THE FLUIDIZED BED PYROLYSIS CHARACTERISTICS OF MOROCCAN OIL SHALE

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ABSTRACT. Pyrolysis characteristics of oil shales from the Timahdit and Tarfaya deposits were investigated in fixed bed, nitrogen swept fixed bed and fluidized bed pyrolysis. The objectives of this work were to determine the effects of pyrolysis conditions on product yields and distribution of the pyrolysed shales. Samples representative of two lithologic units (M_1 and T_4), which comprise part of the richest zone of the Timahdit oil shale formation and samples representative of five zones (R_0, R_1, R_2, R_3 and R_4) of Tarfaya deposit were examined. The shales are primarily carbonates, averaging 12.9 (Timahdit) and 11.3 (Tarfaya) percent organic carbon. Modified Fischer assay for the shales resulted in oil yields ranging between 13.2 and 20.4 gal/ton. Fluidization resulted in shale oil yields ranging from 133 - 157 percent of modified Fischer Assays.

INTRODUCTION. Large deposits of oil shales exist in Morocco. Extensive exploration and processing research has been conducted over the past decades (1). Moroccan oil shale deposits, discovered in the 1960's (1) include those at Guir, Ganntour, Mescala, Oulad Abdown, Tanger, Tarfaya and Timahdit (1-6). Because oil shales are the only abundant indigenous source of fossil fuel in Morocco an extensive resource assessment program has been conducted by Office National de Recherches et D'Exploitations Petroliers (ONAREP). The entire shale oil resources were estimated to amount to 50 billion barrels (2).

Organic carbon contents for Moroccan shales, averaging between 11 and 13 percent, are very similar to both western and eastern US oil shales (2). When western US oil shale technologies are applied to Moroccan shales, a significant amount of carbon is left on the spent shales (2, 4) and large amounts of off-gases are generated. This is similar to the case for eastern US oil shale, where coking and cracking reactions result in high residual carbon and large off-gas volume (7, 8). Fluidized bed retorting has been shown to enhance oil yields when applied to eastern US oil shale by minimizing retrograde oil reactions. This is accomplished by providing rapid heat up and product sweep.

Thus, the objectives of this study are to determine if fluidized bed retorting will enhance oil yields from Moroccan shale and to determine the nature of products produced from the shale. Oil shales from the Timahdit and Tarfaya deposits were selected and the pyrolysis characteristics were investigated using fixed bed, nitrogen swept fixed bed and fluidized bed conditions.

CHARACTERIZATION OF TIMAHDIT AND TARFAYA OIL SHALE DEPOSITS. The Cretaceous Timahdit and Tarfaya oil shale have been under intensive study since 1974 as potential sources of domestic oil (1 - 6). The Timahdit and Tarfaya deposits are among the largest of the

Moroccan oil shales, and are located strategically relative to major cities, potential ports and mining configuration (2). The Timahdit deposit is situated in the Middle Atlas region in the north central part of Morocco, 155 miles southeast of Rabat and 22 miles south of Azrou, and occur in two northeast-southwest trending geosynclines (2). The Tarfaya deposit is located in the south west region along the Atlantic Coast of the Moroccan Sahara. The coastal location is a significant factor in the potential development of this deposit. A comprehensive summary of the previous research relative to the Tarfaya and Timahdit oil shale activities is presented elsewhere (1, 2, 5).

Marlstones, silicious marlstones and limestones comprise the bituminous rocks of the Tarfaya and Timahdit oil shale regions (1, 2). Representative samples from Tarfaya and Timahdit deposits utilized in this study are derived from seven oil shale zones which are further distinguished in 21 sub-zones (Table 1). A considerable variation in zone thickness occurs among the individual beds (Table 1). Samples representative of two lithologic units (M_1 and T_4, see Table 1), which comprise only part of the hydrocarbon section of the Timahdit deposit (2), were available for study. These two shale beds contain predominantly argillaceous marls. In contrast, the Tarfaya oil shales consist mainly of chalks with varying kerogen contents and are characterized by higher moisture contents compared to those of Timahdit (2). The richest Tarfaya oil shale zone, R-zone, is subdivided into 5 lithologic units (R_0, R_1, R_2, R_3 and R_4), all of which were available in this study (see Table 1).

The seven oil shale samples under investigation were obtained from master batches which were produced from bulk samples derived from individual shale beds. The shales were crushed, blended and screened to 18 x 20 mesh for the pyrolysis study. The shale was stored under argon to retard oxidation. Fixed bed, N_2-swept fixed bed and fluidized bed runs were conducted using representative sample aliquotes with the same grain size to allow for more precise comparison of the oil yields.

EXPERIMENTAL.

Modified Fischer Assay

A single fixed bed retorting system was used to determine the Fischer Assay pyrolysis characteristics of the seven oil shale zones. A single retort was utilized to eliminate unaccountable systematic errors and to obtain an unbiased base for comparison. Modifications to standard Fischer Assay procedures were employed because it had been previously shown that these running conditions provide for more reproducible results for eastern US oil shales (9, 12). This study's operating conditions included a linear heating rate of 12 °C/min during oil evolution and a 30 minute soak time at maximum retort temperature of 550 °C. The purpose of the modified Fischer Assay experiments was to establish oil yield data for the shale samples that will be used in the fluid bed retort experiments.

N_2-Swept Fixed Bed Experiments

The fixed bed retorting system is described in detail elsewhere (9). Operationally, a continuous stream of N_2-gas was allowed to enter the pyrolysis zone after being heated to run temperature (550°C). Preheating of the purge-gas was achieved while passing it through a spiral coil that was encased in the reactor furnace. The N_2-stream swept oil vapors and a small amount of fines into the product collection system. The purpose of the N_2-swept fixed bed runs was to determine variations in oil yields caused when the contact time between oil vapors and shale particles was reduced.

Bench Scale Fluidized Bed Experiments

Apparatus: A 1.5 inch diameter reactor as used for fluid bed pyrolysis of Eastern Shales was used in this study. The apparature has also been described in detail elsewhere (9) and only a brief description is offered here. The retort itself was constructed of 316 stainless steel and has a 100 micron stainless steel filter at the bottom which serves as distributor plate. A stand pipe controlled the spend shale overflow from the bed. To closely monitor the retort conditions three thermocouples were located above the distributor plate at lower, medium and upper bed heights. The retort was enclosed in an electrically heated furnace which further accommodates a gas preheater and a fines trap. The preheater served to heat the fluidizing gas to bed temperature before entering the shale zone. The baffled fines trap helped to remove shale particulates from the oil vapor to diminish coke formation before vapors exit the high temperature zone provided by the furnace. A screw feeder was calibrated to add raw shale at a feeding rate of 2.0 + 0.1 g/min into the reactor. N_2 purge-gas was passed down from the feed bin and up through the spent shale reservoir into the reactor. A purge-gas flow rate of 0.25 - 0.30 STP L/min was sufficient to prevent oil vapors from escaping through either inlet or exit pipes. Helium gas was used as fluidizing medium. The volumetric He-flow rate at bed temperature (550°C) and pressure (1 atmosphere) was adjusted to 28 L/min and in combination with a shale feed rate of 2.0 g/min provided for a shale residence time of approximately 20 minutes.

The above fluidized bed pyrolyser provides all of the following: good mixing of the shale solids including both raw shale and pyrolysed ash particles; excellent heat transfer; rapid heating rates of the shale particles; and, a uniform pyrolysis temperature of 550°C. In addition, short residence time of oil vapor in the hot zones favors low oil cracking.

Product Collection Traps: The same configuration of product traps used for eastern US oil shales was employed in this study and the reader is referred to the original work (9). Four traps were used to condense the products generated in the fluidized bed retort. The trap closest to the reactor exit pipe, an air-cooled stainless steel tube, condensed a tarry product. The second trap, an Ice/bath, is designed to remove both oil and H_2O from the vapor phase and consists of a closed pyrex tube with gas in- and outlet openings. The third trap, was developed to condense large amounts of products and utilizes thermal wells and densely coiled stainless steel wire spirals for increased precipitation surface (10, 11). The trap itself was immersed in a Dry Ice/isopropanol bath (-78°C). The final trapping system consists of a 50 ml pyrex tube, sealed with a rubber stopper and was immersed in a Dry/Ice isopropanol bath. The exit tube is connected into a hood system and allows non-condensable vapors to be removed. A gas sample can be drawn for analysis of the vapor phase. Gases leaving the product collection apparatus were monitored on a Carle Gas analyser (Series SX-AGC) to determine off-gas weight.

RESULTS AND DISCUSSION. Operating parameters employed in this study are not necessarily optimum running conditions. They were chosen as a basis for this investigation because a large data base is available from previous bench scale fluidized bed retorting on similar materials.

Ultimate and proximate analyses indicate major differences in moisture, ash and sulfur contents between the Timahdit and Tarfaya oil shales under investigation (Table 2). Results of material balances for modifyed Fischer Assay runs (Table 3) and N_2-swept fixed bed experiments (Table 4) demonstrate that the latter pyrolysis method caused a slight enhancement in oil recovery. Modified Fischer assay for the shales resulted in oil yields ranging between 13.2 and 20.4 gal/ton and oil yields obtained in the N_2-swept fixed bed retorting experiments were in the range of 15.7 - 21.6 gal/ton. Therefore, a maximum oil yield increase of 21 percent was achieved by mobilizing oil vapors with a continuous flow of N_2 gas which reduced the overall residence time of the oil vapors on the shale particles. Also, a decrease in off-gas emission was recorded when N_2 gas mobilized the oil vapors (Table 3, 4), suggesting that vapor phase cracking was reduced. In general, a slightly greater reduction in off-gas emission was recorded for the Tarfaya oil shale samples compared to those of Timahdit. The difference may be related to the higher carbonate and moisture and lower sulfur contents of Tarfaya shales. The results further indicate that oil densities increase for the N_2-swept fixed bed runs (0.956 - 0.971 g/cm^3, Table 4) compared to modified Fischer Assay (0.944 - 0.968 g/cm^3, Table 3).

Fluidized bed pyrolysis resulted in oil yields in excess of the modified Fischer Assay and N_2-swept fixed bed pyrolysis (Table 6 and Figure 1). At this point of study, fluidized bed retorting was performed for three of the seven shale samples. Oil yields obtained from the bench scale fluid bed retort (Table 6) were based on oil collected in the trapping system. The moisture collected simultaneously with the oil was resolved during Karl Fischer water analysis. The C_5^+ hydrocarbon fraction in the off-gas phase was not accounted for in the mass-balance calculations at this time. The C_5^+ concentration was determined to be insignificantly small in the off-gas for either of the fixed bed retort methods employed.

Using the 1.5 inch diameter fluid bed retort, at 550°C operating temperatures 55 to 60 percent of the carbon was removed from the Timahdit shale samples (M_1 and T_4) and 65 percent of the carbon was removed from the Tarfaya shale (R_4). Material balances indicated oil yields for the Timahdit and Tarfaya shale samples to vary between 133 to 157% of those of the Fischer Assay runs (Table 6). A comparison with Eastern shale fluidized bed retorting shows great similarities with respect to overall oil yield and processing behavior.

The fluidized bed retorting of Moroccan oil shales appears very promising from a view point of oil yields. Fluidized beds provide not only enhanced oil yields under relatively non-severe conditions (moderate temperatures of 550°C at atmospheric pressures), but also leave the pyrolysed shale with much less remaining sulfur. This has two potential advantages. The first is lower environmental risks do to lower acid release after exposure to atmosphere. A second is the potential recovery of elemental sulfur, a needed raw material in Morocco.

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TABLE 1 OIL SHALE ZONES FROM TARFAYA AND TIMAHDIT DEPOSITS

DEPOSIT TYPE	SAMPLE ID [sub-zone]	OIL- SHALE ZONES		ZONE THICKNESS [meter]
TARFAYA OIL SHALE DEPOSITS	RON	I	RO	1.1
	R-1A, R-1B, R-1C, R-1D, R-1E, R-1F, R-1G	II	R1	7.45
	R-2A1, R-2A3, R-2B1, R-2B2, R-2C	III	R2	4.4
	R-3A1, R-3A2, R-3A3, R-3A4, R-3A5	IV	R3	4.85
	R-4B1	V	R4	2.2
TIMAHDIT OIL SHALE DEPOSITS	T-4	VI	T	42.15
	M1-COUCH	VII	M	67.35

TABLE 2 PROXIMATE AND ULTIMATE ANALYSES OF MOROCCAN OIL SHALE DEPOSITS

SAMPLE ID	MOISTURE wt %	VOLATILES wt %	ASH wt %	FIXED CARBON wt %	1* C wt %	H wt %	N wt %	2* S wt %
			TARFAYA OIL SHALE DEPOSIT					
RON	2.39	40.3	56.33	1.1	16.88	1.41	0.63	0.19
R-1A	2.77	41.8	54.86	0.6	18.88	1.92	0.84	0.98
R-1B	3.91	39.4	55.87	0.8	14.82	1.29	0.62	0.15
R-1C	4.67	41.8	52.86	0.7	19.02	2.07	0.83	0.35
R-1D	6.61	42.3	49.76	1.3	19.06	2.44	0.76	0.39
R-1E	4.44	44.1	51.73		19.93	2.14	0.83	0.48
R-1F	2.47	47.7	49.62	0.2	21.84	2.01	0.82	0.47
R-1G	7.04	43.2	49.96	0	19.14	2.23	0.79	0.46
R-2A1	1.98	41.5	55.38	1.2	14.7	0.94	0.52	0.17
R-2A3	4.68	39.7	53.37	2.2	17.4	1.74	0.7	0.32
R-2B1	8.12	40.7	49.71	1.5	15.44	1.8	0.52	0.08
R-2B2	5.45	42.9	51.31	0.3	15.43	1.46	0.54	0.19
R-2C	3.01	42.2	53.77	1.1	13.9	1.03	0.57	0.13
R-3A1	6.47	43.6	49.71	0.2	18.31	1.95	0.76	0.29
R-3A2	5.15	40.9	52.83	1.1	17.6	1.78	0.7	0.37
R-3A3	3.54	48.1	48.14	0.3	22.23	2.27	0.31	0.52
R-3A4	5.91	47.1	46.13	0.9	20.98	2.36	0.81	0.39
R-3A5	7.75	38.9	52.36	1.1	15.16	1.8	0.53	0.23
R-4B1	7.05	44.1	48.59	0.3	19.16	2.19	0.67	0.39
			TIMAHDIT OIL SHALE DEPOSIT					
T-4	2.79	29.5	65.31	2.4	15.65	1.63	0.78	1.44
M1-COUCH	1.8	36.4	60.94	0.9	19.77	1.85	0.77	1.9

1* organic + inorganic C 2* organic + inorganic S

TABLE 3 MATERIAL RECOVERY FROM MODIFIED FISCHER ASSAY

SHALE MATERIAL	R0 wt %	R1 wt %	R2 wt %	R3 wt %	R4 wt %	M wt %	T wt %
SPEND SHALE	81.4	76.55	89.57	77.08	75.11	85.07	83.16
H2O	9.26	12.08	4.11	14.02	13.01	4.44	7.27
OIL	6.72	7.94	5.33	8.22	8.19	7.09	6.19
GAS	1.82	3.45	1.02		3.75	3.33	3.41

TABLE 4 MATERIAL RECOVERY FROM N2-SWEPT FIXED BED

MATERIAL	R0 wt %	R1 wt %	R2 wt %	R3 wt %	R4 wt %	M wt %	T wt %
SPEND SHALE	81.45	76.21	88.89	77.52	75.05	83.17	81.74
H20	9.35	12.99	3.99	14.29	14.11	4.97	7.31
OIL	7.41	8.27	6.31	8.41	8.25	8.69	7.88
GAS	1.77	2.56	0.77		2.61	3.12	3.06

TABLE 5 OIL YIELD AND OIL DENSITY OF PYROLOYSED SHALES

ZONE	FA [gal/ton]	OIL DENSITY	N2-FA [gal/ton]	OIL DENSITY
R0	16.97	0.949	18.57	0.956
R1	19.92	0.955	20.66	0.959
R2	13.29	0.959	15.68	0.964
R3	20.39	0.966	20.79	0.969
R4	20.27	0.968	20.38	0.971
T	15.71	0.944	19.66	0.61
M	17.92	0.948	21.58	0.965

TABLE 6

YIELDS FOR FLUID BED RETORT

ZONE	OIL wt %	1* FB vs. FA %
R3	9.28	133
R4	11.96	146
M	11.13	157

1* percent oil yields of Fischer Assays

FIGURE 1 COMPARISON OF OIL YIELDS