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Strengthening the applicability of self-heating retorting process to oil shale via co-retorting

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HIGHLIGHTS

- Facile self-heating retorting of low energy input can well retort Longkou or Huadian oil shale to prepare oil.
- Self-heating retorting of Fushun oil shale with lower oil content is unsatisfying.
- Fushun oil shale can be well utilized by self-heating co-retorting with Longkou or Huadian oil shale.
- Fushun oil shale can be well utilized by self-heating co-retorting with pine needles.
- A new starting point for using renewable biomass to utilize low-grade oil shale is provided.

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ABSTRACT

Recently a facile low-energy-input retorting route but without marked loss in the shale-oil yield is developed, which is achieved by a self-heating effect, that is, spontaneously increasing retorting temperature in the absence of external heat provision (Guo et al., 2013, 2014). In this work, the applicability of self-heating retorting (SHR) process to three Chinese oil shales from different places (i.e., Longkou, Huadian and Fushun) is studied. Of these three oil shales, Fushun oil shale is associated with coal and was previously abandoned during coal mining due to its not high kerogen or oil content. The results show that it's hard for Fushun oil shale to obtain satisfying self-heating effect, while Longkou or Huadian oil shale with higher kerogen or oil content shows satisfactory SHR. However, by adding suitable amounts of Longkou or Huadian oil shale into Fushun oil shale, a satisfying self-heating effect can be obtained as well. Thus, the relatively low-grade Fushun oil shale can also be well utilized to produce shale oil via this facile SHR route. Moreover, to utilize Fushun oil shale with a greener SHR process, the process can be performed by co-retorting Fushun oil shale with pine needles, a kind of renewable biomass. This finding also provides a new starting point for exploring plentiful biomass resources to utilize low-grade oil shale to produce oil in the future work.

1. Introduction

With an increasing demand for energy and a limited reserve of petroleum, the exploitation of energy alternatives has attracted more and more attention. Oil shale, a sedimentary rock with organic matter called kerogen, is plentiful and widespread throughout the world, and thus this kind of unconventional fossil fuel shows great potential as an alternative source for petroleum [1–4]. There are two conventional ways for using oil shale, i.e., burning to generate electricity power and retorting to convert kerogen into petroleum-like shale oil [3–7]. The later way becomes more and more prevalent due to the decreasing petroleum recourses. However, the retorting requires high-energy input to thermally break down the kerogen matrix to shale oil [1,8,9], such as using 700 °C heat-carrier gas to heat raw oil shale to ~550 °C [10], which is the most difficult obstacle to retorting [11].

In order to overcome above problem, Sun et al. [12] demonstrated a low energy-consumption topochemical reaction strategy. In this strategy, the organics retained in the oil shale is partially oxidized by small quantities of air. Subsequently a large amount of heat could be released and accelerate the kerogen self-pyrolysis. The topochemical reaction of oil shale, different from a physical heating process or a complete combustion, is a chemical heat-enhanced process that not only conserves energy but also decomposes oil shale more thoroughly. Almost at the same time with Sun et al., our group

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independently developed a low-energy-input retorting route using low-temperature heat-carrier gas but without marked loss in the shale-oil yield [3,4]. 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 ~300–350 °C by external heating under N_2 and then switching N_2 into oxygen-containing carrier gas. Once N_2 is replaced by oxygen-containing carrier gas, 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 ~300–350 °C (i.e., the required energy input and external-heating terminal temperature are low), the retorting process is significantly simplified. Moreover, like anaerobic retorting processes, self-heating retorting (SHR) process also produces the oil mainly consisting of various hydrocarbons.

However, more research is still required to know this promising retorting route in detail. Oil shales from different places are different in the oil or kerogen content, mineral composition, etc. In this work, the applicability of SHR to three Chinese oil shales from different places (i.e., Longkou, Huadian and Fushun) is studied. Among these three oil shales, Fushun oil shale has the lowest oil content. In Fushun, lots of oil shale is associated with coal and mined during coal mining. Some oil shale, as the waste of coal mining, was abandoned near the mining area and not utilized due to not high organics content. The oil shale stacked on the surface will not only cause a waste of resource, but also pollute ground water due to the leaching or eluviation by rain. If traditional retorting route is used, the low oil content will lead to a low ratio of shale-oil output to energy input. Therefore, the application of SHR to Fushun oil shale with reduced energy input will be particularly meaningful. In this work, we also study improving the applicability of SHR process to Fushun oil shale via co-retorting Fushun oil shale with Longkou (or Huadian) oil shale and plentiful renewable pine needles, respectively. The results show that self-heating co-retorting route is feasible.

2. Experimental

2.1. Materials

The three Chinese oil shales used in this study were obtained from (1) Gonglangtou mine located in Huadian, Jilin province, (2) Liangjia mine located in Longkou, Shandong province and (3) Xilutian mine located in Fushun, Liaoning province. Their results of Fischer assay, proximate and ultimate analyses are shown in Tables 1 and 2. The raw oil shale was crushed and screened to 1–3 mm particles before use. The pine needles were obtained from Chinese red pine (*Pinus tabulaeformis*) and the fallen pine needles were used. The pine needles were cut into short pieces with ~1 mm in length before use.

Table 1
Fischer assay analysis of the used oil shales (wt.%).

Oil shale	Shale oil	Water	Residue	Gas
Longkou	16.96	3.70	73.50	5.84
Huadian	14.90	7.80	70.60	6.70
Fushun	7.82	2.80	87.17	2.20

2.2. SHR of oil shales (or self-heating co-retorting of oil shale with pine needles) for preparing oil

The retorting apparatus used in this study is shown in Fig. 1. The SHR route was as follows: ~60 g oil shale (or oil shale/pine needle mixture) was placed inside a tubular quarts reactor (length: 380 mm; inner diameter: 18 mm). The tubular quarts reactor was installed in a tubular furnace with thermocouples in it. The oil shale (or oil shale/pine needle mixture) was first preheated from room temperature to 350 °C by tubular furnace (i.e., by external heating), during which N_2 passed though the tubular quarts reactor. Then, the N_2 was replaced by the oxygen-containing carrier gas of ambient temperature ($O_2/N_2 = 8/25$ for the retorting of oil shale; $O_2/N_2 = 8/15$ for the co-retorting of oil shale/pine needle mixture). After the N_2 was replaced by oxygen-containing carrier gas, external heating was not required, because the temperature of oil shale (or oil shale/pine needle mixture) in the tubular quarts reactor begins to increase spontaneously owing to the presence of oxygen (i.e., self-heating effect), accompanied by the continuous pyrolysis of oil shale (or oil shale/pine needle mixture). The gaseous pyrolysate outflowed from the tubular quarts reactor with carrier gas, and then passed through a multi-stage water condenser to be condensed as oil. For comparison, anaerobic retorting (i.e., using pure N_2 as the only carrier gas throughout the whole retorting process) was also performed. In the anaerobic retorting, external heating is required at all times until retorting is throughly complete because the pyrolysis of kerogen under N_2 is endothermic.

The oil yield, η, in this work was defined as follows:

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

where m is the weight of the obtained oil and M is the initial weight of the used raw oil shale or oil shale/pine needle mixture.

2.3. Analytical methods

X-ray diffraction (XRD) patterns were measured with a D8 diffractometer (Bruker, Germany) with Cu Ka 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. ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer; the samples were dissolved in deuterated chloroform ($CDCl_3$). Thermogravimetric/differential thermogravimetric (TG/DTG) analysis was carried out on an EXSTAR TG/DTA 6300 thermal analyzer (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 μm film thickness) and a quadrupole analyzer. Mass spectra were obtained at an electron impact potential of 70 eV. Helium was used as the

Table 2
Proximate analysis, ultimate analysis and heating value of the used oil shales.

Oil shale	Proximate analysis (wt.%)				Ultimate analysis (wt.%)				Heating value (J/g)
	Moisture	Volatile matter	Ash	Fixed carbon	C_{ad}	H_{ad}	N_{ad}	O_{ad}	
Longkou	3.51	35.51	50.74	10.24	32.92	4.25	0.80	11.10	11,769
Huadian	5.56	32.65	57.12	4.67	28.92	4.02	0.71	10.90	10,681
Fushun	2.51	17.00	73.8	6.69	14.06	2.22	0.63	6.90	5107