



Effect of minerals on the self-heating retorting of oil shale: Self-heating effect and shale-oil production



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HIGHLIGHTS

- The effect of minerals on the pyrolysis is studied under a special condition, i.e., self-heating retorting.
- Different effects are observed between self-heating retorting and common retorting.
- Using HF or HNO₃ to treat oil shale promotes self-heating temperature, but using HCl markedly lower it.
- Lowering self-heating temperature may not lower oil yield, but it favors the production of heavy components.
- Despite different acid demineralizations, the oils mainly consist of various hydrocarbons.

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ABSTRACT

The effect of the minerals of Huadian oil shale on a low-energy input retorting route was studied. This special retorting route was achieved by a self-heating effect, that is, spontaneously increasing retorting temperature in the absence of external heat provision (Guo et al., 2013) [12]. Oil shale was first demineralized with HCl, HNO₃ or HF before used in the self-heating retorting. The oil shales treated with different acids, and their corresponding semicokes attained after retorting were also characterized. The results showed that using HF-treated oil shale produces the best self-heating effect and the highest oil yield. Using HNO₃-treated oil shale also promotes the self-heating effect. While using HCl-treated oil shale remarkably worsens the self-heating effect, but it gives a higher oil yield than using HNO₃-treated or raw oil shale. The reasons are also analyzed. Although different acid treatments affect the self-heating effect differently, all the attained oils mainly consist of various hydrocarbons, however, the product distributions are different.

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1. Introduction

As the gradual depletion of petroleum sources and the increase in the oil prices, more and more attentions are paid on the utilization of oil shale as an alternative energy source [1,2]. Oil shale is a sedimentary rock containing a high proportion of solid organic matter called kerogen. The kerogen can be released as petroleum-like liquid, i.e., shale oil, when the rock is heated through the chemical process of pyrolysis [3–6]. The known reserves of oil shale are very large, equal to many times [3,7] of the amount of crude oil in the world.

Retorting or pyrolysis of kerogen within the shale into shale oil is a prevalent method for utilizing oil shale [6,8,9]. It requires high-energy input to thermally break down the kerogen matrix to shale oil [2,10], such as using 700 °C heat-carrier gas to heat

raw oil shale to ~550 °C [11], which is the most difficult obstacle to retorting [1]. In order to simplify restoring process, a low-energy-input retorting route using low-temperature heat-carrier gas but without marked loss in the shale-oil yield was developed by us [12]. This route is achieved by a self-heating effect, i.e., spontaneously increasing retorting temperature in the absence of external heat provision. The self-heating process starts with preheating oil shale from room temperature to 300 °C by external heating under N₂ and then switching N₂ into air. When N₂ is replaced by air, the self-heating effect starts. Subsequently, the temperature of raw oil shale increases spontaneously to complete the retorting so that the external heat supply is no longer required. In this process, because external heat supply is needed only for preheating raw oil shale to 300 °C (i.e., the required energy input and external-heating terminal temperature are low), the retorting process is markedly simplified. Moreover, the oil still mainly consists of various hydrocarbons, like the oils obtained from traditional processes.

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However, this promising retorting route has not been investigated in detail yet. Many factors, which may affect the retorting, need to be elucidated. The inorganic minerals compose the major part of the oil shale, in which kerogen is heterogeneously and finely distributed [13,14]. Therefore, it is believed that the minerals will affect the reaction of kerogen physically and chemically [5], and further the choice of process conditions [8,15]. The digestion of minerals by means of acid treatment is a very useful method for studying the effect of minerals on the pyrolysis [5,13]. The minerals mainly consist of silicates, carbonates, pyrite, etc. [5,8,13]. Selective acid treatment can remove these main minerals from the oil shale rock. For example, Ballice and Sert et al. [8,13] used HCl, HNO₃ and HF to remove carbonate, pyrite and silicates of Turkish Göynük oil shale, respectively. By comparing the pyrolytic behaviors of the oil shales treated with different acids, the effect of different minerals on the pyrolytic behaviors in an inert gas atmosphere was elucidated. With acid-demineralizing method, the effect of mineral matrix on the pyrolytic behaviors of various oil shales was also studied by thermo-gravimetric (TG) technique [5,16,17].

Due to the close links of the pyrolytic behavior of kerogen with the mineral matrix, in this work the effect of minerals on the self-heating retorting is investigated with Chinese Huadian oil shale. Oil shale is first demineralized with different acids, HCl, HNO₃ or HF. Then the effects of demineralization using different acids on the structure of oil shale, self-heating effect, pore structure of semicoke, shale oil yield, and the properties of shale oil are studied. In addition, the present self-heating process, where the pyrolysis proceeds spontaneously without the external heat provision, is very different from the previously reported TG analysis [16,17] and common retorting process under N₂ [8,13] for studying the effect of minerals, which were performed by external heating throughout the whole process. Therefore, this work also provides a distinctive standpoint to understand the pyrolysis of oil shale.

2. Experimental

2.1. Materials

The raw oil shale used in this study was obtained from Gonglangtuo mine located in Huadian, Jilin province, China. The main components of the used raw oil shale were shown in Table 1. The raw oil shale was crushed and screened to 1–3 mm particles before used.

2.2. Demineralization of oil shale

First, the raw oil shale was put in a desired acid solution, HCl, HNO₃ or HF solution. Then, the reaction mixture was stirred for 3 h. After that, it was filtrated, washed with 60–70 °C deionized water until the filtrate became neutral. Finally, the solid residue was dried at 60 °C for 10 h. Caution: demineralization with HF was performed in a Teflon container in this work and it cannot be performed in the glass containers.

For the demineralization with HCl, 60 g raw oil shale was put in 240 mL HCl solution (23.8 wt%). For the demineralization with HNO₃, 60 g raw oil shale was put in 200 mL HNO₃ solution

(32.5 wt%). For the demineralization with HF, 80 g raw oil shale was put in 150 mL HF solution (40 wt%).

The retorting process using **HCl-demineralized** oil shale, the retorting process using **HNO₃-demineralized** oil shale, the retorting process using **HF-demineralized** oil shale and the retorting process using **raw** oil shale are denoted as **HCl-D** retorting, **HNO₃-D** retorting, **HF-D** retorting and **Non-D** retorting, respectively.

2.3. Retorting of oil shale for the preparation of shale oil

The retorting apparatus used in this study is shown in Fig. 1. The self-heating retorting route was as follows: ~55 g oil shale was placed inside a tubular quartz reactor (length: 380 mm; inner diameter: 18 mm). The tubular quartz reactor was installed in a tubular furnace with thermocouples in it. The oil shale was first preheated from room temperature to 350 °C by tubular furnace (i.e., by external heating), during which N₂ passed through the tubular quartz reactor. Then, the N₂ was replaced by the air of ambient temperature. When the N₂ was replaced by air as the carrier gas, external heating was not required, because the temperature of oil shale fixed bed in the tubular quartz reactor begins to increase spontaneously owing to the presence of oxygen from air (i.e., self-heating), accompanied by the continuous pyrolysis of kerogen in the oil shale. The gaseous pyrolysate outflowed from the tubular quartz reactor with carrier gas, and then passed through a multi-stage water condenser to be condensed as shale oil. The shale-oil yield, η , in this work was defined as follows:

$$\eta = \frac{m}{M} \times 100\%$$

where m is the weight of the produced shale oil and M is the initial weight of the used raw oil shale.

2.4. Analytical methods

X-ray diffraction (XRD) patterns were measured with a D8 diffractometer (Bruker, Germany) with Cu K α radiation at the step length of 0.05°/s. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer Fourier transform infrared spectrometer. Low-temperature nitrogen adsorption–desorption method was used to measure pore structure. Nitrogen adsorption/desorption isotherms were obtained with a computer-controlled automatic gas sorption system (Autosorb-1, Quantachrome Corporation, USA). Applying the linear part (0.05 < P/P₀ < 0.30) of the adsorption branch to standard Brunauer–Emmett–Teller (BET) equation, specific surface area was calculated. ¹H nuclear magnetic resonance (NMR) and ¹³C NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer; the samples were dissolved in deuterated chloroform (CDCl₃). TG analysis was carried out on an EXSTAR TG/DTA 6300 instrument (SII nanotechnology, Japan). Gas chromatography–mass spectrometry (GC–MS) was performed by a Hewlett–Packard 6890/5973 GC/MS system, which is equipped with a HP-5MS capillary column (crosslink 5% PH ME siloxane, 30 m × 0.32 mm i.d., 0.25 μ m film thickness) and a quadrupole analyzer. Mass spectra were obtained at an electron impact potential of 70 eV. Helium was used as the carrier gas. The data were acquired and processed using Chemstation software with the GC/MS system.

3. Result and discussion

3.1. Influence of demineralization on the structure of oil shale

Generally, the mineral matrix of oil shale mainly consists of quartz (silicates), clay, different types of carbonates (CaCO₃, MgCO₃, and dolomite), pyrite, etc. XRD patterns (Fig. 2) confirm

Table 1
Main components of the used raw oil shale.

Component	Content (wt%)	Component	Content (wt%)
Kerogen	23.8	Calcite	17.8
Water	4.9	Illite	4.2
Quartz	32.1	Pyrite	0.9

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