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Yield and characteristics of shale oil from the retorting of oil shale and fine oil-shale ash mixtures

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HIGHLIGHTS

- The whole formation process of shale oil might be divided into four stages.
- Higher ash/shale mass ratio intensified the cracking and coking of shale oil.
- Ash/shale ratio of 1:2 was recommended for oil shale fluidized bed retort with fine oil-shale ash as solid heat carrier.

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ABSTRACT

For exploring and optimizing the oil shale fluidized bed retort with fine oil-shale ash as a solid heat carrier, retorting experiments of oil shale and fine oil-shale ash mixtures were conducted in a lab-scale retorting reactor to investigate the effects of fine oil-shale ash on shale oil. Oil shale samples were obtained from Dachengzi Mine, China, and mixed with fine oil-shale ash in the ash/shale mass ratios of 0:1, 1:4, 1:2, 1:1, 2:1 and 4:1. The experimental retorting temperature was enhanced from room temperature to 520 °C and the average heating rate was 12 °C min^{-1}. It was found that, with the increase of the oil-shale ash fraction, the shale oil yield first increased and then decreased obviously, whereas the gas yield appeared conversely. Shale oil was analyzed for the elemental analysis, presenting its atomic H/C ratio of 1.78–1.87. Further, extraction and simulated distillation of shale oil were also conducted to explore the quality of shale oil. As a result, the ash/shale mixing mass ratio of 1:2 was recommended only for the consideration of increasing the yield and quality of shale oil.

1. Introduction

With an increasing demand for energy and a limited reserve of fossil fuels, the development of various alternative sources for fossil fuels is required to meet future energy needs. Oil shale, a fine-grained sedimentary rock with organic matter called kerogen, is rich and widespread throughout the world [1]. China has rich oil shale resource; if all the oil shale can be retorted to produce shale oil, a substitute for crude oil, about 47.6 billion tons of shale oil will be obtained [2], which is a considerable amount of potential energy.

According to the heating transfer mode for retorting oil shale, there are two types of retorts in industrial use for shale oil production: gas heat carrier retorts and solid ones. Detailed descriptions of their processes can be found in many literatures [3–5]. However, some technical issues hinder the wide development of these processes. For example, Kiviter and Fushun retort processes produce a large amount of harmful semicoke waste, and Galoter has a complicated multistage technological scheme. As a result, a new comprehensive utilization technology of oil shale was recommended for shale oil production, electricity generation by burning semicoke, and ash building utilization [6–9]. In this comprehensive utilization process, the hot semicoke produced in the oil shale retorts is directly introduced into a circulating fluidized bed (CFB) as a fuel, and the circulating ash of the CFB is directed into the fluidized bed or rotating drum retorts as a high-temperature solid heat carrier. It has been proven that semicoke from Kiviter retorts can burn steadily in a fluidized bed without any additional fuel under a certain condition [10]. The semicoke from the retorts of the comprehensive utilization system of oil shale will have higher physical heat (400–500 °C) and calorific value of combustion than that from Kiviter retorts. Thus, it is easy for it to burn steadily in the CFB of the comprehensive utilization system. A potential issue for the comprehensive utilization system is about the effect of the circulating ash on the low-temperature pyrolysis of oil shale. According to the experimental results of a 65 t/h industrial CFB boiler of oil shale [11], the equivalent diameter of circulating ash is 0.237 mm, far smaller than oil shale particles in the retorts, which will possibly influence the yield and compositions of pyrolytic products of oil shale due to its chemisorption and catalysis properties [12–15]. In addition, if the retorting part of the

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comprehensive utilization system adopts a fluidized bed retort mode, both the circulating ash and fluidizing gases may be combined to supply the heat for retorting oil shale, producing another issue about how to distribute the heat between these two kinds of heat carriers.

For optimizing the comprehensive utilization process of oil shale, a series of investigations have been carried out by the authors, including combustion characteristics of the semicoke CFB, retorting characteristics of fluidized bed retorts, and energy analysis of the whole process, etc. This work focused on the effect of fine oil-shale ash on the yield and characteristics of shale oil during the pyrolysis of oil shale. N_2 adsorption–desorption method and X-ray diffraction were first employed to investigate the pore structure and phase composition of oil-shale ash, respectively. Then retorting experiments of oil shale and oil-shale ash mixture samples were performed by using a lab-scale retorting system. At last, the yield and characteristics of shale oil were comprehensively analyzed to determine an optimum mixing ratio of oil shale and oil-shale ash, providing a set of fundamental data for developing the comprehensive utilization system of oil shale.

2. Experimental

2.1. Samples

Oil shale samples used in this work were obtained from Dachengzi Mine located in Huadian of Jilin province, China. Its composition was studied according to the National Standards of China, shown in Table 1. The lump oil shale was ground as received, sieved to size range of 0–3 mm, and dried at 105 °C to constant weight, and then stored in a desiccator for use.

Oil-shale ash was obtained from the bottom ash of a lab-scale fluidized bed of oil shale at the combustion temperature of 850 °C. It was crushed and sieved to 0–0.2 mm ash which is equivalent with the circulating ash of CFB in particle size.

In consideration that the mixing ratio of ash/shale of at least 2:1 is a common practice based on industrial solid heat carrier retorting units, fine ash was mixed with oil shale samples in six mass ratios of 0:1, 1:4, 1:2, 1:1, 2:1 and 4:1, respectively. These six samples were labeled S_1–S_6, each with increased fractions of oil-shale ash.

2.2. Experimental System

The scheme and detailed instructions of the experimental retorting system of oil shale have been given in Ref. [16]. In this work, mixture samples of oil shale and oil-shale ash (S_1–S_6) were placed inside a small stainless steel retort before each experiment, and heated from room temperature to the final retorting temperature of 520 °C at an average heating rate of 12 °C min^{-1} by using an electrical heater. Pure argon gas was used as a carrier gas at a flow rate of 10 mL min^{-1}. In the heating process, steam, non-condensable gases and shale oil evaporation were formed and passed into a conical flask immerged in a low-temperature trough (~0 °C). The steam and shale oil evaporation were cooled and condensed at the bottom of the conical flask; and the non-condensable gases exited the conical flask through a small mouth and were analyzed online by a Gasmet DX-4000 Fourier transform infrared (FTIR) gas analyzer and a MRU gas analyzer. The experiments ceased after maintaining the final retorting temperature for 20 min. Semicoke, shale oil and pyrolytic water were cooled and weighted, and thus the mass of non-condensable gases might be calculated by difference. Each experimental condition was repeated at least twice to ensure the repeatability and accuracy of the experimental data.

Table 1
Analysis of Dachengzi oil shale.

Proximate analysis (wt.%)[a]		Ultimate analysis (wt.%)[a]		Oil analysis (wt.%)[c,a]	
Moisture	11.54	C	27.33	Shale oil	19.20
Volatile matter	36.20	H	3.59	Semicoke	63.77
Ash	48.24	O[b]	7.89	Water	11.88
Fixed carbon	4.02	N	0.57	Gases	5.15
Lower heating value (kJ kg^{-1})	11076.07	S	0.84		

[a] As-received basis.
[b] Calculated by difference.
[c] Under the national standard of China (SH/T 0508-92).

2.3. Oil-shale ash analysis

An ASAP2010 M + C surface area and porosimetry analyzer was used to measure N_2 adsorption of oil-shale ash at 77.8 K with the relative pressure from 0.01 to 0.995 and the pore size from 1.7 nm to 300 nm. The X-ray diffraction (XRD) spectrum of oil-shale ash sample was obtained using a Rigaku X-ray diffractometer (Rigaku Advanced D/max-2200 X) equipped with a fixed monochromator and a Cu tube (Cu Kα radiation), operating at 40 kV and 20 mA. The diffractogram was obtained by continuous scan from 5° to 90° 2θ at 0.02° intervals.

2.4. Shale oil analysis

2.4.1. Elemental analysis

The obtained shale oil samples were analyzed for CHNO by a Vario EL cube CHNOS elemental analyzer and thus the atomic H/C ratios were able to be obtained. The total sulfur content was analyzed by a Jena EA3100 NS analyzer.

2.4.2. Separation and analysis of different fractions from shale oil

According to the Petroleum Industry Standard of China (SY/T 5119-2008), shale oil was first extracted by organic solvents and then fractionated into four chemical groups: aliphatics, aromatics, non-hydrocarbons and asphaltenes. To investigate the detailed compositions of shale oil, aliphatic and aromatic compositions of each shale oil sample were further analyzed using an Agilent 7890A gas chromatography (GC) and an Agilent 6890-5975C gas chromatograph–mass spectrometry (GC–MS), respectively.

2.4.3. High temperature simulated distillation

The boiling point distribution of shale oil was measured by high temperature simulated distillation (HTSD) using ASTM method HT 750. The HTSD analysis was performed with an Agilent 6890N gas chromatograph which was equipped with an auto-sampler and an automatic injector. Helium was used as the carrier gas with a flow rate of 3 mL min^{-1}. The capillary column was 5 m × 0.53 μm × 0.09 μm, with a cool on-column injector. Temperature programming for the column was from 40 °C to 430 °C at a heating rate of 10 °C min^{-1} and held for 5 min. The on-column injector was programmed from 100 °C to 430 °C in 22 min with a heating rate of 15 °C min^{-1}. The flame ionization detector (FID) was maintained at 430 °C.

3. Results and discussion

3.1. Characteristics of oil-shale ash

N_2 adsorption–desorption isotherms and pore size distribution of oil-shale ash is presented in Fig. 1. The adsorption branch of N_2 adsorption–desorption isotherms rises gradually below $P/$