Oil Shale, 2000, Vol. 17, No. 4
pp. 359-364
ISSN 0208-189X

https://doi.org/10.3176/oil.2000.4.07

SHORT COMMUNICATIONS

RESEARCH ON SOME CHINESE OIL SHALES

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Oil shales samples from five Chinese deposits were studied by proximate analysis, Fisher Assay, Rock-Eval analysis, elementary analysis and differential thermal analysis for evaluation.

Introduction

Oil shale is a kind of lean solid fossil fuel usually consisting mainly of mineral (~80 %) and organic matter (~20 %) [1]. Its resources are abundant in China. They are estimated to be 400 billion tonnes equivalent to 16 billion tonnes of shale oil. So, the research work on oil shale in China is of great importance.

Until now only oil shales of Fushun and Maoming deposits have been extensively researched. In this work, their data are used as comparative material for six other oil shale samples from various deposits. The samples were studied by proximate analysis, Fisher Assay, Rock-Eval analysis, elementary analysis and differential thermal analysis.

All in all eight samples were analyzed:

- Two samples from Jilin Huadian Gonglangtou, 4th (the sample HD-1) and 11th seam (HD-2)
- Two samples from Heilong Jiang Yilan coal mine (YL-3 and YL-4)
- Two samples from Gansu Tianzhu Tianmalong oil shale mine (QZ-5 and QZ-6)
- Samples of Fushun (FS-7) and Maoming (MM-8) oil shales

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Results and Discussion

Proximate Analysis of Oil Shale

Table 1. **Proximate Analysis of Air-Dried Samples, %**

Sample	Water	Ash	Volatile matter	Fixed carbon
HD-1	8.49	49.77	37.37	4.37
HD-2	16.46	12.13	33.79	37.62
YL-3	4.84	34.20	33.18	27.78
YL-4	3.74	58.46	23.32	14.48
QZ-5	1.22	71.53	27.56	-
QZ-6	1.68	40.42	36.78	21.12
FS-7	2.70	73.82	20.13	3.35
MM-8	13.19	65.78	17.19	3.84

Volatile matter content is the highest in HD-1 (more than one third of oil shale), and the lowest in MM-8 (less than one fifth of oil shale).

Ash content is relatively high in QZ-5 and FS-7; these shales can be utilized for making cement. Ash content is the lowest in HD-2.

HD-2 and MM-8 contain mach *water*, which will bring difficulties in commercial processing.

Compared with FS-7 and MM-8, six other oil shale samples have higher content of volatile matter. Except for QZ-5, five samples have lower content of ash. As the characteristics of kerogens are different, shale oil yield is not directly proporational to their content of volatile matter[2].

Fisher Assay of Oil Shale

Table 2. **Fisher Assay of Air-Dried Samples**

Sample	Water, %	Shale oil, %	Spent char	Gas + losses
HD-1	9.00	22.51	62.03	6.46
HD-2	17.20	9.80	66.56	6.44
YL-3	7.20	7.83	80.99	3.98
YL-4	7.20	7.98	80.39	4.43
QZ-5	2.10	7.12	85.29	5.49
QZ-6	3.20	19.19	71.66	5.95
FS-7	4.20	7.93	84.80	3.07
MM-8	4.00	6.87	85.05	4.08

Shale oil yield is the highest from HD-1, rather good from QZ-6, and the lowest from MM-8.

HD-2 contains much *water*.

The samples YL-3, YL-4, QZ-5, FS-7 and MM-8 contain much inorganic matter; their *spent char content* exceeds 80 %.

According to Table 1, YL-3 and QZ-5 contain more volatile matter than Fushun oil shale sample, but their shale oil yield is lower. Maybe, it is due to higher content of structural water in YL-3 and higher gas + losses value for QZ-5.

As a whole, the results of Fischer Assay coincide with those of the proximate analysis.

Rock-Eval Analysis of Oil Shale

Table 3. **Rock-Eval Analysis of Air-Dried Samples**

Sample	TOC, %	S_1, mg/g	S_2, mg/g	S_3, mg/g	$(S_1 + S_2)$, mg/g	PI	S_2/S_3	HI, mg/g TOC	OI, mg/g TOC	PC, %
HD-1	30.65	2.50	262.18	5.59	264.48	0.01	46.90	855	18	21.97
HD-2	36.81	1.42	108.19	8.52	109.61	0.01	12.70	294	23	9.10
YL-3	34.84	2.69	123.03	1.01	125.72	0.02	121.81	353	3	10.43
YL-4	34.34	2.48	105.21	7.27	107.69	0.02	14.47	306	21	8.94
QZ-5	14.44	1.76	115.19	2.05	116.95	0.02	56.19	798	14	9.71
QZ-6	47.85	4.31	295.15	4.52	299.46	0.01	65.30	617	9	24.86
FS-7	16.51	3.76	112.92	2.96	116.68	0.03	38.15	684	18	9.68
MM-8	13.40	1.62	91.62	0.47	93.24	0.02	194.94	684	4	7.74

Notes: Range of type indexes S_2/S_3: I >20; II.1 - 5-20; II.2 - 2.5-5; III <2.5.
TOC - total content of organic carbon; S_1 - free hydrocarbon content; S_2 - pyrolysis hydrocarbon content, S_3 - carbon dioxide content; PI - condensate index; HI - hydrogen index; OI - oxygen index; PC - potential carbon.

Considerable $(S_1 + S_2)$ values for HD-1 and QZ-6 refer them to the group with high potential for producing hydrocarbons. Small $(S_1 + S_2)$ value for MM-8 shows its lowest potential. Compared with FS-7, four of six oil shale samples studied (except for HD-2 and YL-4) have higher potential of producing hydrocarbons.

Total content of organic carbon (TOC) is low in MM-8 as well as PC. TOC in FS-7 is higher than in QZ-5, but lower than in other five samples. These results coincide with the values of oil yield obtained by Fisher Assay.

S_2/S_3 values for all samples, except for HD-2 and YL-4, are higher than 20. According to the range of type index S_2/S_3, they belong to the type I kerogen and samples HD-2 and YL-4 belong to the type II.1 kerogen.

Elementary Analysis of Oil Shale Kerogen

The *kerogen H/C atomic ratios* for FS-7 and MM-8 are higher than those for all oil shale samples under study, except for HD-1. Among the studied samples the HD-1 kerogen has the highest H/C ratio, and that of YL-3 and YL-4 is less than 1.0. These oil shales resemble coal by their appearance.

Nitrogen content of kerogens varies from 1.21 % to 2.49 %. It is the highest in HD-2 and the lowest in HD-1. In four samples (HD-2, YL-4, QZ-6 and FS-7) it is higher than 2.0.

Table 4. **Elementary Analysis of Kerogen of Air-Dried Oil Shale Samples, %**

Sample	C	H	O	N	S	H/C	Formula
HD-1	76.94	10.54	8.77	1.21	2.54	1.64	$C_{100}H_{164}O_9NS$
HD-2	70.43	6.08	15.06	2.49	5.94	1.04	$C_{100}H_{104}O_{16}N_3S_3$
YL-3	75.96	6.02	15.89	1.52	0.61	0.95	$C_{100}H_{95}O_{16}N_2S_{0.3}$
YL-4	77.38	6.38	12.26	2.02	1.96	0.99	$C_{100}H_{99}O_{12}N_2S$
QZ-5	81.66	9.23	3.81	1.47	3.83	1.36	$C_{100}H_{136}O_3N_2S_2$
QZ-6	80.26	7.15	7.71	2.08	2.80	1.07	$C_{100}H_{107}O_7N_2S$
FS-7	79.07	9.93	7.02	2.12	1.86	1.51	$C_{100}H_{135}O_4N_3S_3$
MM-8	79.41	9.64	8.23	1.63	1.09	1.46	$C_{100}H_{96}O_{12}N_2S$

For FS-7 and MM-8 the *sulfur content of kerogen* is lower than for all other samples, except for YL-3 (only 0.61 %). It is the highest in HD-2. Empirical formula shows that in HD-2 and FS-7 there are three sulfur atoms per hundred carbon atoms.

Elementary Analysis of Shale Oil

Table 5. **Elementary Analysis of Shale Oil of Air-Dried Samples, %**

Sample	C	H	O	N	S	H/C	Formula
HD-1	85.85	11.31	1.59	0.94	0.31	1.58	$C_{100}H_{158}O_{1.4}N_{0.9}S_{0.1}$
HD-2	85.92	9.43	3.13	0.95	0.57	1.32	$C_{100}H_{132}O_3N_{0.9}S_{0.2}$
YL-3	89.7	9.0	0.63	0.49	0.18	1.20	$C_{100}H_{120}O_{0.5}N_{0.5}S_{0.08}$
YL-4	89.28	9.03	0.85	0.55	0.29	1.21	$C_{100}H_{121}O_{0.7}N_{0.5}S_{0.1}$
QZ-5	90.46	8.85	-	0.48	-	1.17	-
QZ-6	85.23	8.56	5.55	0.51	0.15	1.21	$C_{100}H_{121}O_5N_{0.5}S_{0.07}$
FS-7	85.39	12.09	0.71	1.27	0.54	1.70	$C_{100}H_{170}O_{0.1}N_{0.2}S_{0.08}$
MM-8	84.82	11.40	2.20	1.10	0.48	1.61	$C_{100}H_{161}O_{0.3}N_{0.2}S_{0.07}$

The *shale oil H/C atomic ratios* exceed 1.0 in all oil shale samples. This ratio is the lowest for QZ-5, and the highest for FS-7. It means that all eight shale oils are rich in low-molecular hydrocarbons. Shale oil H/C atomic ratios of six oil shales under study are lower than those of FS-7 and MM-8.

Sulfur content of HD-2 shale oil is the highest. Sulfur content of FS-7 and MM-8 are also not low.

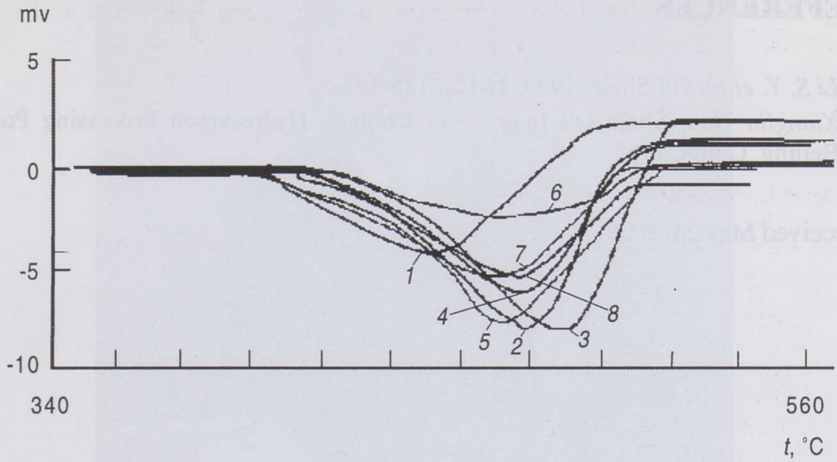
The oils obtained from HD-1 and HD-2 contain more *nitrogen* than other four shale oils. High content of nitrogen probably provides a new way to shale oil utilisation as pyridine is widely used in medicals. In case of producing large amounts of pyridine from these oils, shale oil development in China has great prospects.

QZ-6 content of *oxygen* is the highest attesting a higher amount of oxy-heterocompounds.

Differential Thermal Analysis

According to the Figure, all samples have given endothermic peaks at their differential thermal analysis.

Initial pyrolysis temperature of the sample YL-4 is the lowest and its end temperature is the highest, or, in other words, the range between the initial and end pyrolysis temperature is the widest. Initial pyrolysis temperature of the sample QZ-6 is the highest and end pyrolysis temperature is the lowest. All samples have initial pyrolysis temperature about 400 °C. That for HD-1 is somewhat higher - 418 °C. End pyrolysis temperature varies from 500 °C to 531 °C. Pyrolysis of HD-2, YL-4 and QZ-5 ends at higher temperatures than that of Fushun and Maoming oil shales.



Differential thermal peaks of (*1*) HD-1, (*2*) HD-2, (*3*) YL-3, (*4*) Yl-4, (*5*) QZ-5, (*6*) QZ-6, (*7*) FS-7, (*8*) MM-8

Table 6. **Differential Thermal Temperature, °C**

Index	Sample							
	HD-1	HD-2	YL-3	YL-4	QZ-5	QZ-6	FS-7	MM-8
Initial temperature	418	411	394	394	406	430	403	396
Final temperature	513	530	500	531	524	504	507	517

Conclusion

- The content of volatile matter of the sample HD-1 is the highest, and that of MM-8 is the lowest.
- HD-1 gives the highest yield of oil. QZ-6 is also a rich shale, while the oil yield from MM-8 is the lowest.

- HD-1 and QZ-6 are potentially good hydrocarbon sources, while MM-8 has the lowest potential.
- H/C atomic ratio is the highest in HD-1. Nitrogen and sulfur content is the highest in HD-2. H/C atomic ratio in eight shale oils obtained is higher than 1.0. Sulfur content is the highest in HD-2 oil.
- The area of the DTA curve measured for QZ-6 is the smallest, and those for QZ-5 and YL-3 are biggest. Initial pyrolysis temperatures of all samples are almost the same. End pyrolysis temperature varies from 500 to 531 ℃

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Received May 24, 2000