MAOMING AND HUADIAN OIL SHALE RETORTING USING SOLID HEAT CARRIER

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ABSTRACT

A continuous experimental unit of retorting with capacity 10kg/h using hot spent shale as solid heat carrier was set up. The retorting of Maoming and Huadian oil shale has investigated in the unit. The size range of oil shale sample was 0 — 5mm. Hot spent shale as heat carrier at temperature of 700 — 750℃ was mixed with raw oil shale which was preheated to about 120℃, and the ratio of spent shale to raw oil shale was 3—4. The retorting temperature range was 445—525℃, the optimal temperature was approximately 500℃ for oil yield, it was about 90% of Fischer Assay.

China owns large deposits of oil shale, and oil shale retorting has been carried out for many years. Fushun retorter has been well experienced and famous in the world, but only lump oil shale can be used. The fine grained shale could not be used. The coefficient of recovery oil is not high and need to be developed further. In order to utilize fine grained oil shale, a new retorting process using solid heat carrier has been developed in some countries[1 — 3]. For this purpose an experimental unit for retorting of oil shale with capacity of 10kg/h has been set up in the Dalian Institute of Technology[4]. In this experimental unit many types of oil shale and lignite were tested and the experimental results indicated that it is available for the retorting of oil shale such as Maoming and Huadian oil shale with higher oil yields.

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1. FLOWSHEET OF EXPERIMENTAL UNIT

The experimental unit mainly consists of preparation of raw oil shale, retorting, a lift pipe for combustion and pneumatic conveying, and recovery of oil and gas[4] . A schematic diagram of this unit is shown in Figure 1.

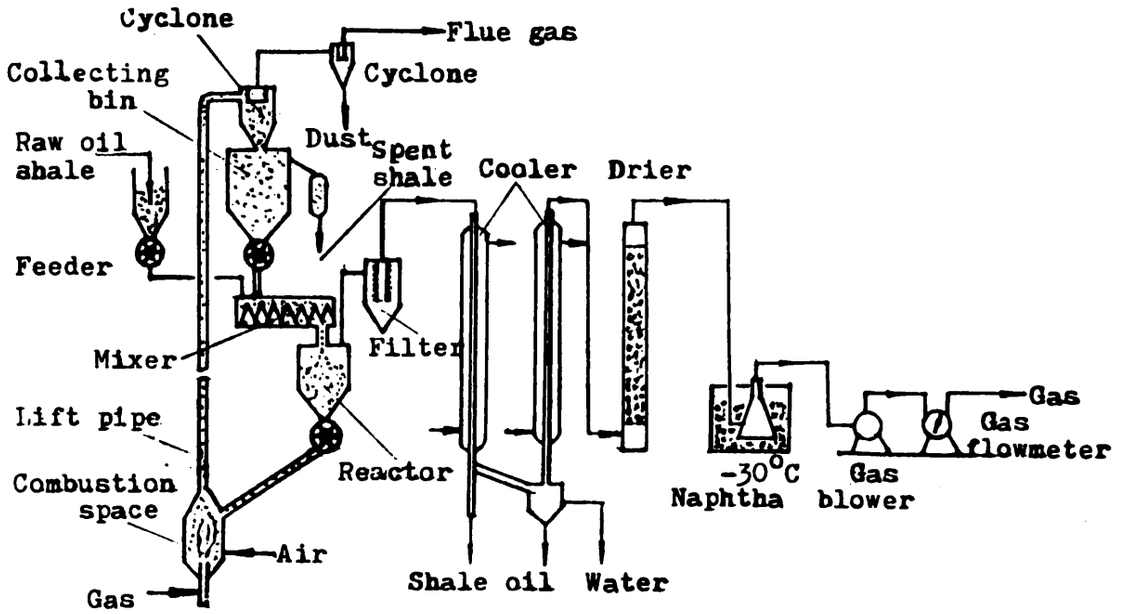

Fig.1. Flowsheet of experimental unit

The raw feed of shale is stored in the raw shale bunker. it is mixed with spent shale, as a heat carrier, in the mixer. Because the mixing is intensive, and the uniform distribution of the fine grained particles, so that the heat exchange between the raw shale and spent shale is very rapid and the heating rate is very high. Thereby the flash pyrolysis of raw shale is taken place. The shale mixture leaving the mixer is passed to the reactor where retorting is completed and devolatilized products are set free. The spent shale from reactor is then transferred to the combustion space which is in the lower section of the lift pipe. The residual carbon from spent shale is burnt in the lift pipe, and the combustion gas simultaneously conveys the spent shale to the first cyclone where spent shale is separated from gas and passed to the collecting bin, and then returned to the mixer,thereby closing the loop.

The spent shale produced is discharged by the draw-off bunker as a by-product.Flue gas dedusted in the second cyclone flows as off-gas.

The volatilized product evolved from raw oil shale passes the reactor and flows to the filter, being dedusted, then it is condensed in cooler, shale oil and liquor are obtained. The gas is dried and refrigerated at -30℃ to obtain naphtha, then it is exhausted by a blower as a product gas.

2. EXPERIMENT

2.1 SAMPLE PROPERTIES

Two samples of Maoming oil shale were applied, the oil content of GM 6 was 6.60% and GM 8 was 8.41%. Another two samples of Huadian oil

Table 1. Analyses of the samples

	Maoming oil shale		Huadian oil shale	
	GM 6	GM 8	GH 6	GH 4
	Proximate analysis			
Moisture(wt%)	13.43	12.92	8.43	7.04
Ash (wt%, dry)	74.03	71.70	61.80	56.12
Volatile matter(wt%,dry)	21.47	21.16	33.12	41.00
Fixed carbon(wt%,dry)	4.50	6.14	5.08	2.88
	Ultimate analysis			
Carbon(wt%,dry)	13.15	15.09	27.71	31.64
Hydrogen(wt%,dry)	2.14	2.30	3.19	3.15
Nitrogen(wt%,dry)	1.87	0.79	0.54	0.63
H/C(Atomic ratio of dry)	1.95	1.83	1.69	1.33
	Analysis, Fischer Assay(20 g)			
Oil (wt%)	6.60	8.41	15.60	18.20
Liquor (wt%)	2.12	2.38	2.57	2.21
Char (wt%)	75.08	73.27	68.40	65.00
Gas+Loss(wt%)	2.77	3.02	4.90	6.70
Heating value(MJ/kg)	6.52	7.44	11.25	13.85

shale, GH 6 and GH4, with higher oil content were also tested. The analyses results of the samples are shown in Table 1.

2.2 OPERATING CONDITIONS

The samples of raw oil shale with size 0 — 2.5mm, 0.6 — 2.5mm and 0 — 5mm were tested. The experimental results indicated that in these size ranges the effect of the size on oil yield was negligible, so the data described in this paper were from the sample with the size 0—2.5mm. The feeding rate was 5 — 7.5 kg/h. The temperature of spent shale as heat carrier was at 700 —750℃. The ratio of spent shale to raw shale was 3 — 4. The air for combustion to the lower section of lift pipe was preheated to about 350℃. The retorting temperature range was 445—525℃.

3. EXPERIMENTAL RESULTS

3.1 PRODUCT YIELD

The oil yields at various retorting temperatures were different, and there was an optimal temperature for pick oil yield[4] . The optimal temperature for retorting of Maoming and Huadian oil shale was between 490 and 505℃. The retorting results are shown in Table 2.

The coefficient of recovery oil is calculated as follows:

$$\eta = \frac{Sr + N}{S_F} \times 100\%$$

where

η — Coefficient of recovery oil, %.
Sr — Retorting shale oil yield, %.
N — Retorting naphtha yield, %.
S_F — Shale oil yield by Fischer Assay, %.

According to the data from Table 2, it can be seen that the η were more than 92%, and the gas yields were between 40 and 60 dm^3 /kg.

Table 2. Products yield

	Maoming oil shale		Huadian oil shale	
Run number	GM6-26	GM8-33	GH6-12	GH4-15
Retorting temperature(℃)	505	507	490	493
Hot spent shale temperature(℃)	700	700	726	740
Shale oil yield(wt%,dry)	7.38	8.71	13.91	15.66
Naphtha yield (wt%,dry)	0.94	0.93	1.82	2.08
Gas yield (wt%,dry)	5.50	3.60	6.17	5.35
Liquor (wt%,dry)	4.05	3.30	4.49	4.09
Coefficient of recovery oil(%)	94.60	93.80	92.30	93.40

3.2 PRODUCT PROPERTIES

The properties of the shale oil are shown in Table 3, it indicated that the oil was lighter, the yield of distillation fraction with b.p. <300℃ was 50%. The main component of the shale oil was paraffin, in which the amount of the components of C_7 $-C_{25}$ was up to 70 $-$80% and C_7 $-C_{12}$ was about 27 %.

The main components of the naphtha were C_4 $-$ C_8 , in which the components of C_5 and C_6 were 60% of the total amount. When the refrigeration temperature of recovery naphtha being lower, the lighter components became more, and the higher the retorting temperature, the more the contents of benzene and toluene were in the naphtha.

The gas component is shown in Table 4. Ethylene in gas was about 5-6%, and combustible components were 60 $-$70%, gas heating value was more than 18.10 MJ/m^3 .

Table 3. Shale oil properties

	Maoming oil shale		Huadian oil shale	
Run number	GM6-26	GM8-33	GH6-11	GH6-12
Retorting temperature(℃)	505	507	497	490
Density(g/cm^3 ,at 25℃)	0.937	0.894	0.891	0.894
Viscosity(℉,at 40℃)	1.399	1.295	1.210	1.230
Ash content(wt%)			0.23	1.06
Solidification point(℃)			17	16
Free carbon(wt%)			0.24	3.40
Initial point (℃)	93	52	70	80
(Vol.%)				
5 %	175	95	145	160
10 %	195	125	180	180
20 %	225	165	215	215
30 %	255	200	241	255
40 %	275	240	293	290
50 %	300	270	300	300
65 %		320		
Average molecular weight				312

The carbon content in spent shale was lower. The size of spent shale was finer than raw shale, but its effect on operation was not significant.

4. MATERIAL BALANCE

The material balances calculated from the data of Maoming GM6-31 and Huadian GH6-12 runs are shown in Table 5.

Table 4. Gas components

	Maoming oil shale		Huadian oil shale	
Run number	GM6-26	GM8-33	GH6-12	GH4-15
Retorting temperature (℃)	505	507	490	493
CO_2 (Vol. %)	36.70	33.14	34.01	32.10
CO (Vol. %)	8.01	8.13	13.85	7.00
H_2 (Vol. %)	24.63	30.40	22.50	34.80
CH_4 (Vol. %)	17.44	13.48	13.72	11.00
C_2H_4 (Vol. %)	5.64	5.12	6.42	5.80
C_2H_6 (Vol. %)	5.24	5.19	5.43	4.50
C_3 (Vol. %)	2.35	4.54	4.08	3.40
Heating value (MJ/m^3)	18.81	19.73	20.33	18.10

Table 5. Material balance of runs(wt%,dry)

	Maoming oil shale	Huadian oil shale
Run number	GM6-31	GH6-12
Retorting temperature (℃)	505	490
Shale oil	6.57	13.91
Naphtha	0.64	1.82
Gas	3.96	6.17
Liquor	3.87	4.49
Spent shale	78.49	69.20
Combustion + Loss	6.47	4.41
Sum	100	100

REFERENCES

1.Губергриц М. Я. et al.
Химия Твердого Топлива 1977, No.3, 164.

2.Hendrikson T. A., Rammler A.
Ullmanns Encyklopädie der Technische Chemie, 4 Auflage, Band 17, 437, 1979.

3.Rammler R. et al.
Chemie Ind. Tech. 53, No.2, 96, 1981.

4.Guo Shu-cai et al. J. Dalian Institute of Technology(in Chinese). Vol.25, No.4, 25, 1986.