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SHALE HOLD TIME FOR OPTIMUM OIL SHALE RETORTING INSIDE A BATCH-LOADED FLUIDIZED-BED REACTOR

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Abstract. *An optimum thermal decomposition (retorting) of the Jordanian Lajjun oil shale was examined using a laboratory-scale batch-loaded fluidized-bed reactor. The effects of the retorting temperature (450–600 ºC), shale hold time (5–40 min) and size of shale particle (0.6–4.5 mm) on oil yield were investigated. Findings showed that for maximum oil yield achievement, a shale particle size close to 1.4 mm was optimal. For this, two optimum retorting zones were proposed; in the first zone, retorting should be performed at higher temperatures (540–600 °C) and short shale hold times (5–20 min) and in the second zone, at lower temperatures (450–510 °C) and long hold times (> 20–40 min).*

Keywords: *retorting, oil shale, fluidized bed, oil yield.*

1. Introduction

For many countries, oil shale represents a valuable potential source of liquid hydrocarbons and energy. Jordan's huge reserves of oil shale exceed 50 billion tons, which is approximately equivalent to 5000 million tons of oil [1]. In Jordan, there are about 26 known deposits of oil shale, some of which are large and of relatively high-grade quality [2, 3]. The most important eight deposits, listed in Table 1, are located in west central Jordan within 20 to 75 km east of the Dead Sea. The Lajjun, Sultani and Juref ed Darawish deposits have been explored by boreholes most extensively, and many samples have been analyzed. Table 1 summarizes some of the geological and resource data for these eight deposits. Calcite, quartz, kaolinite, and apatite make up the major mineral components of the Lajjun oil shale, along with small amounts of dolomite, feldspars, pyrite, illite, goethite, and gypsum [4].

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The sulfur content of Jordanian oil shale ranges from 0.3 to 4.3%. The sulfur content of shale oil from the Lajjun deposit is about 3%.

Table 1. Resource data for eight oil shale deposits in Jordan

Deposit	No. of boreholes	Area, km^2	Overburden, m	Thickness of oil shale, m	Shale oil, wt%	Oil shale, 10^9 tons	Shale oil, 10^6 tons
Lajjun	173	20	30	29	10.5	1.3	126
Sultani	60	24	70	32	7.5	1.0	74
Juref ed Darawish	50	1500	70	31	?	8.6	510
Attarat Umm Ghudran	41	670	50	36	11	11	1245
Wadi Maghar	21	19	40	40	6.8	31.6	2150
Wadi Thamad	12	150	140–200	70–200	10.5	11.4	1140
Khan Ezzabib	–	?	70	40	6.9	?	–
Siwaga	–	–	–	–	7.0	–	–
Total	–	2385	–	–	–	64.9+	5246+

Previous research works on oil shale pyrolysis inside fluidized-bed reactors showed dissimilar relationships between oil yield and retorting temperature. Chen et al. [5] pyrolyzed fine oil shale particles (0–0.95 mm) in an experimental fluidized-bed reactor. They showed that the yield of shale oil reached 5.13% under optimum experimental conditions, i.e. particle size of oil shale less than 0.47 mm, feeding rate 14 kg/h, and reactor temperature 450–500 °C. The residence time, however, was kept constant at 11 min. Nazzal and Williams [6] pyrolyzed oil shale in a semi-continuous fluidized-bed reactor at 400–650 °C at a constant residence time of 45 min and shale grain size of 1.20–3.33 mm. They found that the oil yield was increased with temperature increase from 400 to 520 °C, while it was decreased at temperatures higher than 520 °C. Also, Wall [7] reported an oil yield increase when the pyrolysis temperature was increased from 450 to 500 °C upon pyrolyzing oil shale in a bench-scale fluidized-bed reactor at 450–550 °C. However, no dependency of oil yield on retorting temperature was established by other researchers like Carter et al. [8] and Dung et al. [9], who reported that the oil yield was independent of temperature in the 450–550 °C range. Similarly, Dung and Wall [10] and Dung and Udaja [11] found that the oil yield was independent of temperature in the 450–525 °C range.

Therefore, it is a rewarding task to investigate the relation between the retorting temperature and shale hold time, and their sequential effect on oil yield through an optimum retorting process. This was experimentally studied in the current work by varying the shale hold time (between 5 and 40 min) and retorting temperature (450–600 °C) only with oil shale of pre-determined optimum particle size (found to be around 1.4 mm).

2. Experimental

2.1. Apparatus

The schematic diagram of the fluidized-bed apparatus is shown in Figure 1. The apparatus was a vertical laboratory-scale electrical reactor (Carbolite STF 15/-610, USA; 6.0 kW power, 240 V input). The reactor tube was made of carbon steel with 7.5 cm in inside diameter and 120 cm in height with a maximum operating temperature of 1500 °C. The heated length was 610 mm. The fluidizing medium, silica glass (inert material) with a mean diameter of 0.35 mm, was placed in a static bed 70 mm in height over the gas distributing wire mesh (100 straight-hole carbon steel plate). The temperature of the bed was monitored with an R-type thermocouple placed about 20 mm below the bed surface. The fluidizing gas was provided from a nitrogen cylinder at a superficial velocity equaled to about 2 times the minimum fluidization velocity. In a typical experimental run, the sweep gas flow rate was kept constant at 30 ± 1 l/min corresponding to the vapor residence time varying between 15 to 20 s depending on the retorting temperature as well as on the vapors evolution rate from the oil shale. At this flow rate, the bed appeared smoothly fluidized. The vapor products leaving the top of the reactor were

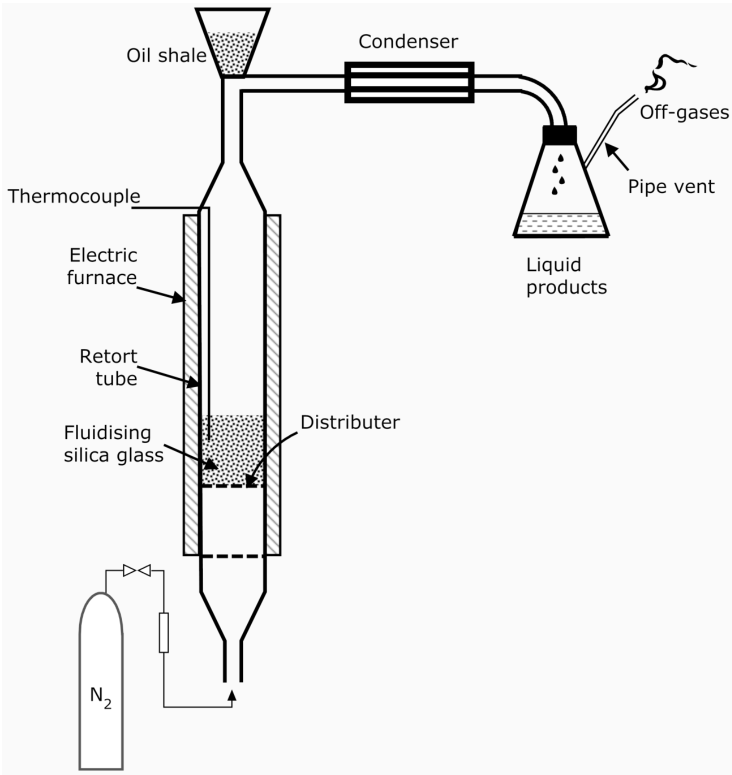

Fig. 1. Schematic diagram of the batch-loaded fluidized-bed reactor.

condensed through an ice water-cooled glass condenser. The oil was then separated from water in accordance with the ASTM D244 standard test method.

2.2. Oil shale materials

The oil shale samples utilized in this work were collected from the Lajjun deposit in the crest central part of Jordan. Table 2 presents the chemical composition of a typical oil shale sample. The received oil shale was ground in a ball mill, and sieved into six different average particle sizes of 0.6, 0.9, 1.4, 2.1, 3.3 and 4.5 mm. In a typical run, a weighed shale sample (about 55 g) was introduced from the top of the preheated reactor by quickly dropping it into the reactor as soon as a steady temperature was reached, producing a negligible temperature drop in the bed temperature.

Table 2. Chemical composition of an arbitrary sample of Lajjun oil shale

Component	wt%
Moisture	4.39
Ash	54.68
CO_2	18.88
Total S	3.12
Organic C	14.88
H_2	1.64
N_2	0.38
O_2	1.87
Fisher assay, wt%:	
Oil content	11.00
Spent shale	80.61
Moisture	4.00
Off-gases	4.39

3. Results and discussion

Table 3 shows one set of experimental runs on the thermal decomposition of oil shale conducted at a constant shale hold time of 40 min inside the reactor. The yields of oil shale, off-gases, moisture and spent shale were measured at various parameters, i.e. shale particle size between 0.6 and 4.5 mm and retorting temperature between 450 and 600 °C. The calculated percentage relative oil yield was based on the oil yield obtained from the standard Fisher assay as follows:

$$\text{Relative oil yield\%} = \frac{\text{Attained shale oil}}{\text{Shale oil (Fisher assay)}} \cdot 100$$

Table 3. Experimental set of retorting conditions at oil shale hold time of 40 min

Run No.	Shale particle size, mm	Retorting temperature, °C	Oil, g	Water, g	Spent shale, g	Off-gases, g	Relative oil yield, %
1	0.6	450	5.79	2.26	44.18	2.78	95.62
2	0.6	480	5.92	2.27	43.82	3.00	97.78
3	0.6	510	6.02	2.38	44.00	2.60	99.50
4	0.6	540	5.65	2.48	43.95	2.92	93.36
5	0.6	570	5.40	2.12	43.70	3.77	89.26
6	0.6	600	5.12	2.16	43.41	4.32	84.58
7	0.9	450	6.16	2.44	43.97	2.43	101.87
8	0.9	480	6.32	2.31	43.87	2.50	104.40
9	0.9	510	6.45	2.21	44.25	2.10	106.57
10	0.9	540	6.00	2.13	43.99	2.87	99.18
11	0.9	570	5.87	2.17	43.76	3.20	97.08
12	0.9	600	5.42	2.35	43.57	3.66	89.53
13	1.4	450	6.32	2.34	44.13	2.22	104.40
14	1.4	480	6.47	2.11	44.27	2.15	106.99
15	1.4	510	6.62	2.19	44.39	1.79	109.49
16	1.4	540	6.14	2.32	44.02	2.53	101.44
17	1.4	570	5.90	2.08	43.95	3.07	97.51
18	1.4	600	5.48	2.45	43.51	3.57	90.56
19	2.1	450	6.15	2.39	43.77	2.68	101.71
20	2.1	480	6.29	2.32	43.63	2.76	104.03
21	2.1	510	6.48	2.14	43.84	2.54	107.11
22	2.1	540	5.97	2.21	43.63	3.18	98.75
23	2.1	570	5.69	2.34	43.08	3.90	94.06
24	2.1	600	5.35	2.36	42.75	4.54	88.40
25	3.3	450	5.98	2.21	44.04	2.77	98.91
26	3.3	480	6.18	2.12	43.61	3.09	102.14
27	3.3	510	6.38	2.08	43.78	2.76	105.45
28	3.3	540	5.82	2.43	43.49	3.26	96.21
29	3.3	570	5.32	2.33	43.30	4.06	87.86
30	3.3	600	4.93	2.19	43.25	4.63	81.45
31	4.5	450	5.83	2.21	43.94	3.02	96.38
32	4.5	480	6.19	2.07	43.49	3.25	102.30
33	4.5	510	6.34	2.15	43.77	2.74	104.83
34	4.5	540	5.67	2.23	43.65	3.44	93.79
35	4.5	570	5.24	2.21	43.44	4.11	86.53
36	4.5	600	4.85	2.13	43.34	4.67	80.21

3.1. Optimal retorting temperature

Figure 2 represents the percentage relative oil yield variation with temperatures ranged from 450 to 600 °C at different shale particle sizes ranged from 0.6 to 4.5 mm (shale hold time was fixed at 40 min). Oil yields were found to increase with increasing temperature from 450 to 510 °C, and reached a maximum at around 510 °C for all shale grain sizes. The oil yield increase (from 450 to 510 °C) and subsequent decrease (from 510 to 600 °C)

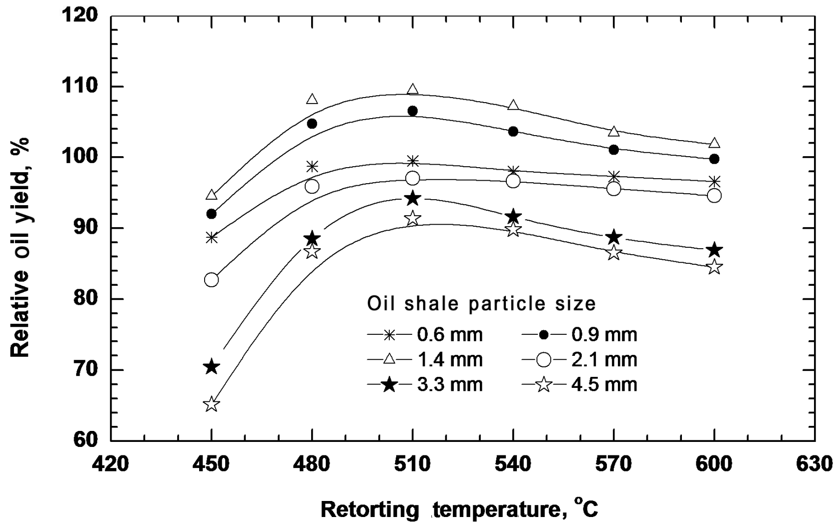

Fig. 2. Change of percentage relative oil yield with retorting temperature at different shale particle sizes (shale hold time = 40 min).

were found to be less sensitive to temperature with smaller shale particle sizes (0.6–2.1 mm) compared to those with larger shale particle sizes (3.3–4.5 mm). This result, in fact, is not unexpected, due to the exceedingly complex and competing process steps during the thermal decomposition of oil shale. The increased oil yield at temperatures below 510 °C is a result of the shale bitumen compounds conversion and volatilization to oil, water and off-gases (hydrocarbons) vapors. At elevated temperatures (> 510 °C), in addition to the volatilization due to continued evaporation of heavier oil molecules, thermal cracking and coking of oil compounds to volatile fragments also occur, which will result in a decreased oil yield and simultaneous increased off-gases yield [12, 13, 14, 15]. This was experimentally observed by the almost ceased oil drops down to the collecting flask which was accompanied by an increased off-gases emission out from the flask pipe vent. The collected oil amount dropped from 6.62 to 5.48 g, while there was an increase in the emitted off-gases yield from 1.79 to 3.57 g (see Table 3). Interestingly, at this decreased oil yield and subsequent increased off-gases yield with temperature rise from 510 to 600 °C, the spent shale yield was found to be nearly unaffected as illustrated in Figure 3. This trend most likely suggests that either no coking occurred or it was of scant extent since small shale particles produce less coking [16], and/or the released coke was continuously eliminated by the sweeping nitrogen gas.

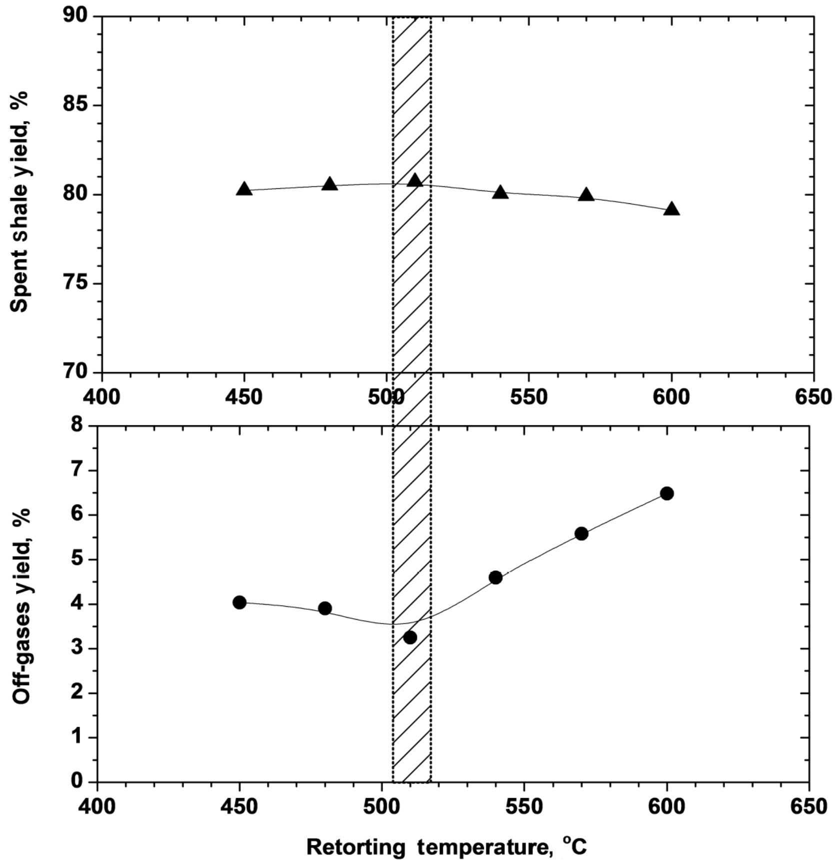

Fig. 3. Change of yield of off-gases and spent shale with retorting temperature (shale particle size 1.4 mm, shale hold time 40 min).

3.2. Optimal shale particle size

In the oil yield against shale particle size plot at the optimum temperature (510 °C) at the shale hold time of 40 min (Fig. 4), a fast increase in the obtained oil yield with small shale grain sizes of 0.6–1.4 mm was followed by a reduction in the oil yield with large shale particle sizes of 2.1–4.5 mm. The relative oil yield increased from 99.5% at a 0.6 mm shale grain size to about 110% at a 1.4 mm shale particle size, and then fell to around 105% at a 4.5 mm shale grain size. The low oil yield associated with small shale particles might be explained by the fact that small shale particles often possess a large specific surface area and pore volume. Therefore, the oil evolved, during the first decomposition process (volatilization), would be retained on the particles surface and inside the pores for an additional time to undergo a further cracking (secondary decomposition) into non-condensable off-gases.

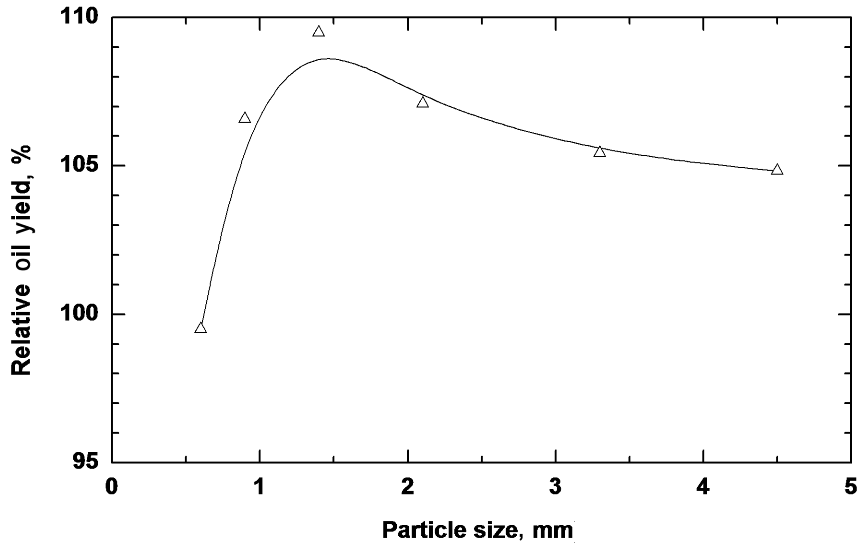

Fig. 4. Change of percentage relative oil yield with shale particle size at optimum retorting temperature of 510 °C (shale hold time 40 min).

On the other hand, with large shale particles, the extremely low heat conductivity of shale causes a bigger difference in temperature between the center and outside surface of the particle; for the formed oil in and near the cold center of particles it will take a longer time to diffuse outward to the hot outer surface. This will eventually result in a similar cracking process of oil and thus in the formation of greater amounts of off-gases and sequential reduction in oil yield. Table 3 shows that the oil yield dropped from 6.48 to 6.34 g when the shale grain size increased from 2.1 to 4.5 mm, while the off-gases amount increased from 2.54 to 2.74 g. Optimum oil shale grain size close to 1.4 mm is, accordingly, recommended for a maximum yield of shale oil.

3.3. Optimal shale hold time

Figure 5 illustrates the effect of shale hold time on percentage relative oil yield at different retorting temperatures for the optimal shale grain size (i.e. 1.4 mm). As can be seen, the first retorting zone (zone I in the figure) belonging to the short shale hold time (5–20 min) shows that maximum oil yield could be attained in the high temperature range (510–600 °C), and the yield increase was found to be proportional to the retorting temperature rise. This observation is close to that of Chen et al. [5] who found that shale oil yield gradually increased in the 250–450 °C reaction temperature range, and a maximum yield was obtained at 450–550 °C at a constant residence time of 11 min. The apparent increase of oil yield with increasing temperature in this zone, as was explained in the previous section, was due to the primary oil

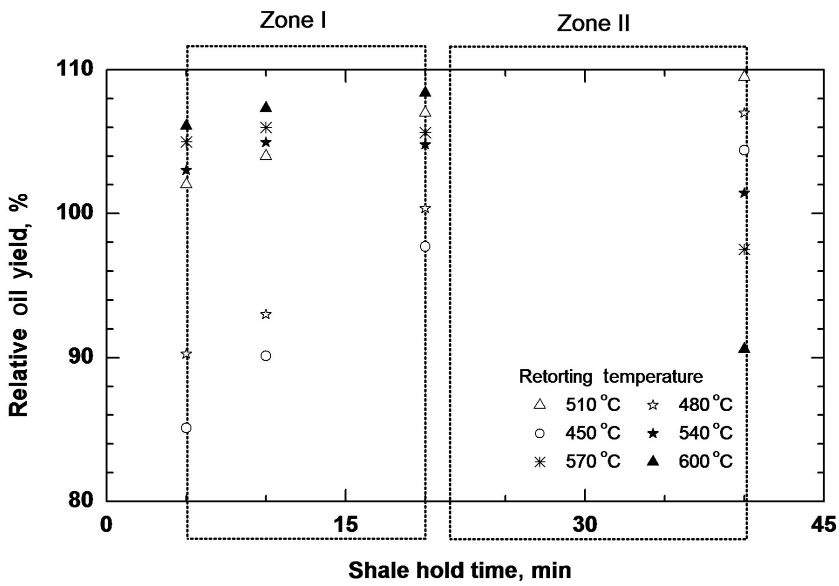

Fig. 5. Change of percentage relative oil yield with shale hold time at different retorting temperatures (shale particle size 1.4 mm).

shale volatilization process and continued evolution of oil vapors with no cracking chances during hold time periods as short as < 20 min. So, the retorting process in this zone can be considered as a time-controlled process.

In the second zone (zone II in Figure 5) of long shale hold time (>20–40 min), however, both the shale hold time and temperature played an important role in the retorting process. There are, accordingly, two regimes. In the low temperature regime (450–510 °C) the initial decomposition rate is likely higher than that of the successive cracking. So, the oil yield kept increasing with temperature increase from 450 to 510 °C. In the high temperature regime, however, the completeness of the cracking step is stronger, and thus, reduces the oil yield. This result agrees with the finding of Nazzal and Williams [6] at comparable shale particle sizes, retorting temperatures and residence time: 1.20–3.33 mm, 400–650 °C and 45 min, respectively. Han et al. [17], upon retorting 0.6 mm oil shale at a residence time of 40 min, observed that the rate of shale oil formation was fast at 460–490 °C (a result close to that zone II shows), and almost ceased close to 520 °C; a result which does not really clash with that of zone II, considering the smaller size of their oil shale (0.6 mm).

For application in integrated burning technologies based on circulating fluidized-bed combustion (CFBC) fired with a mixture fuel of fine oil shale and spent shale (shale char), the second zone would be practically favorable since fine shale retorting at temperatures below 550 °C would produce spent shale possessing good combustion properties in terms of fixed carbon and residual organics [18].

4. Conclusions

For optimal retorting process, an optimum oil shale grain size of 1.4 mm gave maximum oil formation at all retorting temperatures ranging from 450 to 600 °C, at which there were two retorting zones:

- zone I (short shale hold time varying from 5 to 20 min): recommended retorting in the high temperature range (510–600 °C), the retorting process in this zone could be considered as a time-controlled process;
- zone II (long shale hold time varying from > 20–40 min): recommended retorting in the low temperature range between 450 and 510 °C.

Zone II retorting would be quite applicable to integrated burning technologies based on CFBC combustion fired with the fine oil shale/spent shale fuel mixture, as retorting in this zone would most likely produce spent shale possessing good combustion properties.

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