05	0.04	0.11	0.10	0.12	0.19	0.60	0.10	0.12	0.19	0.60	0.19	0.60
Carbon monoxide	0.15	0.13	0.17	0.41	0.85	0.40	0.19	0.27	0.31	0.35	0.67	0.57	0.31	0.35	0.67	0.57	0.67	0.57
Carbon dioxide	1.57	2.96	0.99	2.92	3.84	2.02	1.47	3.57	2.23	2.30	8.21	12.81	2.23	2.30	8.21	12.81	8.21	12.81
Water	1.69	ND	3.67	3.79	ND	3.17	3.10	ND	3.21	ND	4.41	ND	3.21	ND	4.41	ND	4.41	ND
Hydrogen sulfide	0.00	0.30	0.01	0.02	0.35	0.03	0.00	0.11	0.00	0.42	0.00	1.27	0.00	0.42	0.00	1.27	0.00	1.27
Spent shale	88.79	85.91	89.16	83.31	78.18	86.95	84.92	81.68	78.32	75.07	72.53	66.97	78.32	75.07	72.53	66.97	72.53	66.97
Unaccounted	0.07	2.12	0.06	0.11	5.78	-0.02	0.31	2.65	0.31	3.99	1.23	2.58	0.31	3.99	1.23	2.58	1.23	2.58
RECOVERY OF ORGANIC CARBON (%)																		
Oil	54.8	63.3	44.6	33.4	39.9	46.9	61.4	69.4	59.5	69.2	41.1	49.1	59.5	69.2	41.1	49.1	41.1	49.1
Spent shale	38.2	29.8	45.4	57.6	48.0	42.8	30.3	18.6	33.4	21.9	47.4	35.5	33.4	21.9	47.4	35.5	47.4	35.5
Gas	5.8	5.2	7.9	7.4	10.4	8.9	8.1	7.8	7.5	4.9	7.2	11.2	7.5	4.9	7.2	11.2	7.2	11.2
Unaccounted	1.2	1.7	2.1	1.6	1.7	1.4	0.2	4.2	-0.4	4.0	4.3	4.3	-0.4	4.0	4.3	4.3	4.3	4.3
ANALYSIS OF OIL (wt%)																		
Carbon	84.42	84.79	84.83	83.64	84.43	84.84	84.53	84.84	84.31	84.18	84.30	84.44	84.31	84.18	84.30	84.44	84.30	84.44
Hydrogen	11.95	10.91	12.08	11.50	10.55	11.96	12.33	11.57	12.16	11.43	11.44	10.46	12.16	11.43	11.44	10.46	11.44	10.46
Sulfur	0.42	0.43	0.68	0.59	0.76	0.50	0.35	0.46	0.35	0.41	0.50	0.57	0.35	0.41	0.50	0.57	0.50	0.57
Nitrogen	1.40	1.81	0.98	1.11	1.25	0.97	1.02	1.06	0.96	1.14	1.22	1.55	0.96	1.14	1.22	1.55	1.22	1.55
H/C atomic	1.71	1.54	1.72	1.67	1.49	1.71	1.77	1.64	1.75	1.63	1.64	1.49	1.75	1.63	1.64	1.49	1.64	1.49
Density (g/cm ³ 60°C)	0.88	0.96	0.89	0.88	0.97	0.88	0.85	0.94	0.85	0.93	0.91	0.97	0.85	0.93	0.91	0.97	0.91	0.97

NA = Not available.

ND = Not determined.

FA = Material balance modified Fischer assay.

SBFP = Bench scale fluidised-bed pyrolysis with steam.

basis. A shale of high organic carbon content tended to give a high oil yield (Table 1). However, in some cases the correlation was poor owing to the conversion of only a small fraction of the organic carbon to oil. Figure 1 shows that, with the exception of the data for Duaringa shale, there is a strong correlation between organic carbon conversion and the atomic hydrogen-to-carbon ratio (H/C) of the shale kerogen for both the FA and steam BFP conditions. A shale of high kerogen H/C had a high conversion and was likely to produce a FA oil of high H/C.

Sweep gas

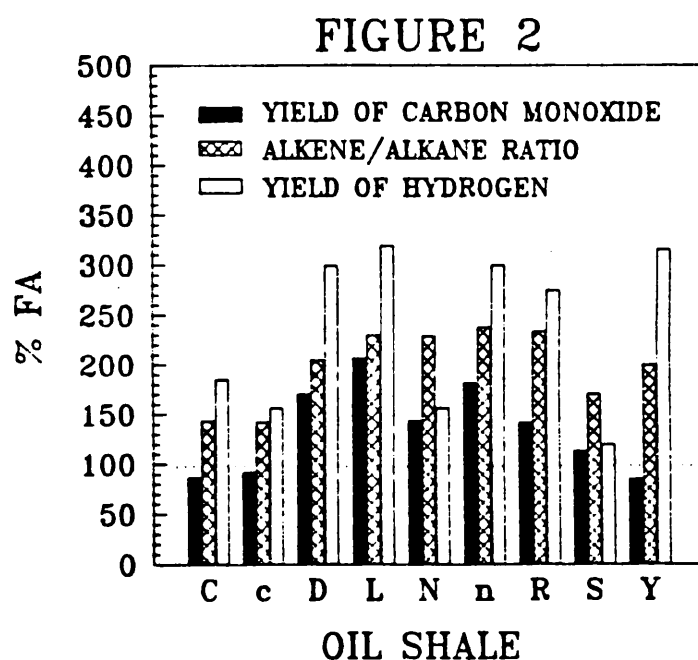
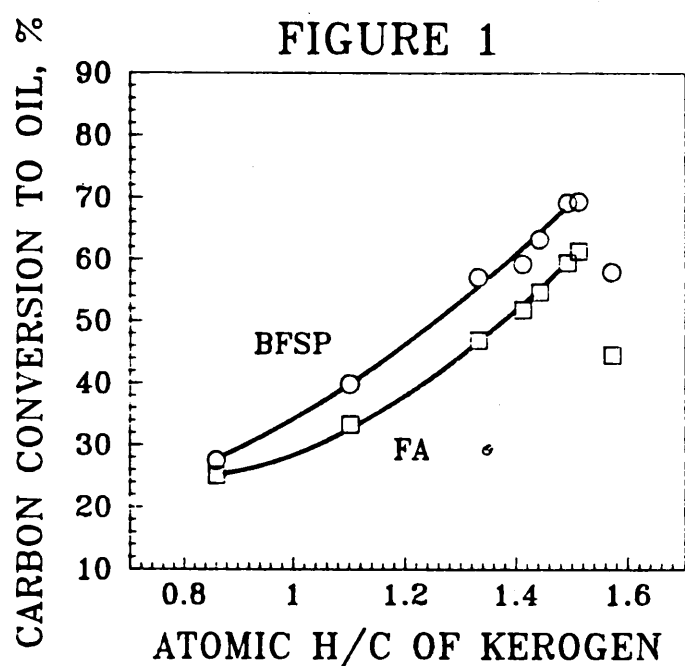
Compared to the FA oil yield, fluidised-bed steam pyrolysis gave about 10-20% more oil for all shales except Duaringa which showed a 33% increase in oil yield. Under similar conditions, Wall⁴ measured increases in oil yield of 10-34% for Condor, Nagoorin and Rundle oil shales. By comparison, the fluidised-bed nitrogen pyrolysis of Condor, Duaringa, Nagoorin and Stuart shales gave a 7% average increase in oil yield³; fluidised-bed pyrolysis with carbon dioxide gave an oil yield increase of 11% for a Condor sample¹. In all cases, oil yield increases were associated with increases in the conversion of organic carbon to oil and equivalent decreases in organic carbon conversions to char in the spent shale. For Kentucky oil shale, Carter and Taulbee⁶ found that oil yields obtained from fluidised-bed steam pyrolysis were only about 2% higher than those obtained with nitrogen pyrolysis; both exceeded FA oil yields by 20 to 30% for temperatures between 475 and 575°C.

Table 1 shows the inferiority of the steam BFP oils to the FA oils for all shales; the BFP oils had lower atomic H/C, higher sulfur contents and higher nitrogen contents (except for Duaringa). In particular, the sulfur content in the BFP oil from Duaringa shale was 5.6 times that in the FA oil and the total sulfur in this oil was about twice the kerogen sulfur in the shale. This indicated that at least part of the sulfur in oil originated from pyrite.

The FA produced trace amounts of hydrogen sulfide from all shales except Nagoorin. In contrast, the steam BFP gave very high yields of hydrogen sulfide (0.1 to 1.3 wt% of dry shale) from all shales. This is probably due to the reaction between steam and pyrite to give hydrogen

sulfide, sulfur dioxide and pyrrhotite.

Compared to the FA, the steam BFP produced less hydrocarbon gases for most samples. Figure 2 shows that in general the steam BFP gas had a higher alkene/alkane ratio, more carbon monoxide and considerably more hydrogen than the FA gas. High alkene/alkane ratios were attributed to the chemical equilibria, which favoured alkenes and hydrogen, owing to the high degree of dilution of the retort gas, rather than the thermal cracking of oil vapour. However, the amount of hydrogen produced from the alkene-alkane equilibria was not sufficient to account for the additional hydrogen.



Since the rapid heating of shale in a fluidised-bed has been found to have no effect on the oil yield⁴, and oil loss due to thermal cracking was small, an oil yield increase under nitrogen can be attributed mainly to enhanced oil evaporation caused by high gas sweeping. For Australian oil shales, we do not have a satisfactory explanation for further oil yield increase in the presence of steam. However, we think that this enhancement of oil yield by steam is related to the reduction of coking losses.

Pyrolysis temperature

The influence of temperature on oil yield for steam pyrolysis of Condor 7090 and Stuart samples is shown in Figure 3. Oil yields appeared to be independent of temperature in the range 450 to 525°C. This is

consistent with data on nitrogen fluidised-bed pyrolysis of Condor, Duaringa, Nagoorin and Stuart samples from our previous work³, and a Rundle sample investigated by Litster et al.⁷. Data for both shales indicated that the oil yields decreased as temperature increased above 525°C. By contrast, data of Carter and Taulbee⁶ showed maximum oil yields at about 520°C for both steam and nitrogen pyrolysis of Kentucky oil shale between 475 and 575°C. The loss of oil yield in the higher temperature range is likely to have been caused by significant thermal cracking of the oil vapour. This was supported by our data which showed the increases in hydrocarbon gas yield and ethylene/ethane ratio with increase in temperature. Low oil yields for Kentucky shale at the lower temperature range may be caused by shale residence times of 3 to 6 minutes, which was not long enough for complete conversion of kerogen in a continuous single-stage fluidised-bed retort.

Studies with Condor and Stuart shales showed that the temperature of the steam pyrolysis had little effect on the chemical characteristics of the shale oils produced. The atomic H/C ratios and nitrogen contents of the oils decreased slightly and sulfur contents increased only slightly as temperature increased above 525°C. A similar trend was observed for the nitrogen pyrolysis of Condor, Nagoorin and Stuart samples³.

Shale ash

Results for steam and nitrogen pyrolysis of Condor 7090 and Stuart samples in the absence and presence of shale ash are compared in Table 2. Shale ash was prepared by complete combustion of spent shale at about 800°C in a fluidised-bed combustor. For both shales and both retorting atmospheres, oil yield decreased as the ash-to-shale ratio (the ratio of the amount of shale ash initially charged into the fluidised-bed to the total amount of oil shale fed) increased. We have also observed this detrimental effect of shale ash on oil yield in the pyrolysis of Condor and Stuart oil shales in a 150 mm diameter continuous fluidised-bed pyrolyser⁸. Simulated distillations of shale oils in this study confirmed our previous conclusion that the lost oils were mainly heavy fractions which adsorbed and coked onto shale ash. This reaction which produces coke as the major product^{8,9} is distinct from the vapour phase and catalytic

FIGURE 3

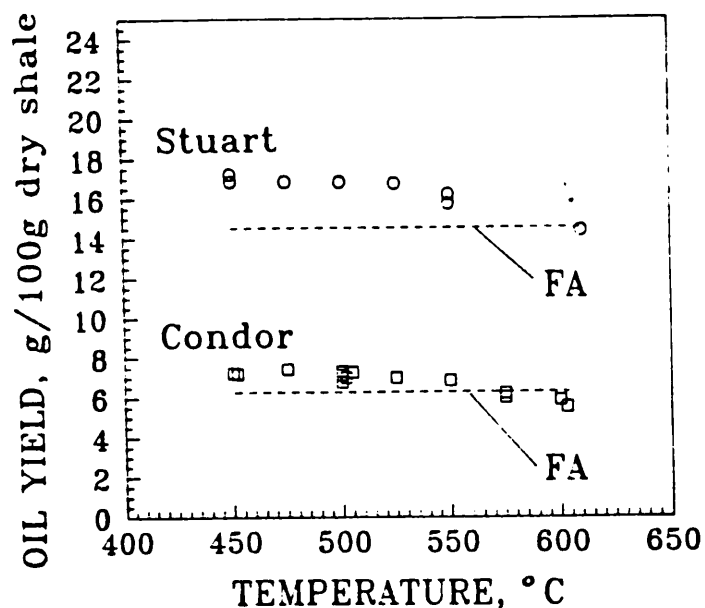


TABLE 2 EFFECT OF ASH-TO-SHALE RATIO ON BFP OIL YIELD (%FA)

SHALE	ASH-TO-SHALE RATIO	N ₂	STEAM
Condor	0.00	108	114
	0.25	95	ND
	0.50	90	101
	0.75	88	ND
	0.50*	101	109
Stuart	0.00	99	118
	0.25	96	ND
	0.50	94	109
	0.75	89	104
	0.50*	ND	116

ND: Not determined.

* : Ash treated at 1000°C for 24 h.

cracking reactions which yield predominantly lower molecular weight products.

Australian Tertiary oil shales are abundant in clay minerals (montmorillonite and kaolinite)¹⁰ which have high specific internal surface areas and were once used as cracking catalysts for petroleum gas oils. By contrast, Western USA (Green River) shales are rich in carbonate minerals. Our FA retorting of 50 g Anvil Point shale with its shale ash, fully combusted at 550°C, gave oil yield of 98% FAs. By comparison, 18% oil loss occurred in FA experiments on a Condor sample at ash-to-shale of one.

Table 2 also shows that for the same ash-to-shale ratio, pyrolysis with shale ash treated at 1000°C in a muffle oven for 24 hours gave less oil loss than pyrolysis with untreated shale ash. This treatment reduced the specific internal surface areas of shale ashes, for example from 23 to 8 m²/g for the Condor sample. The coking reactivities of Condor shale-oil on 15 different shale ashes have been found to correlate reasonably well with the internal surface areas of the shale ashes⁹. Also, Espitalie et al¹¹ showed that the amount of coked oil increased with the specific surface areas of clay minerals and except for Ca²⁺ montmorillonite, clays did not have any catalytic activity. We therefore consider high active internal surface areas to be one of the major factors in the reduction of oil yield.

ACKNOWLEDGEMENTS

This work was partly funded through a collaborative research agreement with Southern Pacific Petroleum NL/ Central Pacific Minerals NL. It was supported by grants Nos. 701 and 931 administered by the National Energy Research Development and Demonstration Council (NERDDC). The authors gratefully acknowledge the experimental assistance of B.H. Stratten, A.R. Tibbett, A.K. Hutchings and L.T. Roberts.

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