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Research article

Characterization of oil shale pyrolysis by solid heat carrier in moving bed with internals

Dengguo Lai [a,b], Guangyi Zhang [a,*], Guangwen Xu [a,c,**]

[a] State Key Laboratory of Multi-phase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] Southwest Research and Design Institute of Chemical Industry Corporation Limited, Sichuan 610225, China

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ABSTRACT

Oil shale pyrolysis by solid heat carrier in moving bed with internals (MBI) was investigated with the aim to identify the effect of oil shale properties (moisture content and particle size) and heat carrier types on the physicochemical properties and distributions of pyrolysis products. Pyrolysis of oil shale with high moisture content of 10 wt% caused obvious increase in shale oil yield due to the protective effect of steam atmosphere by its reducing secondary reactions and also catalysis action of shale ash. The obtained highest shale oil yield was close to the yield of Fischer Assay. Pyrolyzing dried oil shale produced shale oil containing more light oils (gasoline and diesel) and allowed higher gas yield. Pyrolysis of large size (i.e. >10 mm) oil shale reduced oil yield but increased light oil content due to the required long time for heat transfer and intra-particle volatile diffusion. Comparing with ceramic balls, shale ash as the heat carrier presented a favorably catalytic effect on cracking and upgrading of shale oil. With increasing pyrolysis temperature from 465 to 525 °C, using shale ash greatly raised light oil content by 10.24% (relatively), considerably reduced the content of heteroatomic compounds, and promoted the conversion of aliphatics to aromatics. Shale ash carrier particles enabled better dust removal than ceramic balls did to attain oil product with a dust content below 0.2 wt%. Generally, oil shale pyrolysis using shale ash heat carrier in MBI process has obvious effects of in-situ shale oil upgrading and in-bed dust removal to allow good pyrolysis performance.

1. Introduction

Oil shale can be pyrolyzed to produce shale oil, an alternative fuel of petroleum with a vast resource [1]. The commercialized technologies for oil shale pyrolysis are mainly based on internal heating by introducing either gas heat carrier or solid heat carrier into the retort (pyrolyzer) [2]. The successful ones using gas heat carrier, such as Fushun, Kiviter and Petrosix retorts, only can treat large oil shale particles (e.g. >10 mm), causing about 40% of mined oil shale to be abandoned [3]. The technologies based on solid heat carrier have better adaptabilities for small-size oil shale and appears to have the advantages of high oil yield and low effluent gas volume. Low gas volume enables easier recovery and control of gaseous pollutants in comparison with the case for gas heat carrier processes [4,5].

The solid heat carrier processes utilize solid particles (shale ash or ceramic balls) preheated by outside combustor to mix with and thus heat raw oil shale in order to realize its pyrolysis. Comparing to other heat carriers such as ceramic balls in Toscoal process, we prefer hot shale ash as the heat carrier because the former requires additional expenses due to its abrasion and separation. For mixing hot solids and oil shale, the vertical mixer with overlapping inclined baffles reported by Lewis [6] is considered to be superior to fluidized bed in the Chevron STB process [7,8] and to screw mixer in the DG (Dagong) [9] and L-R [10] processes. In addition, moving bed reactor has such advantages as limiting the movement of solid particles inside the reactor as compared to rotary kiln and fluidized bed reactors, which can reduce the intake of fine particles in the produced oil vapor [11]. By contrast, the ATP process [12] is too complicated for commercial operation, while the Galoter process [13] running in Estonia is still unable to fully solve the ash-intake problem. To sum up, almost all the existing solid heat carrier processes suffer, to a certain degree, from the technical problems including high intake of dust (>10 wt%), high content of heavy components in produced shale oil [2,14], and high degree of complexity or high capital cost.

Separation of dust or fine particles from pyrolysis volatile is suggested to be the last technical challenge of fine oil shale pyrolysis [15]. Great attention has been paid to find practical methods to solve this problem, including heavy oil recycling and high temperature online separation (i.e., high temperature cyclone, ceramic filter, gauze screen

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[*] Corresponding author.
[**] Correspondence to: G. Xu, State Key Laboratory of Multi-phase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China.
E-mail addresses: gyzhang@ipe.ac.cn (G. Zhang), gwxu@ipe.ac.cn (G. Xu).

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filter and granular filter). However, up to now there is yet not efficient way or mature technology to thoroughly smooth over the dust-intake problem in pyrolysis processes because of the blockage of filter and troubles owing to special properties of heavy volatiles such as corrosivity, stickiness and high tendency of phase transition [16,17]. External granular filter is expected to be effective for dust separation because of its tolerance of high temperature, corrosive gas and chemical stability [18–20]. Nonetheless, disadvantages including severe abrasion of filter medium, high recycling energy consumption and difficulties in system temperature and pressure control limited its utilization in industrial practices.

With an intention to develop a new pyrolysis technology for small-size oil shale to produce shale oil with both high yield and good quality, a kind of moving bed reactor with internals (MBI) was proposed [2,21–23]. The application of internals in moving bed reactor can regulate pyrolysis volatiles to flow laterally across particle bed, endowing the particle bed with in-bed dust removal via filtering and in-situ oil upgrading through selective secondary reactions to heavy species [23]. Shale ash has a desirable potential to incur cracking and coking reactions when oil vapor flows through a shale ash bed, which can upgrade shale oil to generate oil product with lowered heavy oil content [24,25]. Consequently, the MBI process well combines moving bed pyrolysis and in-situ granular filtration, thus being a promising method for producing low-dust shale oil from pyrolyzing small-size oil shale. In fact, Huadian oil shale pyrolysis by solid heat carrier in this reactor has been investigated in a continuous laboratory facility, and the results showed that high-quality shale oil with low contents of dust and heavy oil was obtained at high yields [2].

Oil shale pyrolysis in steam-containing atmosphere is of particular interest when considering wet feedstock, and several studies in fixed or fluidized bed pyrolysis have reported obviously high shale oil yields in excess of the Fischer Assay yield if using steam as the sweep gas [26–30]. The differences caused by addition of steam into reaction atmosphere may be arisen from the fact that steam is more effective for recovering oil product and avoiding retrogressive char forming reactions [28]. However, little can be concluded about how steam affects oil shale pyrolysis by solid heat carrier. Several papers introduced oil shale pyrolysis using sand or ceramic balls as heat carrier, but no comparison was available with the pyrolysis using the practically possible shale ash carrier [13,31]. There are also very few studies regarding solid heat carrier pyrolysis of oil shale in different particle sizes [6,25].

This study is a continuous work of our studies about oil shale pyrolysis in MBI using solid heat carrier to further understand its performance under different conditions including varying steam content in atmosphere, oil shale particle sizes and type (property) of solid carrier particles. Pyrolysis product distribution and shale oil composition variation are particularly tested against conditional parameter changes.

2. Experimental section

2.1. Facility and operation

The continuous operation system shown in Fig. 1 was used for experiments, and it contained five major sections: heating solid heat carrier particles, feeding controls for heat carrier and oil shale, mixing of solid particles, moving bed reactor for oil shale pyrolysis and pyrolysis product recovery. A heat carrier bin in an electric furnace was used to store and preheat the heat carrier in each test. Preheated heat carrier and oil shale were quantitatively delivered into the mixing section by two respective screw feeders. The mixed solids in turn fell into the moving bed reactor to initiate pyrolysis reactions. The produced volatiles including oil and water vapor and non-condensable gas laterally passed through the particle bed (between the reactor wall and central internals) to enter the central gas collection channel and finally flew out of the reactor through the outlet connected to the central internals. Through cooling and condensation by water and glycol in succession, most shale oil and water were stripped from the gaseous product stream, and the residual oil was further recovered via acetone adsorption in a few scrubbing bottles. The non-condensable gas flew through a volumetric meter and was further sampled using gas bags for analysis in GC before it was vented. More details about the apparatus and operating procedures can be found in our previous publication [2].

2.2. Materials and analysis

The tested oil shale was the abandoned oil shale by Fushun retort in sizes below 13 mm. Table 1 shows the general characteristics of oil shale samples. The received oil shale has a moisture content of about 10 wt% and its shale oil yield determined by the Fischer Assay retort is 10.15 wt% on dry basis. The used shale ash was from an industrial combustion furnace of Huadian oil shale and it was also sieved into sizes below 13 mm for testing. Shale ash was characterized with the X-ray fluorescence (XRF) analysis, and the results in Table 1 shows that the main components in ash include SiO_2, Al_2O_3, CaO, Fe_2O_3 and SO_3. A kind of ceramic balls below 3.0 mm was also used as heat carrier in this study and its major components were Al_2O_3 and SiO_2. All the yields of products referred to in this article were on the dry basis of oil shale.

Analysis of non-condensable gas in a micro GC (Agilent 3000A) gave its concentrations of major gas species including H_2, CH_4, CO, CO_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8. In the context, the hydrocarbons C_2H_4 and C_2H_6 were denoted as C_2 and C_3H_6 and C_3H_8 as C_3. The obtained shale oil was analyzed in a simulated distillation GC (Agilent 7890B) to determine its distillate fraction distribution according to the ASTM D2887 method. On the basis of distillate fraction distribution, shale oil was characterized in terms of boiling points (BP) according to gasoline at BP below 180 °C, diesel at 180–350 °C, vacuum gas oil (VGO) at 350–500 °C and heavy oil over 500 °C. In this study, the so-called light oil fraction includes fractions of gasoline and diesel, while heavy oil fraction contains those for VGO and heavy oil components. The aromaticity of shale oil was detected by high-resolution NMR spectroscopy (Bruker Avance III spectrometer) at 700 MHz for ^{13}C. GC–MS (Shimadzu QP2010Ultra) analyses were performed to clarify the variation of major chemical components in shale oil. Concentration of an individual compound was calculated by its corresponding peak area against the total areas of all identified peaks (i.e., normalized to 100%). In this study, the mass content of dust in shale oil was determined as the content of toluene-insoluble matters. The amount of the insoluble matters was obtained by adding 20 ml toluene into 20 g shale oil and then filtering the mixture.

3. Results and discussion

3.1. Varying moisture content of oil shale

Fig. 2 (a) shows the yields of shale oil and pyrolysis gas (against dry oil shale) for dried and un-dried oil shale. The tested un-dried oil shale contained 9.40 wt% water. Raising pyrolysis temperature from 465 °C to 495 °C increased the shale oil yield for dried oil shale but almost unchanged for un-dried oil shale. The presence of moisture in oil shale (9.40 wt%) caused a visible increase in oil yield but obvious decrease in gas yield by about 10 l per kilogram dry oil shale, regardless of pyrolysis temperature (465 or 495 °C). For un-dried oil shale its shale oil yield was 10.51% relatively higher than that for dried oil shale at 465 °C (9.67 wt% vs. 8.75 wt%). At 495 °C this rise was 7.60% by rising from 8.95 wt% to 9.63 wt%. Thus, pyrolyzing oil shale containing certain moisture content, its volatiles are released in steam-containing atmosphere, which would facilitate oil production by about 10% (relative to dried material) and meanwhile to reduce gas production by about 20% (relatively).

Fig. 2 (b) reports the effect of moisture content on oil composition and yields of oil distillate fractions. Clearly, the total yield of gasoline and diesel from dried oil shale was higher than that from un-dried oil