A study of pyrolysis of oil shale of the Leningrad deposit by solid heat carrier

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Abstract. The investigation of the oil shale pyrolysis with a solid heat carrier was carried out using the experimental retorting system that simulates the Galoter industrial process. This system allows verifying both fractional composition of the oil shale and solid heat carrier, and their ratio and temperature. The oil shale of the Leningradsky deposit was used in the work, and quartz sand was used as the solid heat carrier. It is shown that the yield of the shale oil under the pyrolysis with solid heat carrier exceeds by more than 20% the results received in the standard Fisher retort. Using ash as the solid heat carrier results in a decrease in the yield of oil and gas with simultaneous increase in the amount of the solid residue. This is due to the chemical interaction of the acid components of the vapor-gas mixture with the oxides of alkaline-earth metals that are part of the ash.

1. Introduction

Despite the fact that Russia occupies one of the leading places on the potential resources of hydrocarbons, the explored reserves at the existing rates of production will last for 20-30 years. The depletion of easily accessible reserves and the increase in the number of oil and natural gas fields concentrated in the northern regions with complex operating conditions lead to a significant increase in the cost of their extraction. In this connection, the interest in alternative energy sources is growing. One of such sources can become oil shale [1]. Oil shales are characterized by a high content of mineral components, closely related to organic matter [2]. This significantly complicates the direct combustion of this fuel due to contamination of furnace walls and superheaters with ash deposits, as well as corrosive and abrasive wear of steam superheaters and water economizers [3]. An alternative to direct burning of shales is their thermal processing (pyrolysis). This process allows converting the organic mass of oil shale to vapor products and produce not only high-quality boiler fuel, but also motor fuels, as well as valuable chemical raw materials.

The most advanced technology for the thermal processing of oil shale at present is the Galoter one, implemented in the industrial units UTT with a solid heat carrier (oil shale ash) [4]. However, despite the long run of existing UTT units, the yield of shale oil, which is the main factor determining the efficiency of shale processing, is lower than at semi-cooking under laboratory conditions using a standard Fisher retort. This negatively affects the cost of producing synthetic oil from the oil shale and reduces the competitiveness of the process with respect to traditional methods of liquid fuels production.
A large number of investigations, which study the effect of the main parameters of the oil shale pyrolysis on the efficiency of the process, have been conducted lately [5]. They include the effect of the process temperature, the heat transfer characteristics, and the pyrolysis kinetics on the oil yield. The main purpose of this work is to elucidate the features of heat and mass exchange processes of the oil shale pyrolysis with a solid heat carrier and to determine the conditions, under which the maximum yield of shale oil is reached.

2. Experimental

The oil shale samples from the Leningradsky deposit (Russia) were used in the experiments. After milling and sifting, the shale samples with particles size from 0.2 to 5.0 mm was dried to constant weight and placed in a germetic container. A sample of oil shale was investigated using standard techniques. Table 1 presents the results of a proximate and ultimate analysis of the tested oil shale. The shale organic mass is equal to 36.85%. The composition of the mineral part of the oil shale is as follows: SiO₂ - 31.0%; Al₂O₃ - 8.2%; Fe₂O₃ - 5.9%; TiO₂ - 0.5%; CaO - 39.5%; MgO - 4.8%; SO₃ - 5.0%; K₂O - 4.2%; Na₂O - 0.3%; P₂O₅ - 0.1%; others – 0.5%. Quartz sand with an average particle size of 0.35 mm was used as a solid heat carrier.

| Proximate analysis (wt.%) | Ultimate analysis (wt.%) |
|---------------------------|--------------------------|
| Moisture                  | C                        |
| Volatile matter           | H                        |
| Ash                       | S                        |
| Fixed carbon              | N                        |
| Lower heating value (kJ/kg)| O                        |

Pyrolysis of the oil shale was carried out with use of the standard Fisher retort and the experimental retorting system for the processing of oil shale with a solid heat carrier. The retorting system scheme and its general appearance are shown in Figure 1. The main element of the system is the hermetic steel retort with the mixing device 1, placed in the shaft furnace 2, in which a solid heat carrier (quartz sand) is heated. The retort is equipped with thermocouples that fix the temperature both inside the solids layer and on its outer wall. The preliminary experiments showed that the temperature difference at different points of the material layer under mixing device work does not exceed 10 °C. The upper part of the retort is a dust precipitation chamber connected to the condensation system 3 - 7. The non-condensible part of the vapor-gas mixture (pyrolysis gas) comes from the condenser 7 to the gas meter 8 and the flow meter 9, and after it to the burner 10, where it is burned.

![Figure 1a](image1a.png)  
**Figure 1a.** Scheme of the experimental retorting system.
As a result of heat and mass transfer processes, the thermal decomposition and evaporation of the organic mass of oil shale particles occurs. Approximately 1-2 minutes after the start of the experiment, the temperature inside of the retort is stabilized and the process of mixture cooling begins. Upon completion of the experiment, the amounts of obtained products such as gas, tar, pyrogenetic water and char were determined.

Another task of the work was to evaluate the effect of alkaline-earth metal oxides in shale ash, which is used as the solid heat carrier in the UTT units, on the process of oil shale thermal processing. The shale ash contains a significant amount of calcium oxide (CaO), so it was chosen for research. Thermal decomposition of the mixture of oil shale with CaO (5%, 15%, 30%, and 50%) was investigated. The shale particles were thoroughly mixed with CaO particles before the experiment, after which the mixture was placed in the reaction volume of the Fisher retort. The retort was heated to a final temperature of 520 °C, and then the amount of semi-coking products obtained was determined. In addition to quantifying the yield of pyrolysis products, the change in the group composition of the shale oil and the pyrolysis gas was also investigated.

3. Results and discussion
On the first stage of the work, a series of experiments was conducted on the pyrolysis of oil shale in a standard Fisher retort. In turn, the Galotex technology uses the solid heat carrier for heat transfer, which allows heating of the entire fuel mass to the specified temperature much quicker. A significant difference in the rate of heating does not allow transferring the results of quantitative evaluation, obtained in the Fisher retort, to industrial UTT units. Therefore, the only acceptable option for modeling the thermal processing of oil shale in installations with a solid heat carrier remains experimental study on a reduced physical model of the process.

3.1. Oil shale thermal decomposition in Fisher retort
The experiments on the pyrolysis of oil shale in a standard Fisher retort were performed at a heating rate 10 °C/min in the temperature range 480-520 °C. The results are shown in Table 2. It can be seen that the maximum yield of the shale oil corresponds to a temperature of 490 °C. Since the data scattering is small, it can be attributed to the error of the experiment. Nevertheless, it is clear that for the oil shale of the Leningrad deposit the pyrolysis process is completed already at a temperature of 480 °C.

Table 2. Pyrolysis of shale oil in Fisher retort

| Products yield, % | Process temperature, °C |
|-------------------|-------------------------|
|                   | 480        | 490        | 520        |
| semi-coke         | 71.31      | 71.35      | 71.42      |
| shale oil         | 21.96      | 21.99      | 20.02      |
| pyrogenetic water | 1.39       | 1.41       | 2.85       |
| gas and loss      | 5.34       | 5.25       | 5.71       |

3.2. Pyrolysis of oil shale in retorting system with solid heat carrier
The main objective of the study is the thermal decomposition of oil shale under conditions close to real in the UTT unit. Data on the yield of pyrolysis products as a function of the experimental temperature $T_{exp}$, which is the final temperature of the mixture of oil shale and heat carrier, are shown in Figure 2.
Figure 2. The yield of pyrolysis products.

It can be seen that the gas yield decreases with increasing $T_{\text{exp}}$, and then begins to increase sharply. This growth may be due to the decomposition of the pyrolysis shale oil in the free volume of the reactor. The yield of pyrogenetic water has the opposite tendency. It should be noted that its yield is quite large and reaches 20% at $T_{\text{exp}} = 500$ °C. There is a constant tendency to decrease the yield of semi-coke with the growth of $T_{\text{exp}}$. The residual organic mass of the semi-coke at $T_{\text{exp}} > 550$ °C does not exceed a few percent. The shale oil yield increases with the temperature rising up to 550 °C. A further decrease in this parameter is due to the presence of secondary reactions of decomposition of the shale oil into lighter components of the gas.

As already mentioned above, the main difference between the pyrolysis process in the standard Fisher retort and in the retorting system with solid heat carrier is the heating rate of the fuel. In this connection, it is interesting to compare the data on the oil yield in these two experiments (see Figure 3). For experiments in the standard Fisher retort at the heating rate of 10-15 °C/min, the yield of the shale oil does not exceed 60% of the organic mass. The optimum process temperature is ca. 480 °C. The maximum yield of the shale oil in the experimental retorting system at the heating rate ca. $10^3$ °C/min and $T_{\text{exp}} = 560$ °C was 73%, which exceeds the Fisher’s retort value by 20%. The high heating rate in the retorting system is achieved through the effective mixing of materials by a mixing device capable of ensuring in a short period of time the complete homogeneity of the mixture and, accordingly, the uniformity of heating of the shale particles.
3.3. Reaction of shale oil with oxides of alkaline earth metals

The Galoter technology is based on the employment of shale ash as the solid heat carrier. The semi-coke particles that are formed in the pyrolysis reactor are burned up in the fountain type furnace at the temperature 750-850 °C. The resulting heat is used for heating of the heat carrier, which is then separated from the ash and flue gas stream and returned to the pyrolysis reactor. Simultaneously, carbonate compounds contained in the mineral mass of the oil shale are destroyed with the formation of oxides of alkaline earth metals and free carbon dioxide. The oxides of alkaline earth metals are returned in the pyrolysis reactor and then react with products of oil shale pyrolysis, which leads to decrease of the shale oil yield [6].

Therefore, one of the tasks of the work was to evaluate the effect of alkaline-earth metal oxides in shale ash, which is used as the solid heat carrier in the UTT units, on the yield of the shale oil. The corresponding experiments on the yield of pyrolysis products of the mixture of oil shale with CaO particles were performed with use of the standard Fisher retort. The results are shown in Table 3. It can be seen from Table 3 that the yield of the oil and the pyrolysis gas decreases with a corresponding increase in the proportion of pyrogenic water and char as the concentration of calcium oxide in the mixture increases. An increase in the concentration of CaO by more than 30% does not lead to a further redistribution of the pyrolysis products.

Table 3. Yield of pyrolysis products in Fisher retort at various CaO concentrations

| Products yield, % | Concentration of CaO in mixture, % |
|-------------------|-----------------------------------|
|                   | 0       | 5       | 15      | 30      | 50      |
| shale oil         | 20.50   | 19.32   | 17.79   | 16.27   | 16.45   |
| pyrogenetic water | 2.06    | 2.93    | 4.33    | 5.30    | 4.79    |
| semi-coke         | 72.03   | 73.44   | 74.85   | 76.73   | 76.70   |
| gas and loss      | 5.41    | 4.32    | 3.03    | 1.70    | 2.06    |
Of particular interest is the analysis of the group composition of the oil for various mixtures, the results of which are shown in Figure 4. As can be seen from the result of the analysis, a significant reduction in the total phenols and an increase in the content of hydrocarbon compounds occur in the shale oil for mixture with 30% calcium oxide addition. The pyrolysis gas analysis shows almost complete absence of acid components (CO₂ + H₂S).

4. Conclusions
A series of experiments in the experimental retorting system with solid heat carrier was performed to determine the yield of the oil shale pyrolysis products as a function of the process temperature. It was found that the maximum yield of liquid products of ca. 73% (from the organic mass of oil shale) is achieved in the temperature range 540-560 °C, which exceeds by more than 20% the corresponding value received in the standard Fisher retort. The conducted studies also confirmed the assumption of chemical interaction of the acid components of pyrolysis products with the alkaline-earth metal oxides, in particular, with CaO. It was found that as a result of the chemisorption in the UTT unit, the solid phase can absorb up to 20% of the oil and a significant amount of pyrolysis gas, which are then burned in the fountain furnace.

References
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Figure 4.a The group composition of the shale oil for the mixture of shale and CaO, %

Figure 4.b The group composition of the gas for the mixture of shale and CaO, %