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INVESTIGATION OF THE THERMAL DECOMPOSITION PROCESS OF KENDYRLIK DEPOSIT OIL SHALES

Abstract. In the article, experiments on the thermal treatment of Kendyrlik shale by its carbonization and activation were carried out. First, shale was carbonized in an inert argon medium in the temperature range 25-700 °C and then activated by water vapor at a temperature of 850-900 °C. The analysis of the elemental composition of the resulting synthetic gas showed that the highest concentration of combustible gas components (CO, H_2, CH_4) is observed at 900°C (in the absence of H_2S, low CO_2 and a small amount of liquid products - resin). Shale pyrolysis was also carried out in argon medium up to 900 °C. As a result of the analysis of the component composition of liquid products, it was found that mainly isoalkenes, alkanes and isocycloalkanes are formed. However, the elemental composition of the produced gas showed that the volume of gas and its caloric content are significantly lower in comparison with similar parameters for the gas produced during the activation of shale.
Keywords: shale, Kendyrlik, activation, carbonization, pyrolysis, gas.

Introduction. Globally, the significance of shale is its value as a source of energy, an alternative to other types of fossil fuels (for example, oil and coal) [1]. The solution to the problem of the use of oil shale, especially abroad, is mainly considered in the direction of their processing, with the production of shale resin - a substitute for oil and artificial gas (a substitute for natural gas). At the same time, the determining qualitative characteristics are: the content of organic matter and the yield of resin; calorific value (by class); the content of sulfur, rare and dispersed elements in the initial shale, semi-coking resin, gas products and ash residue; composition of the products obtained (resin, gas mixture); the ratio of the yield of the semi-coking resin to the heat of combustion (in groups) [2].

Possessing a high calorific value of combustible mass, shaleis one of the low-grade fuelsdue to the huge amount of ash. The high content of hydrogen (up to 11%) in kerogen and volatile substances (combustible mass), reaching 80%, makes it possible to utilize shale as a raw material for pyrolysis and gasification processes, as well as chemical processing for the production of various oils, motor fuels, phenols, tanning beds, combustible gas, various valuable chemical products for the chemical industry [3]. Liquid hydrocarbons (shale oil-resin), obtained by pyrolysis, are similar in composition to petroleum hydrocarbons and can be considered unconventional (shale) oil [4].

At present, considerable experience in ground processing of oil shale in off-shore retorting technology has been accumulated [5]: Galoter Process (GALOTER, Russia-Estonia), Enefit (modification of Galoter process), Kiviter (Estonia), Alberta-Taciuk Process (ATP) (Australia) , Petrosix (Brazil), ToscoII (USA), Fushun (China), Paraho Process (USA), Lurgi-Ruhrgas (Germany), Chevron STB (USA), etc. Energy efficiency of technologies is provided by technological operations optimizing physical and chemical conditions of the main process - pyrolysis process. The obtained industrial results [5, 6] showed the high efficiency of the use of oil shales.

One of the most effective shale processing technologies is the Galoter Process technology for the production of shale oil, motor fuels. This technology is mastered on a large industrial scale in Estonia (Narva). Using the potential heat of raw materials and economic efficiency, it surpasses all the technologies of thermal processing of oil shale that exist in the world today.

According to the Kazakhstan Research Institute of New Chemical Technologies and Materials, at least 25 deposits of oil shale, related to sediments of the Upper Devonian, Lower Carboniferous, Upper Paleozoic, Middle and Upper Jurassic and Paleogene, have been identified on the territory of Kazakhstan. They differ in the composition of the initial substance and in the conditions of formation, which to a large extent determined their quantitative and technological characteristics. The deposits of oil shale in Kazakhstan are extremely poorly studied [7, 8].

One of the promising and largest coal-shale basins is the Kendyrlyk basin (East Kazakhstan region), whose total reserves are estimated at 4,075 million tons, including balance reserves - 708 million tons [8,9]. It is followed by the Baykhozhinskoye (in Southern Kazakhstan) and the Priuralsky group of deposits in the west of the country [8].

The main advantage of Kendyrlyk resin is a low sulfur content, which is removed by conventional methods used in refining petroleum products. In Kendyrlyk shale, the sulfur content usually does not exceed 1%, and in many other deposits, the sulfur content in shale is 4-7%, and sometimes 9%. The total thickness of the shale horizons is more than 100 m, the thickness of the beds varies from 1 to 12 m, the calorific value is 4-15 MJ/kg, the yield of the resins is 4-20% [10, 11].

Therefore, the aim of this work is to study the processes of thermal processing of Kendyrlyk shale for the production of hydrocarbon products.

Research methods

Humidity, ash content and volatility of oil shales were determined on the Thermogravimetric Analyzer "ThermosterEltra" (according to ASTM D7582-12 "Standard Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis"). The bulk density, the pH of the aqueous extract, the adsorption activity by methylorange were determined in accordance with [12, 13].

Elemental shale analysis was performed using energy dispersive X-ray spectroscopy on a SEM (Quanta 3D 200i) instrument with an attachment for energy dispersive analysis from EDAX at a resolution of: 3.0 nm at 30 kV (high vacuum mode); <12 nm at 3 kV (low vacuum mode); with an accelerating voltage from 200 V to 30 kV and with an increase from x50 to x100000. Elemental analysis is determined from Be to U. Samples were attached to a copper holder using conductive adhesive paper. Previously, a thin conducting layer of carbon was deposited on the surface of the samples in a special vacuum installation for better passage of charges. The energy of the exciting electron beam in the analysis was 15 keV, the working distance was 15 mm.

The thermal decomposition of oil shale was carried out as follows. Previously, the shale was crushed on a hammer mill (Molot-200) to a fraction of 0.1 mm and granular samples with a diameter of 0.8 cm were obtained using a tablet press (model 1000). The obtained shale samples were first subjected to heat treatment at a heating rate of 1-2 deg/min in an inert argon medium in the temperature range of 25-700 °C, and then activation of shale with water vapor within 850-900 °C. Also, the process of pyrolysis of shales in an inert argon medium in the temperature range 25-900 °C was carried out at a heating rate of 10-15 deg/min, in order to obtain mainly liquid products (resins).

The elemental composition of the gas (released in the processes of carbonization and activation) and liquid products (after distillation with the selection of hydrocarbon fractions) was determined on a Chromos GC-1000 chromatograph.

Results and discussion

TheKendyrlyk oil shale was selected as a subject for research. The results of analyzes of the technical and chemical composition of shales are presented in tables 1, 2.

Table 3 and figure 1 show the temperature dependences of the gas components obtained as a result of the carbonization and activation of the Kendyrlik shale. The formation of combustible gas components (CO, H_2, CH_4) occurs in accordance with the basic chemical reactions:

$$2H_2O \rightarrow 2H_2 + O_2 - 115\ 700\ \text{kcal} \quad (1)$$

$$C + H_2O \rightarrow CO + H_2 - 28\ 150\ \text{kcal} \quad (2)$$

$$C + CO_2 \rightarrow 2CO - 38\ 400\ \text{kcal} \quad (3)$$

$$C + 2H_2 \rightarrow CH_4 + 18\ 600\ \text{kcal} \quad (4)$$