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Research article

Experimental study of kukersite oil shale pyrolysis by solid heat carrier

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ABSTRACT

The investigation of oil shale pyrolysis in the experimental retorting system by solid heat carrier (silica sand) was conducted. Modeling of the heat and mass transfer processes in the retorting system was performed with use of simplified mathematical model. It was shown that the radiation heat exchange plays the main role in the heat transfer between oil shale particles and solid heat carrier under the conditions of volatiles release. The maximum yield of the shale oil amounts to 73% at temperature of experiment of 560 °C, which exceeds the data obtained in the Fisher assay on 20%. The conditions that lead to increase in maximum yield of shale oil in the industrial UTT units with the rotary drum reactor were ascertained. They are mainly associated with a decrease in the solid heat carrier (ash) temperature, which leads to the inhibition of secondary reactions between ash and the acidic compounds of the shale oil.

1. Introduction

The continuous growth in energy use in the world results in the exhaustion of traditional energy resources such as oil, gas, and coal. Therefore, the retrieval of alternative energy sources has a great importance at the present. One these sources can be oil shale primarily due to the enormous reserves and the valuable chemical composition [1]. Oil shale has a high content of mineral material that is closely integrated with organic matter (kerogen) [2]. And that is why its direct combustion in boilers is faced with some technical difficulties [3]. The oil shale kerogen contains a large amount of hydrogen. The mass ratio C/H is approximately equal to eight, which is close to the corresponding ratio for raw oil [4]. Therefore, pyrolysis or retorting of oil shale makes it possible to process up to 90% of kerogen into vapor products, which are raw materials for the production of boiler and motor fuels [5] as well as of valuable chemicals [6].

The oil shale retorting has a long history, and different technologies were developed [7]. The most advanced retorting technology is the Galoter one, the commercial realization of which put into practice in the industrial units UTT-3000 with a capacity of 3000 t of shale per day [8]. This technology is based on the oil shale pyrolysis in the horizontal rotary drum reactor at temperature of the order of 500 °C. The oil shale ash is used as a solid heat carrier. The semicoke particles after the reactor are transported into aerated fountain furnace, where their combustion occurs at temperatures 750-850 °C, thus providing the necessary temperature of ash for subsequent heating of oil shale in the pyrolysis reactor.

A large number of investigations that aim to study the influence of main parameters of oil shale pyrolysis on the process efficiency have been conducted over the recent years. They examine the effect of retorting temperature on the products yield [9], the heat transfer characteristics of oil shale particles [10], the pyrolysis kinetics [11–13], etc. To better understand the pyrolysis mechanism as applied to the Galoter technology, the numerical analysis of the oil shale pyrolysis in rotary drum reactor was performed [14]. The developed model includes such processes as the motion of solids in the reactor, the heat transfer between solid heat carrier and fuel particles, the kinetics of kerogen decomposition, etc. The theoretical description of these processes requires some simplifications and concretization of the model parameters, which can be received on the base of experimental investigations. The main objective of this study is to clarify the specific features of heat transfer between oil shale particles and solid heat carrier under the conditions of volatiles release as well as the identification of conditions that lead to maximum yield of shale oil.

2. Experimental

2.1. Materials

Oil shale samples used for experiments were obtained from Leningradsky deposit of the kukersite oil shale, Russia. These samples were crushed and sieved to three fractions with mean grain sizes of 0.35, 1.5, and 4.0 mm, respectively. After crushing and drying at room temperature to constant weight, oil shale was kept in hermetic volume.

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A representative sample of oil shale was investigated by standard methods. Table 1 shows the results of proximate and ultimate analysis of the tested oil shale. The mineral part of the kukersite consists mainly of limestone (of the order of 45 wt.%). The Fisher assay yields are as follows (wt.%, dry basis): shale oil – 20.50; pyrogenic water – 2.06; coke residue – 72.03; gas and loses – 5.41. The inert particulate material (silica sand) with mean grain size of 0.2 mm was used in experiments as the solid heat carrier.

2.2. Experimental system

During the first stage of the work, the investigation of oil shale processing with solid heat carrier using experimental retorting system was conducted. The scheme of the retorting system is shown in Fig. 1. The main element of the system is the hermetic steel retort with mixing device 1, which is placed in the shaft furnace 2, where the heating of the solid heat carrier (silica sand) occurs. The mass ratio of oil shale and solid heat carrier in the experiments was chosen so that the final temperature of the process is in the range 450-600 °C. Upon reaching the desired temperature of the heat carrier (550-700 °C), the retort is disconnected from the external heating source and at the same time it is filled with a portion of the shale.

The uniform mixing of shale with solid heat carrier is carried out by using the vertical mixing device. The time of oil shale adding and full mixing of the materials was not specially controlled, but it was determined in the range of 5-10 s based on results of separately conducted measurements. As the result of the heat and mass transfer processes, the thermal decomposition of kerogen occur followed by the volatiles emission. The temperature inside the retort is stabilized approximately one-two minutes after the start of the experiment.

The upper part of retort represents a dust precipitation chamber that is connected with the condenser of heavy oil 3, which is equipped with the collector of heavy oil 5. After passing the condenser 3, the vapour-gas mixture enters the condenser 4 for medium-light oil, which is connected with the collector of this oil 6. The final condensation of the vapour-gas mixture occurs in the condenser 7, which is located in thermostat with negative temperature. A non-condensable gas mixture (pyrolysis gas) is supplied from the condenser 7 to the gas meter 8 and the flow meter 9, and then to the burner 10, where it is burned. During the experiment, the temperature and pressure in the retort as well as the gas-flow rate after the condensation system were registered. After the end of the experiment, the determination of quantity of received products such as gas, oil, pyrogenic water, and semicoke was made.

During the second stage of the work, the impact of alkaline-earth metals oxides contained in the shale ash on the retorting process was estimated. The kukersite oil shale contains a significant amount of calcium oxide. Therefore, this mineral was used for investigation. The experiments were performed in the Fisher retort using mixtures of oil shale and calcium oxide in ratio of 19:1, 17:3, 7:3 and 1:1. The heating rate of the retort up to the final temperature of 520 ºC did not exceed 15 ºC/min.

Separately, the carbonates decomposition in the oil shale depending on the treatment temperature was examined. For this purpose, parallel samples of oil shale were placed in the muffle furnace and heated to final temperatures of 600, 800, and 950 °C. Upon reaching the set temperature, the sample is kept for 2 h and then is cooled in a exsiccator. The content of carbon dioxide in received samples was determined by gravimetric method, which allowed judging the degree of carbonates destruction.

Table 1
Analysis of the tested oil shale.

Proximate analysis (wt.%)[a]		Ultimate analysis (wt.%)[a]	
Moisture	1.30	C[b]	30.52
Volatile matter	46.25	H	2.73
Ash	47.88	S	0.52
Fixed carbon	4.57	N	0.16
Lower heating value (kJ/kg)	10,576.30	O[c]	16.89

[a] As-received basis.
[b] Total carbon.
[c] Calculated by difference.

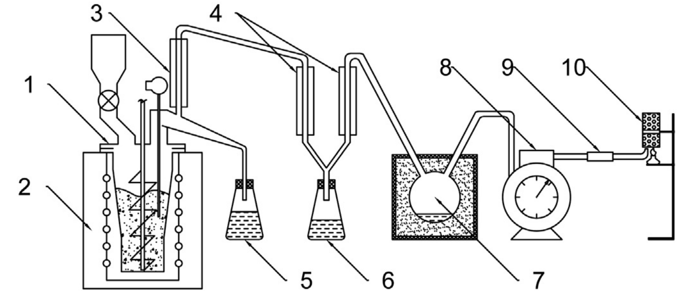

Fig. 1. Schematic diagram of the experimental retorting system.

3. Model description

Modeling of the heat and mass transfer processes in the experimental retorting system was performed with use of simplified mathematical model, which includes the equation of enthalpy balance between solid heat carrier and fuel, the equation of heat conductivity describing the heating of fuel particles, and the kinetic equation of the kerogen decomposition. The kerogen behavior at high temperatures is determined by the kerogen type, heating rate, final temperature, particle size, etc. [15–16]. The decomposition process begins with kerogen conversion into a plastic state – tar (TAR), which disintegrates then into the mixture of liquid hydrocarbons (OIL) and gas (GAS).

It is assumed that the heat transfer in the layer of heat carrier that surrounds fuel particles is high, so the layer is considered as isothermal. Since the size of the fuel particles is sufficiently small, they are considered as isothermal also. The heat transfer between reactor walls and the filling is ignored. At these conditions, the enthalpy balance equation can be written as:

$$c_{hc}m(T_{hc,0}-T_{hc}) = c_f(T_f-T_{f,0}) + (1-Y_{tar})\Delta H, \quad (1)$$

where c_{hc} and T_{hc} are the heat capacity and temperature of the heat carrier; $m = G_{hc}/G_f$ is the ratio of the flow rates of the solid heat carrier G_{hc} and the fuel G_f; Y_{tar} is the tar concentration, kg/(kg of kerogen); ΔH is the heat of reaction.

Fuel particles are assumed to be spherical, and any change of the particle mass and shape during devolatilization process is not taken into account. The heat transfer equation that describes heating of fuel particles can be expressed as follows:

$$d(\rho_f v_p c_f T_f)/dt = (h+h_{rad})s_p(T_{hc}-T_f)-\rho_f v_p k_{tar} Y_{tar}\Delta H, \quad (2)$$

where ρ_f is the fuel particle density; $v_p = (1/6)\pi d^3$ is the volume of the fuel particle with the diameter d; $s_{p.} = \pi d^2$ is the particle surface; h is the conductive and convective heat transfer coefficient; $h_{rad} = \sigma\beta(T_{hc} + T_f)(T_{hc}^2 + T_f^2)$ is the radiation heat transfer coefficient, where $\sigma = 5.67 \times 10^{-8}$ W/(m^2·K^4) is the Stefan-Boltzmann constant, and $\beta = 0.8$ is the particle emissivity; k_{tar} is the rate constant of the tar decomposition. In general, the heat exchange between solid heat carrier and fuel particles is carried out by conduction, convection, and radiation [17,18]. At the conditions of intensive volatiles emission from the fuel particle, one can expect that the radiation heat transfer will be predominant.