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RETORTING PROPERTIES OF OIL SHALE FOUND AT THE NORTHERN FOOT OF BOGDA MOUNTAIN, CHINA

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On the basis of pyrolysis gas chromatography (PGC) technique, the retorting process of oil shale found at the northern foot of Bogda Mountain was simulated by a step-by-step procedure. The dynamic changes in recovery of all kinds of oil (gas) products, and their total recovery rate at different temperature ranges during pyrolysis were studied. Meanwhile, the reasons for these changes were analyzed, and the properties of oil shale were discussed. This paper provides some parameters to evaluate these properties precisely. The results show that the retorting process and the corresponding pyrolysis occur in three stages: 1) a few hydrocarbon products are generated below 410 °C, their amount increasing slowly with temperature; 2) the amount of hydrocarbon products increases rapidly in the range of 450–510 °C, accounting for 70% of the total, and the yield has maximum at about 490 °C; 3) gaseous hydrocarbons are the main products above 510 °C, whereas their yield is small. Oil shale found at northern foot of Bogda Mountain is characterized by the advantage to yield light oil. In future processing and refining, the temperature should be maintained between 450 °C and 510 °C to recover oil (gas) products, especially light oil, effectively. Original hydrocarbon-generating potential is the principal factor in controlling the behavior of oil shale during the process. The greater the original hydrocarbon-generating potential, the larger the amount of heavy oil products generated at the high-temperature stage.

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Introduction

Oil shale, also known as oil forming shale, is a kind of sedimentary rock rich in organic matter (usually 15–50%). It can be used for generating shale oil, which is similar to crude oil, at low-temperature retorting.

The extraction techniques of oil shale have already been an important research and development line worldwide. Oil extraction techniques can be classified as the underground dry distillation and overground dry distillation. Underground dry distillation, also named *in-situ* retorting, is still under development since at the industrial scale the process is hard to control. Overground dry distillation techniques can be divided into two categories: direct and indirect heat transfer method. The first one is faster and more effective in heat transmission. So, modern dry distillation techniques mainly use the heat carrier and direct contact with heat transfer. Direct heat transfer method can also be sub-divided depending on whether gaseous or solid heat carrier is used. Gaseous heat carrier is used at oil shale dry distillation mainly in Russia, Estonia (Kiviter retorts) [1–2], Brazilia (Petrosix) [3], America (SGR) [4], Japan (Joseco) [4] and China (Fushun-type retorts) [5]. The methods with solid heat carrier include American Tosco-II [6], Estonian Galoter [7–8], German LR [6], and Canadian ATP technique [9].

Levent and Tulay [10] investigated the pyrolysis characteristics of Göynük oil shale by the non-isothermal method. The results indicated that the heating rate of pyrolysis was relatively limited, and the pyrolysis reaction occurred in accordance with the first-order kinetics model. There was no direct relationship between activation energy and heating rate, and activation energy was the lowest (3.0 kJ/mol) when the heating rate was 20 °C/min. Dogan and Uysal [11] also studied the pyrolysis behavior of Turkish oil shales by the non-isothermal method. The results showed that the conversion rate increased with final pyrolysis temperature. Activation energy and conversion rate of pyrolysis were almost irrelevant to particle size. It was found that pyrolysis of Seyitömer and Himmetoglu oil shales occurs in two stages with different values of activation energy. Thakur and Nuttall [12] studied pyrolysis kinetics of oil shale by isothermal and non-isothermal thermogravimetry. The pyrolysis process could be divided into two steps, which were both characterized by the first-order kinetics, and the pitch was regarded as the intermediate state. Tao et al. [13] simulated the hydrocarbon generation and expulsion of low-maturity oil shale in three different conditions: without water but with variation in temperature, with various amount of water under constant temperature, and with constant amount of water at different temperatures. The changes in the phase state and compositions of hydrocarbon products in three different thermal simulation conditions were analyzed. Kök et al. [14–19] studied the factors influencing kinetic data, such as sample order geometry, heating rate and atmosphere, under non-isothermal conditions. It was observed that the composition of products obtained through pyrolysis and combustion depends on oil shale composition and conditional variables, such as temperature, time, rate of heating, pressure, and gaseous environment. A general trend that the activation energy in the low temperature oxidation region was higher than that in the high-temperature oxidation region was established.

Oil shale is an important alternative energy resource. Nowadays, the primary way in industrial utilization of oil shale is obtaining and refining oil products at retorting [20]. After oil shale is extracted, oil and gaseous products can be obtained after crushing and dry distillation of oil shale. From shale oil gasoline, kerosene, diesel oil and other oil products can be obtained after further processing, and the fuel gas can serve as a supplementary heat resource at retorting or as supply for the domestic users [21–22]. The technique of oil extraction from oil shale has been widely used and extended, but not so much research has been done in the field of retorting properties of oil shale. In this study, we use step-by-step pyrolysis gas chromatography technique to evaluate the retorting processes of oil shale samples taken from the northern foot of Bogda Mountain. It helps us to establish the total recovery of shale oil in different temperate ranges and the yields of different hydrocarbons. The knowledge is very important for controlling pyrolysis temperature of oil shale, saving energy consumption, extracting special shale oil products, assessing the development value of oil shale resource, etc.

Samples and experimental

The experimental samples (DZB06 and DZB23) were taken from Lucaogou oil shale layer series, which are located in the northern foot of Bogda Mountain, Xinjiang, China. The samples were prepared according to ASTM standards. The main industrial indexes of these two samples are close and their oil yields are 7.0% and 9.5% respectively, characterizing medium-quality oil shale (Table 1). However, the chemical parameters and compositions of pyrolysis products show great differences. As shown in Table 2, the sample DZB06 contains relatively little total organic carbon (TOC) and yields more light hydrocarbons.

A step-by-step PGC experiment was carried out in the organic geochemistry laboratory of Exploration and Development Institute of Daqing oil field, China, using the instrument PY-GC14B. The equipment was calibrated before the experiment. The applicable standard was SY/T6118-1996, and the chromatographic column HP-5 was used. The preferable pyrolysis conditions were: 1) solid particles ground into particles 20–25 μm (to ensure that

Table 1. **Main industrial indexes and chemical parameters of samples**

Sample No.	Oil_{ad}, %	$CR_{,ad}$, %	S_1, mg/g	S_2, mg/g	Organic matter type	TOC, %
DZB06	7.0	88.7	1.17	49.40	II_1	7.10
DZB23	9.5	85.9	2.04	202.75	I	25.48

Table 2. **Composition of one-step pyrolysis products**

Sample No.	Gas (C_1-C_5), %	Gasoline (C_6-C_{10}), %	Kerosene (C_{11}-C_{13}), %	Diesel (C_{14}-C_{18}), %	Heavy oil (C_{19}-C_{25}), %	Lubricating oil (C_{26}-C_{40}), %
DZB06	29.18	29.83	11.59	13.28	9.93	6.19
DZB23	15.72	21.27	8.10	11.41	17.13	26.37

the organic matter in oil shale will be fully cracked), 2) heating rate 5 ℃/min (provides sufficient heat to reach a certain reaction rate), 3) ten heating temperature ranges including 150–300, 300–370, 370–410, 410–430, 430–450, 450–470, 470–490, 490–510, 510–540 and 540–600 °C, 4) flow rate of carrier gas (helium) 26 ml/min (improves the sensitivity and ensures safety), 5) separation of products in liquid nitrogen trap, 6) trap temperature – 320 ℃. The preferable gas chromatography conditions were: HP-5 capillary columnar model, initial temperature 30 ℃, final temperature 320 °C, heating rate 3 °C/min, flow rate of carrier gas (helium) – 26 ml/min, split ratio of 1/25–1/50, and hydrogen flame detector detection. In order to verify the consistency and repeatability, the experiments were performed twice.

Results and discussion

The distribution of products was measured in 10 temperature intervals, and the temperature interval 410–510 ℃ corresponding to the high-temperature region was encrypted. Based on the different boiling points of hydrocarbons, we summed the peak areas in the gas chromatograms as follows: C_1-C_5, C_6-C_{10}, C_{11}-C_{13}, C_{14}-C_{18}, C_{19}-C_{25} and C_{26}-C_{40}, that correspond to gas, gasoline, kerosene, diesel, heavy oil and lubricating oil, respectively. The results are shown in Tables 3 and 4.

Table 3. **Yield of each component in different temperature ranges at the step-by-step pyrolysis of sample DZB06**

Pyrolysis temperature range	Gas (C_1-C_5), %	Gasoline (C_6-C_{10}), %	Kerosene (C_{11}-C_{13}), %	Diesel (C_{14}-C_{18}), %	Heavy oil (C_{19}-C_{25}), %	Lubricating oil (C_{26}-C_{40}), %	Total recovery rate, %
150–300 °C	0.196	1.028	0.704	0.901	0.597	0.318	3.744
300–370 °C	0.232	0.591	0.292	0.345	0.263	0.159	1.881
370–410 °C	0.654	1.145	0.443	0.583	0.391	0.286	3.503
410–430 °C	1.077	1.553	0.687	1.061	0.882	0.62	5.88
430–450 °C	2.596	3.59	1.552	2.019	1.569	1.262	12.588
450–470 °C	4.613	6.573	2.77	3.469	3.224	4.601	25.25
470–490 °C	6.513	7.486	3.429	3.973	3.514	2.65	27.565
490–510 °C	3.869	3.233	1.138	1.409	0.86	0.253	10.762
510–540 °C	2.695	1.007	0.252	0.195	0.061	0.005	4.214
540–600 °C	3.802	0.535	0.11	0.114	0.048	0.003	4.613
Total, %	26.247	26.74	11.378	14.069	11.41	10.156	100

Table 4. **Yield of each component in different temperature ranges at the step-by-step pyrolysis of sample DZB23**

Pyrolysis temperature range	Gas (C_1-C_5), %	Gasoline (C_6-C_{10}), %	Kerosene (C_{11}-C_{13}), %	Diesel (C_{14}-C_{18}), %	Heavy oil (C_{19}-C_{25}), %	Lubricating oil (C_{26}-C_{40}), %	Total recovery rate, %
150–300 °C	0.016	0.053	0.087	0.137	0.061	0.063	0.416
300–370 °C	0.036	0.076	0.112	0.069	0.014	0.307	0.036
370–410 °C	0.112	0.225	0.083	0.099	0.086	0.014	0.619
410–430 °C	0.242	0.536	0.181	0.235	0.239	0.046	1.479
430–450 °C	0.937	1.655	0.599	0.736	0.768	0.183	4.880
450–470 °C	2.616	4.956	1.859	2.427	2.867	1.047	15.772
470–490 °C	4.434	7.976	3.386	5.135	7.867	9.985	38.784
490–510 °C	4.24	5.457	2.435	3.578	5.685	11.797	33.192
510–540 °C	1.288	0.84	0.264	0.369	0.287	0.314	3.361
540–600 °C	1.186	0.156	0.043	0.043	0.021	0.011	1.461
Total, %	15.106	21.93	9.05	12.829	17.894	23.769	100

Recovery dynamics of different oil (gas) products during pyrolysis

During the low-temperature retorting, abundant insoluble organic matter (similar to kerogen in source rock) containing in rock breaks down, so shale oil and gaseous hydrocarbons are formed. At the preheating phase of medium-low temperature (<410 °C), thermally unstable bonds in the polymer structure absorb heat and break. Polymer degrades into numerous macromolecules soluble in organic matter which is difficult to volatilize. That is shale oil. In this process, only a small quantity of gasified and highly-volatile products (light oil) are produced and detected. The generated shale oil is similar to natural crude oil, containing a large number of hydrocarbons. However, natural crude oil is mainly composed of saturated hydrocarbons, whereas shale oil contains more organic heterocyclic compounds or un-saturated hydrocarbon compounds, which contain nitrogen, oxygen and so on. Therefore, the components of shale oil are relatively complicated and difficult to refine. When the temperature reaches 410 °C, shale oil begins to degrade, generating gaseous hydrocarbons and liquid products which can be gasified at the experimental temperature. The boiling points of liquid products obtained in different temperature ranges are different. They leak out through the internal voids in the rock and can be taken into collecting traps along with carrier gas (helium), thereafter being cooled into liquid. During this stage, the yield of oil products increases rapidly, and the yield of gaseous hydrocarbons increases slowly. When the temperature is extremely high (540–600 °C), the retorting process ends, and the residual organic matter loses its oil-generating capacity. Apart from continuing to break the heteroatomic functional groups and side chains, forming small quantity of water, carbon dioxide and nitrogen, the main reaction is breaking of a large number of C-C bonds, including ring-opening and rupture of naphthene. So, the yield of liquid hydrocarbon decreases rapidly, and the yield of macromolecular oil products (> C_{25}) drops to zero gradually (Tables 3 and 4).

As shown in Fig. 1, the recovery ratio of various kinds of oil (gas) products increases slowly with temperature below 410 °C, thereafter the ratio increases rapidly with increasing temperature, and reaches the maximum at 410 °C. At higher temperatures, the recovery ratio of oil and gas components decreases rapidly due to rapid exhaustion of hydrocarbon generation potential of shale.

Changes in total recovery of oil (gas) product during pyrolysis

As the recovery ratio of the oil (gas) products changes with pyrolytic temperature, the total recovery of products also has a similar variation tendency (Figures 2 and 3). It can be seen that the yield of various compounds increases substantially only when the heating temperature is about 450–510 °C, although the pyrolysis of oil shale organic matter reaches the maximum above 410 °C. The temperature range in which 70% of products are generated is narrow, only around 60 °C. In addition, when the process enters an extremely high-temperature phase, the total recovery of oil and gas reduces greatly. The yield of gaseous components is less than it is in the previous stage, but their yield is still very high compared to other compounds. During this stage, the amount of gas accounts for 40% of the total yield in the whole heating process.

Overall, when the temperature rises to around 450 °C, the process of kerogen degrading into asphalt is completed, macromolecular asphalt begins to break up into gaseous and liquid products which will be gasified under experimental temperature. After the heating temperature reaches 510 °C, the retorting process is ended, and the residual organic matter in oil shale has lost its oil-generating capacity. Therefore, most of the hydrocarbons (about 70%) are generated within the temperature range of 450–510 °C.

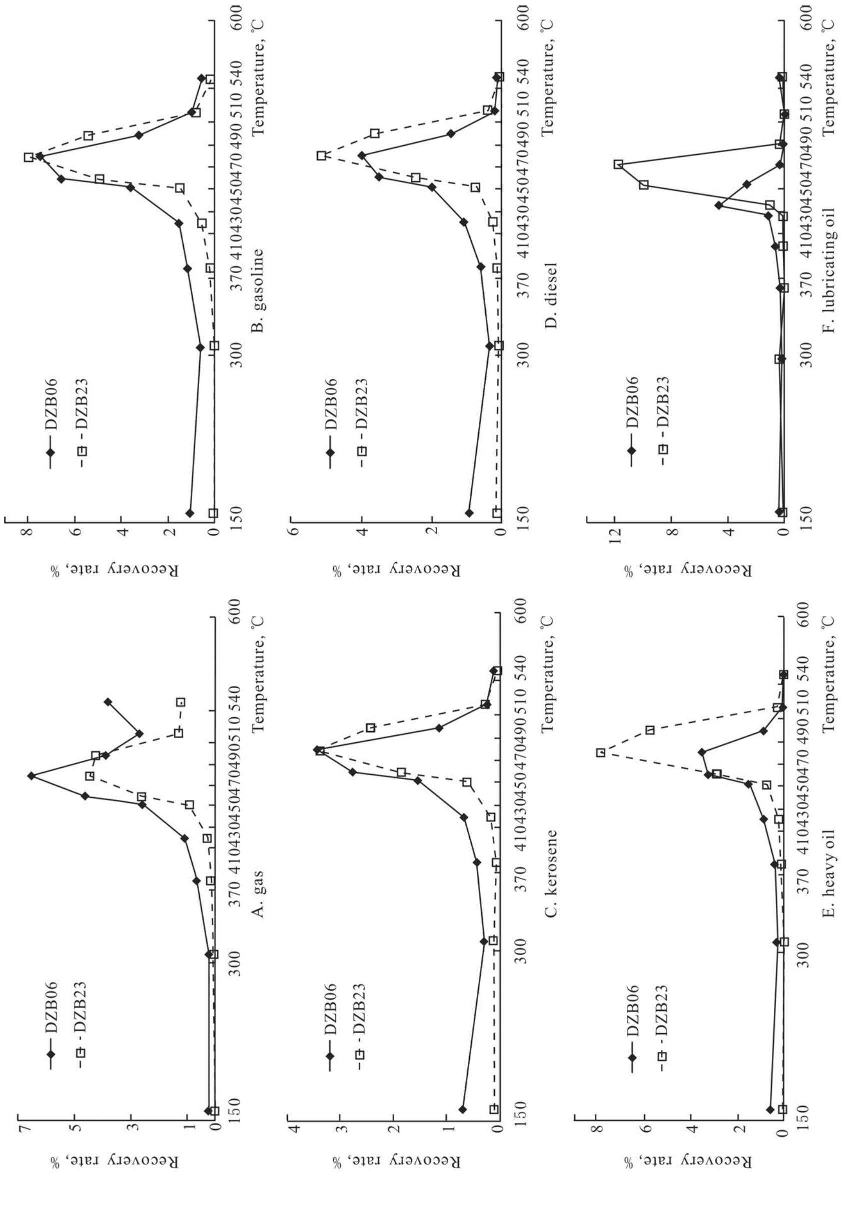

Fig. 1. Dynamic recovery changes of different oil (gas) products during pyrolysis.

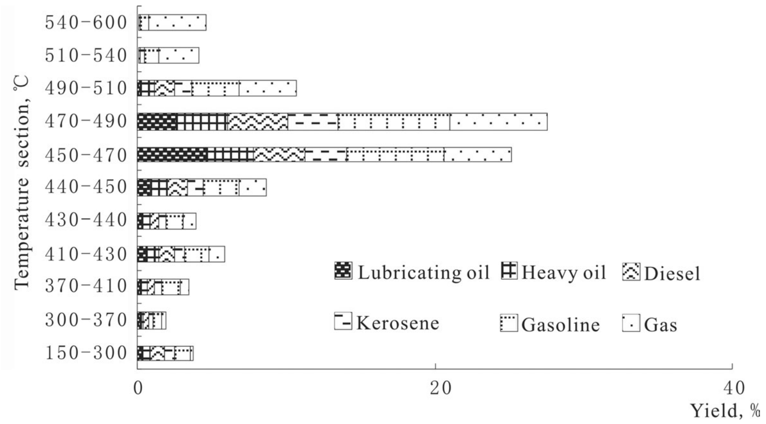

Fig. 2. Yield of each component at different temperature ranges at step-by-step pyrolysis of sample DZB06.

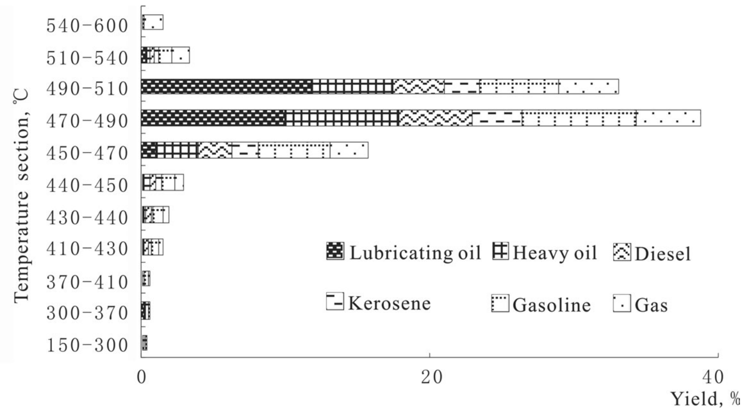

Fig. 3. Yield of each component at different temperature ranges at step-by-step pyrolysis of sample DZB23.

General characteristics of oil shale retorting process

The analysis above shows that gasoline, kerosene, diesel oil and other chemical products can be obtained by hydrocracking and refining of shale oil. A few pyrolysis products of oil shale come from hydrocarbons adsorbed in rock, but most of them form at cracking of parent material (kerogen). The quantity and quality of the pyrolysis products are directly related to the processing technology of oil shale. Further analysis indicated that oil (gas) products of oil shale are different under different reaction conditions. It is favorable to generate light oil in the process of cracking at medium-low temperature (<410 °C), but in this case total recovery of products is extremely limited. The recovery rate of heavy components (heavy oil and lubricating oil) increases significantly at high temperatures (about 490 °C). Moreover, the relative proportions of gas and light oil are markedly increased at extremely high temperatures (540–600 °C). It is shown that high temperature evokes the secondary cracking of products and makes the relative yield of light oil and gas increasing.

Conclusions

It can be seen that the recovery rate of products from two samples reaches a maximum at around 490 °C, and 70% of pyrolysis products are generated between 450 °C and 510 °C. Oil shale located in the northern foot of Bogda Mountain is characterized by high light oil generating potential, which is as much as 60–80%. Thanks to this feature, the temperature range 450–510 °C, will guarantee the maximum recovery of oil (gas) in order to obtain high yield of light oil. Regarding oil shale with great original hydrocarbon potential, the heating should be prolonged to facilitate the formation of heavy oil and to evoke the cracking conversion of heavy oil to light oil. Excessively high temperature, however, cannot increase the yield of oil, and it is uneconomical as well. Consequently, it is important to control the pyrolysis temperature and heating time in the retorting process of oil shale.

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