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Oil shale pyrolysis in indirectly heated fixed bed with internals under reduced pressure

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ABSTRACT

Our previous studies have shown evident technical superiorities of oil shale pyrolysis in a newly devised fixed bed reactor with particularly designed internals (Fuel Processing Technology, 138, 2015: 147-155). This study is furthered to optimize the operating conditions by focusing on the reaction pressure to enhance the yield and quality of shale oil in the fixed bed reactor with internals. Reducing the pyrolysis pressure increased the shale oil yield in comparison with the pyrolysis under atmospheric pressure. This influence due to reducing reaction pressure appeared to be higher in the reactor with internals than in the reactor without any internals. Moreover, there were higher yield of aliphatic components and fewer aromatic species in the reactor with internals, essentially indicating the suppressed secondary reactions to the produced primary shale oil in the new reactor. In this reactor the shale oil yield reached 97.57% of the Fisher Assay yield (8.24 wt.% dry basis) at a furnace heating temperature of 1000 °C under reduced pressure conditions. Consequently, there is actually some synergistic effect between internals and reducing pressure so that adopting internals and using vacuum condition can grant the indirectly heated fixed bed reactor great potential to achieve high yield and high quality of shale oil in oil shale pyrolysis.

1. Introduction

The demand for alternative oil is continuously growing due to the foreseen shortage of petroleum supply. Oil shale is the major unconventional oil resource and exists in a number of countries and its pyrolysis for producing shale oil has been attractive for decades of years [1]. There are thus many studies about oil shale pyrolysis conducted to understand the effects of major fundamental parameters on shale oil yield and shale oil quality with the intention of optimizing the reaction conditions. They include pyrolysis temperature [2–4], heating rate [3–6], particle size [7–9], residence time for pyrolysis reaction [10], composition of pyrolysis atmosphere [11,12], mineral matrix [13] and so on. Burnham et al. [14] observed that with increasing reaction pressure and also decreasing heating rate it significantly reduced the shale oil yield because of the delayed oil evolution rate that caused serious secondary reactions. The result implies that the condition of rapid heating and low reaction pressure facilitates shale oil production in oil shale pyrolysis.

Vacuum pyrolysis was found to enable higher oil and volatile yields in comparison with the pyrolysis under atmospheric pressure [15–17]. Indeed, a reduced pressure facilitates the removal of pyrolysis products to shorten the residence time of condensable vapors in reactor and thus to decrease the degree of secondary reactions. Li et al. [18] reported the increase of tar yield and the less aromatic species in the generated tar under vacuum conditions. This indicates the improvement on the oil production by having higher yield and better quality through pyrolysis under reduced pressures.

There are different oil shale pyrolysis or retorting technologies based on either direct or indirect heating. The direct heating method has to use either gas or solid heat carrier. The indirect heating pyrolysis has usually low oil yield and low efficiency because of its low heat transfer efficiency. Recently, Zhang et al. [19] have reported the use of internals in an indirectly heated fixed bed reactor for coal pyrolysis to reinforce the heat transfer and also pyrolysis performance. While the heating rate to coal can be doubled, it also increased the coal tar yield and quality through regulating the gaseous pyrolysis product in the reactor to flow from high-temperature zone to low-temperature zone. This reactor was also applied to oil shale pyrolysis by Lin et al. [20] and showed the similar improvement on both heating rate and shale oil production. The particularly designed internals have also been applied to pyrolysis of coal or oil shale in different fixed/moving bed reactors either indirectly heated or using solid heat carrier, and all showed higher performance to enhance yield and quality of the produced coal tar or shale oil [21–23]. The high oil quality refers to the high content of light oil, high H/C atomic ratio and low dust content in the produced shale oil.

This study is devoted to investigating the oil shale pyrolysis in the preceding indirectly heated fixed bed reactor with internals under reduced pressures. The operating conditions will be optimized to get further better

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pyrolysis performance by taking advantage of the benefits granted to pyrolysis by both internals and low pressure. It is expected to have higher shale oil yield under reducing pressure to further facilitate the oil production of oil shale pyrolysis in the reactor with internals, in comparison with that in the reactor without any internals. In addition, the product distribution and shale oil composition will be also compared for different reaction pressures in the fixed reactor with internals.

2. Experimental section

2.1. Facility and procedure

The pyrolysis facility and method are basically the same as used in Lin et al. [20]. Fig. 1(a) and (b) presents the testing facility and two types of fixed bed reactors, respectively. The used two reactors were made of stainless steel and had the same internal diameter of 100 mm and effective volume of 1900 ml for loading oil shale. The reactor A had not any internal, while the reactor B was mounted with the two kinds of internals. The first type of internals was the four metallic plates of 35 mm wide and 120 mm high, which were perpendicularly connected to the reactor wall with a 90° angle between two neighboring plates to enhance the heat transfer of oil shale bed. Another type of internals was a central gas collection pipe connected to the exit of the reactor to adjust the flow direction of gaseous pyrolysis products in the reactor.

Batch-wise pyrolysis was conducted by loading about 1400 g oil shale in the reactor. Before loading the reactor, the furnace was first preheated to a temperature about 200 °C higher than the required pyrolysis temperature. This is for achieving quickly the operating temperature after putting the reactor into the furnace and adjusting the furnace heating to its controlling temperature. Silica wool was used to insulate the furnace and reactor to keep the possibly maximal uniform heating to the reactor.

The pyrolysis products from the reactor were immediately cooled down in a condenser (4). While the formed liquid shale oil and water were collected into the bottle (5), the left gaseous stream further passed through three acetone washing bottles (6) immersed in an ice-water bath to collect shale oil with the possibly highest degree. The non-condensable pyrolysis gas was metered in a wet gas meter (10) to record the gas volume, and it then passed through a sodium bicarbonate solution (11) and a silica gel bottle (12) to remove sulfur species and moisture in the gas, respectively. The cleaned gas was sampled in every 5 min using gas bags to measure its composition in a micro GC. The pressure inside the reactor was adjusted using a valve before the vacuum pump and it was constantly kept in the whole procedure of an experiment. The reaction pressure was presented in terms of the minus pressure value relative zero for the atmospheric pressure. The temperature of oil shale in the core or near the wall of the central gas collection pipe was measured and recorded throughout the experiment as the controlling reference. For every individual experiment, the test was ended when the temperature of oil shale at the same central position reached 520 °C. Then, the reactor was quickly taken out from the furnace to cease the reaction, and char was further taken for characterization after the reactor reached room temperature. Table 1 summarizes the operating conditions adopted for all experiments, showing that the study involved two series of experiments, with S1 and S2 for clarifying the effects of pressure and temperature (but under reduced pressure), respectively.

Table 1
Operating conditions of all experimental tests.

Test series	Reactor	Furnace temperature (°C)	Relative pressure[a] (kPa)
S1	A	800	0, −40, −60
	B	800	0, −40, −60
		700	0, −40
S2	B	800	0, −40
		900	0, −40
		1000	0, −40

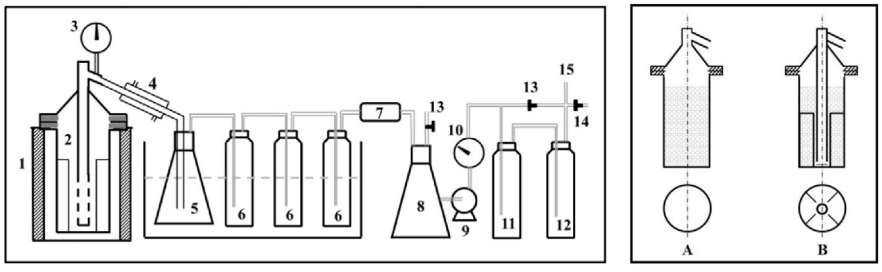
[a] Relative pressure = reactor pressure − 1.0 atm.

2.2. Material and analysis

The tested oil shale in this article was from Huadian, Jilin province, China. For tests, the oil shale was ground and sieved into particles below 5 mm and further dried at 110 °C for 24 h in an air oven. Table 2 lists the proximate and ultimate analyses for the tested Huadian oil shale. More than 70 wt.% is ash (A), and the volatile content (V) is about 24 wt.%. The Fischer Assay gave an oil yield of 8.24 wt.% against dry oil shale mass.

After each experiment, both the cooled char and the liquid product in the collection bottle, which is a mixture of shale oil and water, were collected and weighed. The condenser and entire pipeline were washed using acetone and the received washing liquid was mixed with the acetone-absorption liquid from three acetone scrubbing bottles. Acetone in the mixed liquid was in turn removed via vacuum rotary evaporation to recover shale oil. The recovered shale oil was mixed with the liquid mixture in the collection bottle, which was finally weighed and analyzed to determine the moisture content of the produced shale oil using the water-toluene azeotropic distillation method.

The shale oil after water removal was analyzed using simulated distillation GC (Agilent 7890A) according to ASTM D2887-01a standard to determine its distillation fractions at different boiling points. The oil components with different boiling points were distinguished into light oil (boiling point below 350 °C), vacuum gas oil or VGO (boiling point 350–500 °C) and heavy oil (boiling point above 500 °C). The chemical composition of the shale oil was further measured using a GC–MS spectrometer (Shimadzu QP 2010 Ultra). The temperature of injector and detector was 280 °C, and the column temperature program included the steps of keeping the column at 50 °C for 5 min, heating it to 280 °C at 6 °C/min and finally holding the column at 280 °C for 10 min. The solvent delay time was 1.7 min, and the scanning range was from 20 to 900 m/z. The relative content of each component was evaluated with



(a) (b)

Fig. 1. Schematic plots for (a) experimental system and (b) side view and cross-sectional view of two fixed bed reactors of A without internals and B with internals (Ref. [20]).