PRODUCTION OF OIL FROM ISRAELI OIL SHALE

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ABSTRACT. Oil shale can be utilized in two ways: direct combustion to generate steam and power or retorting to produce oil and gas. PAMA has been developing both direct combustion and retorting processes. Its main effort is the combustion. An oil shale fired steam boiler was erected in the Rotem industrial complex for demonstration purposes. PAMA also has been looking into two alternative retorting concepts — slow heating of coarse particles and fast heating of fine particles. The present paper provides operating data of oil shale processing in the following schemes: (a) retorting in a moving bed, pilot and bench scale units, and (b) retorting in a fluidized bed, bench scale unit.

INTRODUCTION

The term "oil shale" has been given in Israel to bituminous marls of the Senon era. Deposits of oil shale have been found all over the country, but mainly in the north-eastern part of the Negev. The overall reserves are estimated at over 10 billions of tons.

The Rotem deposit, located near the Negev town of Dimona, has been studied extensively. Table 1 presents a list of its main components — organic material, calcite and clay minerals, mainly kaolinite. Minor amounts of quartz, apatite, gypsum and pyrite also have been found. The concentration of organic carbon is not constant but increases significantly towards the bottom of the deposit; a typical content is about 10%, as shown in Table 2. The organic material, the kerogen, consists of about 66.5% carbon, 7.6% hydrogen, 2.3% nitrogen, 14.6% oxygen and 9.0% sulfur.

Table 1. *Typical Israeli oil shale composition*

	(% wt. — dry basis)
Organic material	10 - 27
Calcite	45 - 65
Clays	10 - 30
Moisture	22%
Quartz, Apatite, Gypsum, Pyrite	balance

Oil shale is a friable, porous and dusty material. Its compressive strength is relatively low, about 100 kg/cm^2, while its porosity is very high - 30 to 35%. The raw mine material may have a moisture content of about 20%.

Table 2. *Typical analysis of Rotem's oil shale*

		(% wt.— dry basis)
Organic material	C	9.70
	H	1.12
	N	0.33
	O	2.13
	S	1.31
Pyritic sulfur		0.60
Bound water		1.80
CO_2 (carbonate)		23.68
Non-volatile		59.33

Although the oil shale of the Rotem deposit has a very low calorific value (LHV = 750 Kcal/kg), two of its characteristics make it suitable for fluidized bed combustion:

- very high reactivity due to the high porosity of the rock and the weak S-C bond in the organic material;
- high calcium content which serves as a natural absorbent for sulfur oxides; the Ca/S molar ratio is over 10:1.

Therefore, it was decided to utilize the oil shale mainly for combustion. A fired steam boiler using 50 tons per hour (tph) of oil shale was erected for demonstration purposes and has been operating continuously since October 1989. As expected, the carbon utilization and the sulfur capture have been very high — over 99%.

A second way of extracting energy from oil shale is the production of liquid fuel. Although this process is not economically justified today, as the price of conventional crude oil is very low, the Ministry of Energy and PAMA have decided to continue research and development of oil production from shale for the following reasons:

- starting a commercial operation once the price of crude oil goes up;
- as of today, shale's oil is the only significant source of liquid fuel in Israel and therefore should be exploited if and when necessary;
- shale oil may be a source of special chemicals and other products.

ISRAEL OIL SHALE AS A SOURCE OF LIQUID FUEL

The following discussion is based on the well known Fischer Assay (F.A.) evaluation standard (ASTM D3904). Although this procedure was originally developed for coal, it is also considered as a good estimate of the liquid fuel production potential of oil shale.

Table 3 presents a typical F.A. yield of Rotem's oil shale as well as high heating value of raw shale and products. Tables 4 and 5 list the analyses and the composition of the F.A. products. Typical F.A. oil properties are illustrated later in Table 9. The following points need to be highlighted:

- the oil yield of the shale's original organic material is about 43%. However, the yield of thermal energy, carbon and hydrogen is over 50%;

Table 3. *Israeli oil shale—typical F.A. yields and heating values*

	Yield on dry basis (% wt.)	HHV (Kcal/Kg)
Raw oil shale		1060
Oil	6.23	9550
Gas	3.14	5580
Spent shale	88.13	310
Water	2.5	-

Table 4. *Analysis of F.A. products (% wt.)*

Composition	Kerogen	Oil	Char
C	66.5	78.5	72.1
H	7.6	9.5	3.5
N	2.3	1.1	4.2
O	14.6	3.7	15.6
S	9.0	7.2	4.6
H/C Ratio	1.37	1.45	0.58

- the raw shale oil is characterized by high content of sulfur and nitrogen — 7.2% and 1.1%, respectively. It is also highly unsaturated — the bromine number is about 100 and the H/C ratio is only 1.45. Therefore, this oil should be severely hydrotreated before its processing in the oil refinery;
- the residual organic matter of the spent shale (char) is a very low quality fuel; its nitrogen and sulfur contents are high, while it is very hydrogen deficient. Its best use would be as a source of heat for the oil production process;
- the shale's gas is rich in H_2S, CO_2 and CO, which normally cannot be found in natural or refinery gases. The H_2S should be scrubbed away from the gas before it can be used.

Table 5. *Typical F.A. gas analysis*

	% vol.
H_2	19.49
NH_3	0.69
CO	3.94
CO_2	23.84
H_2S	22.87
CH_4	14.99
C_2H_4	1.27
C_2H_6	4.59
C_3H_6	1.92
C_3H_8	1.90
C_4H_8	0.33
C_5	1.30
C_6	0.66

SHALE OIL PRODUCTION PROCESSES

Shale's oil is the product of thermal cracking of the organic matter contained in the shale. The cracking is achieved by heating the rock to a temperature of about 500°C and maintaining it for a few minutes; this process is called retorting. There are two main types of retorting processes — slow and fast heating.

Slow heating of coarse particles:

Processes of this type are characterized by slow heating of raw shale at a high temperature for up to 30 minutes. The shale particles are coarse, having a diameter of up to 3". Normally, gas is used as heat carrier. Installations using this technology include the Paraho and Petrosix vertical shaft moving bed, the Union oil upflow vertical shaft, the Superior and Dravo circular grate and the Soviet Union's Kiviter process.

Fast heating of fine particles:

Finely ground oil shale, with a maximum diameter of less than 7 mm, as presented in Table 6, is heated within seconds to 500°C and maintained at that temperature for a few minutes. Theoretically, the short residence time results in high throughput. The spent shale is sent to a combustor, and the ash is then recycled back to the retorting chamber as a heat carrier. The retort is designed to ensure good mixing of the oil shale with the ash. Facilities using this process include the Lurgi screw retort, the Chevron stage fluidized bed, the Galoter rotary drum, the Hebrew University split stage reactor and the PAMA fluidized bed process.

Figure 1 is a simplified scheme of an indirectly heated moving bed retort. Oil shale moves downward by gravity through a vertical shaft. At first, the shale is dried and preheated by an upflowing gas, then retorted and finally cooled by a cold recycle gas. Heat is supplied to the process by the externally heated recycle gas. The off-gas with the oil mist and the spent shale leave the retort at a low temperature of 100°C. The oil mist is collected in a coalescer and by an electrostatic precipitator. This process is very simple and reliable.

The main disadvantage of the indirectly heated moving bed retort is the low thermal efficiency — the char is not utilized, while the product gas is consumed in the recycle gas heater.

The directly heated moving bed retort was developed to solve this problem. Figure 2 presents a scheme of this process. Air is injected into the bed under the retorting zone and the heat is generated by partial combustion of the char and the gas. The process was developed in the late 1970s by the Paraho Company, USA. The oil yield of this process is 90-95% of the Fischer Assay.

The particle size of the feedstock in the moving bed is between 7 and 75 mm. As is shown in Table 7, these particles account for only about 75% of the crushing oil shale. Consequently, the moving bed retorting process must be integrated with a process which is able to utilize the fine particle — either a fluidized bed combustor or a fast heating retort. Figure 3 depicts such an integration.

There is another disadvantage of the direct heated moving bed retort — it produces a large volume of low heating value gas. This gas has a calorific value of about 100 BTU/SCF and H_2S content of about 0.5%. Therefore, it is very expensive to treat the gas and very difficult to use it in conventional boilers. PAMA recommends using this gas in co-combustion with oil shale, in a fluidized bed combustor.

Table 6. *Sieve analysis of oil shale*

mm	% wt.
9.0 +	1.2
8.0 - 9.0	1.6
6.3 - 8.0	3.8
4.0 - 6.3	9.3
2.8 - 4.0	10.4
2.0 - 2.8	11.3
1.4 - 2.0	14.1
0.8 - 1.4	15.4
0.5 - 0.8	9.3
- 0.5	23.6
"top size" — 7mm	

Figure 4 presents a simplified scheme of a fluidized bed retort and combustor. Raw oil shale is mixed in the retort with hot recycled ash, whereby it is heated to about 500°C. The vapors of oil, gas and steam are sent to a fractionation section, via a cyclone. The mixture of spent shale and recycled ash enters the combustor where the char is oxidized. The circulation of the ash is achieved by pneumatic conveying from the retort to the combustor. Rotary valves are used to control the flow of solids as well as for sealing.

Figure 5 is a block diagram of this process. It includes dryer, retort, combustor, ash cooler, heat

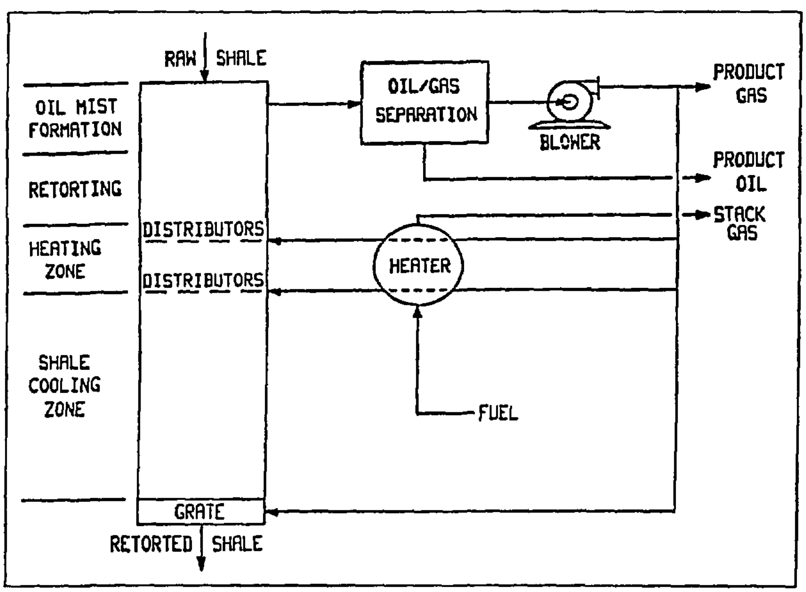

Fig. 1. *Moving bed retort — indirectly heated*

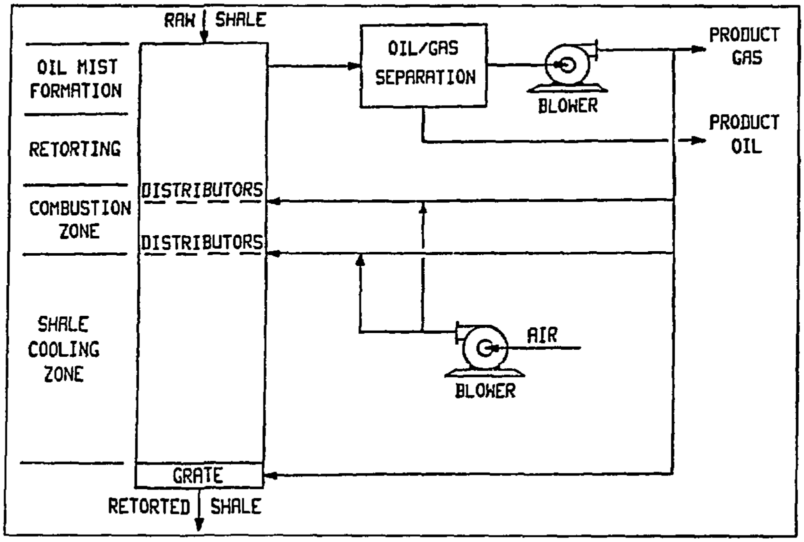

Fig. 2. *Moving bed retort — directly heated*

Table 7. *Sieve analysis of oil shale after primary crushing*

mm	%wt.
75.0 +	16.4
53.0 - 75.0	27.7
37.5 - 53.0	14.6
19.0 - 37.5	17.8
9.5 - 19.0	16.2
7.0 - 9.5	2.9
2.8 - 7.0	5.2
1.4 - 2.8	1.8
0.5 - 1.4	1.6
- 0.5	1.8
suitable as feedstock to a moving retort:	
7.0 - 75.0	73.2

recovery unit and dust collector. Although the process is complicated compared to a moving bed, it has some potential advantages:

- all mined shale can be processed;
- the process has high thermal efficiency;
- product gas has a calorific value of over 500 BTU/SCF.

PAMA RESEARCH AND DEVELOPMENT PROGRAM

For more than 10 years, PAMA has been working on the development of processes for oil shale utilization. It should be noted that PAMA's work is part of a national effort. Many research groups have worked in this field. Two of these groups are still working in cooperation with PAMA: the Fuels Research Group of the Hebrew University and the Energy Center of the Weizmann Institute.

Table 8 summarizes PAMA's effort on retorting processes. Tests on slow heating, moving bed retorting were carried out in various units, using direct as well as indirect heating. Most of the tests were highly successful, with an oil yield of about 95% of the Fischer Assay value. As can be seen in Table 9, the processed shale's oil is heavier than the F.A. oil, but has a similar composition. It almost completely lacks the naphtha fraction.

The data obtained from the tests were used by PAMA in the design of a demonstration plant. The moving bed, vertical shaft design was completed in 1985. The unit, with an internal diameter of 11 ft was proposed. This demonstration plant would be able to process 30 tph of oil shale and produce 250 BPD of synoil. The required investment was estimated at 15 million dollars.

PAMA has also been working on fast heating fluidized bed retorting. A bench scale unit has been operating since 1985, and the testing program will be

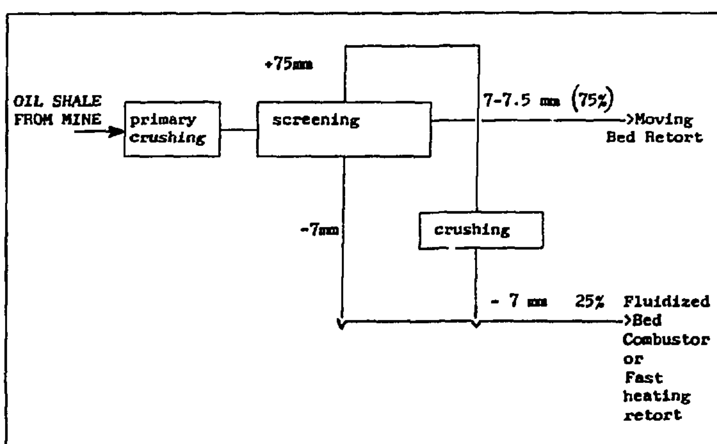

Fig. 3. *Integration of moving bed retort and oil shale fines utilization*

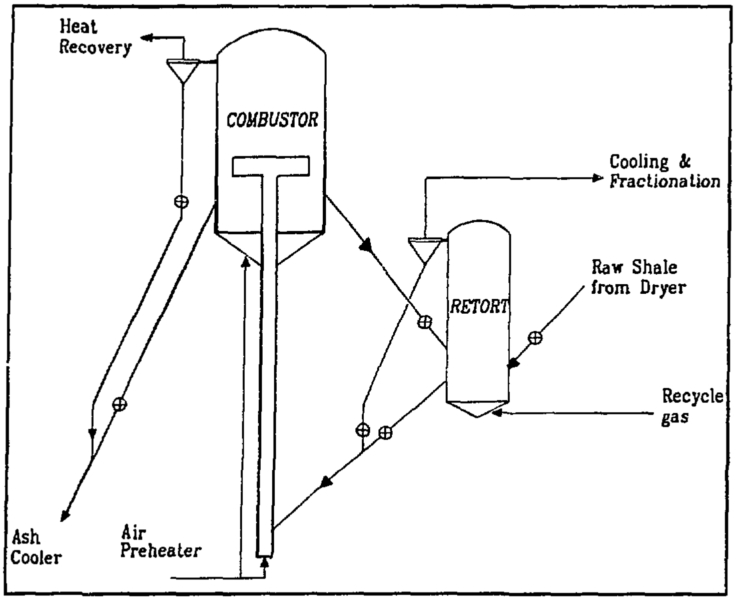

Fig. 4. *Simplified scheme of fluidized bed retort and combustion system*

produced in the bed process, as can be seen in Table 9;

- no significant scrubbing of H_2S from the gas was observed; it was expected that the H_2S would react with the recycled ash to form CaS and FeS. The phenomenon was observed by PAMA's lab, as shown in Figure 6, and by other laboratories.

The fast heating process proved to be much more complicated than the moving bed retort. However, we believe that the 3 main operation problems have been solved:

- controlling the ash circulation;
- preventing the leakage of gases between the retort and the combustor;
- preventing clogging of the gas cooling and oil collection systems by entrained fine particles.

This year, PAMA intends to

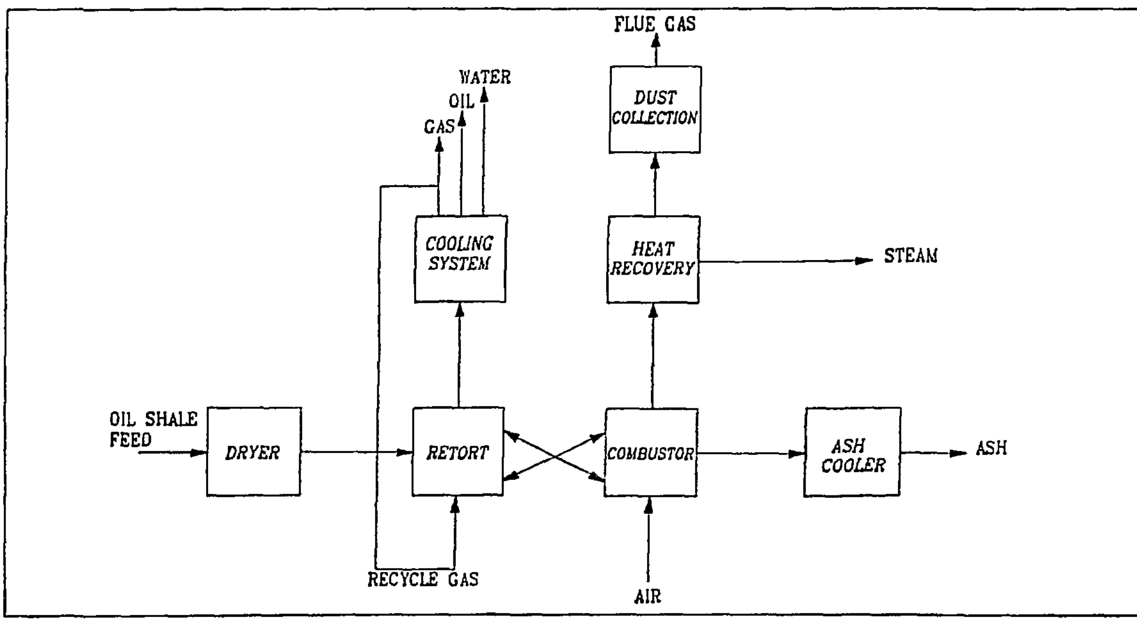

Fig. 5. *Block diagram of fast heating retort process*

completed this year. Here are the main results:

- the average oil yield is 80% of the F.A. value. This value is lower than expected, probably due to the low temperature in the retort, lower than optimal temperature;
- the shale's oil is very similar to the oil

evaluate the fast heating process and to compare it with the moving bed retorting. A joint team of the Ministry of Energy and PAMA will then select the best process. If the moving bed would be selected, as mentioned, we will recommend to erect and run the 30 tph demonstration plant. If the fast heating

Figure 8. *Summary of PAMA's R&D program on shale oil production*

Moving Bed Retort	
1979-80,83	Pilot tests in Paraho pilot plant.
1983-84	Feasibility study of 18,000 bpd plant.
1985	"Pre-project" - preliminary design and cost estimate for a 250 bpd Demonstration Plant.
1988	Pilot tests in Petrosix pilot plant.
1989-90	Tests at PAMA Lab Scale Unit.
Fast Heating - Fluidized Bed	
1985	Erection of a Bench Scale Unit.
1986-87	First Phase Testing.
1989-90	Second Phase Testing.
1991	Process Evaluation.

Table 9. *Comparison between shale oil from different processes*

	Fischer Assay	Moving bed	Fluidized bed
Density (gr/ml at 15°C)	0.9646		
Simulated distillation (°C)			
IBP	70	146	139
10% vol. over at	147	232	228
30%	227	311	297
50%	299	374	353
70%	369	440	418
90%	445	510	499
FBP	513	598	633
Total:			
Sulfur (% wt)	7.2	6.9	6.8
Nitrogen (% wt)	1.1	1.3	1.1
n-Heptane ins. (% wt)	1.0	5.3	7.6
Kin. visc. at:			
40°C (cst)	6.6	31.6	33.1
50°C (cst)	5.0	19.9	24.2
Pour point (°C)	0	12	9

process is decided upon, the pilot with a capacity of about 6 tph of oil shale will be constructed.

As stated earlier, raw shale oil must be hydrotreated before it is fed to a refinery. In 1985 Israeli shale oil was hydrotreated in the pilot plant of a USA company. Table 10 lists the properties of the obtained syncrude. It can be classified as a high quality crude oil; the sulfur content is low, less that 0.05%, and it has no residue.

It is possible, however, that better oil would be obtained with new catalysts. Therefore, PAMA and researchers of the Ben-Gurion University are working on the development of novel catalysts which will enable hydrotreating and hydrocracking of the raw shale oil in one plant. It is expected that the product would be of better quality than the syncrude of Table 10, thereby improving the economics of shale's oil production in Israel.

Table 10. *Properties of Israeli oil shale syncrude*

Gravity (°API)	31.2
Sulfur (% wt.)	<0.05
Nitrogen (ppm)	1000
Kin. viscosity at 50°C (cst.)	5.5
Pour-point (°C)	35
Yields: (% vol)	
Naphtha	5
Jet fuel	15
Gas Oil	40
HVGO	40

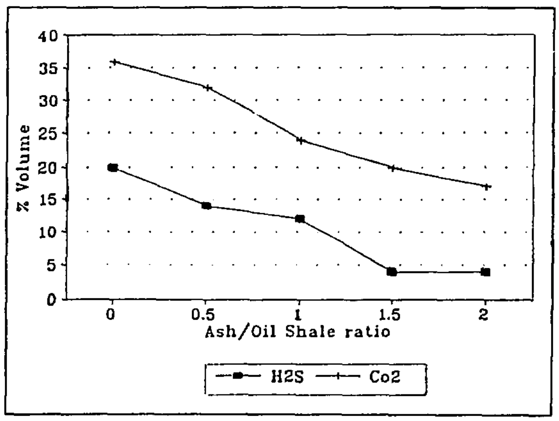

Fig. 6. Gas composition at different ash/oil shale ratios