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Composition of the Thermal Degradation Products of Oil Shale from the Kotsebinskoe Deposit

S. B. Romadenkina, V. A. Reshetov†, A. V. Kruzhalov, E. V. Lobankov, and R. I. Kuz'mina
Saratov State University, ul. Astrakhanskaya 83, Saratov, 410012 Russia
e-mail: romadenkina@yandex.ru
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Abstract—The pyrolysis of oil shale from the Kotsebinskoe deposit for the manufacture of solid, liquid, and gaseous products was studied. The composition of the resulting oil shale products was determined. The areas of application for the oil shale products are proposed.

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The processes that occur on heating in the absence of any reagents are referred to as thermal processing. The thermal processing of solid fuels is used for the production of refined carbonaceous solid materials and liquid and gaseous products. Depending on the purpose of the products, natural bituminous shale from different deposits can be a source material [1]. As a rule, the thermal processing of oil shale is performed in the absence of catalysts; because of this, the apparatus is sufficiently simple. In connection with this, specific capital expenditures for thermal processing are considerably lower than those in any other oil shale conversion processes [2].

At the same time, specific limitations because of environmental requirements imposed on the processes of the thermal conversion of oil shale should be taken into consideration. In any versions of the process, solid, gaseous, and liquid products of complex composition, which essentially depends on the elemental composition of the initial oil shale, are simultaneously obtained.

Not all of the lines of bituminous shale application are industrially used. The assortment of shale-chemical products should be noticeably expanded and revised. Furthermore, many environmental problems caused by the release of toxic and chemically aggressive gas components into the environment appear upon the processing of high-sulfur bituminous shale.

The occurrence of the above problems is related to an insufficient level of the development of physicochemical laws governing the processing of oil shale and the production of materials on its basis.

The development of new energetically advantageous and ecologically sound technologies for the complex processing of bituminous shale is a problem of considerable current interest.

Natural bituminous shale from the Kotsebinskoe deposit served as a test material.

The natural bituminous shale from the Kotsebinskoe deposit was chosen for this study because this is a new deposit in Saratov oblast. This region is rich in the heavy stocks of natural bituminous shale. Studies on the processing of bituminous shale are of current interest for our region.

Shale for studies was taken directly from the deposit. For the studies, the oil shale was taken from different layers for comparative characterization. Intermediate layers (shale clay) were also studied. The chemical composition of shale clays is close to the composition of bituminous shale; the main difference consists in a smaller organic matter content (to 10%).

The bituminous shale contains from 90 to 70 wt % mineral components, which carbonates, aluminosilicates, anhydrite, dolomite, hydromica, titanium and silicon oxides, pyrites, and organic matter (kerogen), which accounts for 10–30% on a rock weight basis. The amount of kerogen in high quality oil shale can reach 50 wt %. The organic matter consists of a complex structure multipolymer—kerogen (approximate formula, $C_{68}H_{94}O_{16}S_4N$).

The aim of this work was to obtain solid, liquid, and gaseous products from the natural oil shale from the Kotsebinskoe deposit for their further use.

A systems approach to a study of oil shale includes the preliminary physicochemical characterization by thermogravimetric and X-ray diffraction analysis, which makes it possible to quantitatively determine

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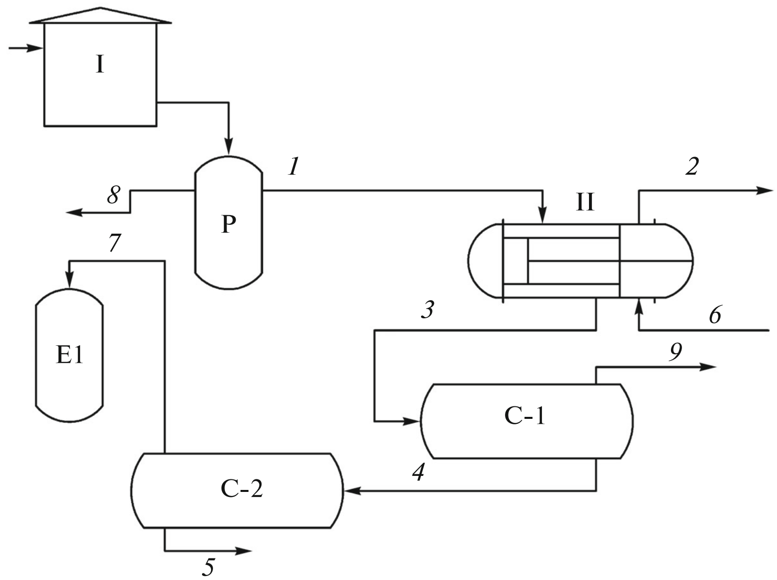

The flow chart of pyrolysis (preparation unit I and heat exchanger II): (*1*) a hot gas–liquid mixture, (2) water after the heat exchanger, (*3*) a cold gas–liquid mixture, (*4*) a liquid fraction, (*5*) phenol water, (*6*) water to the heat exchanger, (*7*) shale oil, (*8*) solid residue, and (*9*) pyrolysis gas; (P) reactor; (E-1) vessel for the liquid fraction; and (C-1, C-2) separators.

the moisture, organic matter, and ash contents and also to establish the phase composition of the oil shale.

Oil shale was subjected to thermolysis, whose conditions were substantiated by the data obtained with the aid of thermogravimetric analysis. The characteristic temperature points of the process of oil shale heating at a rate of 10 K/min are as follows:

(1) 100–105°C(the yield of unstructured water);

(2) 160–230°C (the temperature of the onset of thermooxidative degradation);

(3) 410°C (the onset of the parallel processes of thermobitumen and pyrite oxidation);

(4) 550°C (the onset of the process of crude shale oil pyrolysis);

(5) 700°C (the end of the burnout of organic matter and the decarbonization of magnesite and siderite);

(6) 900°C (upon the completion of the process of calcite decarbonization).

The pyrolysis of oil shale from the Kotsebinskoe deposit was carried out [3–5]. The figure shows a schematic diagram of the setup. The oil shale was preliminarily ground in a ball mill to a size of 1 cm^3. Then, the fuel arrived at a reactor, where it was heated to 700°C (or until the completion of the release of a gas phase).

The gas product of pyrolysis was directed to a water cooler, where it was cooled to 50°C. After cooling, the product arrived at a separator, where it was separated into gaseous and liquid fractions. The liquid product arrived at a separator, where the mixture was separated into tarry water and crude shale oil. The crude shale oil was accumulated in a receiver. The obtained products of pyrolysis were analyzed for determining their chemical composition.

For establishing the chemical composition of shale ash, X-ray fluorescence analysis was carried out on an EDX-720 spectrometer in an atmosphere of nitrogen; Table 1 summarizes the data.

It was found that the shale ash is a mixture of oxides (CaO, MgO, FeO, TiO_2, and SiO_2), which can be subsequently used as binding agents in building or as adsorbents. The specific surface area of the shale ash was 27 mg/cm^3.

The gaseous component of the oil shale was analyzed on a Kristall-2000 chromatograph. Table 2 summarizes the chromatographic data, which indicate

Table 1. Composition of the shale ash of the Kotsebinskoe deposit

Substance	Concentrations of oxides in shale ash, wt %
CaO	59.44
SiO_2	13.72
Al_2O_3	11.26
Fe_2O_3	7.66
K_2O	6.57
TiO_2	1.35
Total	100.00

Table 2. Composition of the gas phase of bituminous shale

Gas	Value, vol %
H_2	12.80 ± 0.02
CO	12.82 ± 0.03
CO_2	45.48 ± 0.01
SO_2	3.04 ± 0.01
H_2S	2.11 ± 0.02
CH_4	18.09 ± 0.04
C_2H_6	0.28 ± 0.03
C_3H_8	1.93 ± 0.01
C_4H_{10}	0.92 ± 0.05
C_5H_{12}	0.27 ± 0.04
C_2H_4	2.26 ± 0.03
Total	100.00

that the main components of a gas phase are methane, ethane, hydrogen, hydrogen sulfide, carbon(II) oxide, and carbon(IV) oxide. In terms of calorific value, hydrocarbon gases and also hydrogen and carbon(II) oxide are the most valuable components. Thus, on the one hand, the mixture of gases (H_2S, CO_2, SO_2, and CO) released upon the thermolysis of the bituminous shale is the most valuable fuel product; on the other hand, it is harmful to the environment.

One more product—crude shale oil (to 9% on an oil shale weight basis)—was formed upon the pyrolysis. Infrared-spectroscopic analysis was carried out for the determination of functional groups in the liquid shale oil product.

The determination of functional groups in the organic shale oil was performed on a Specord 75IR spectrophotometer in cells with organic solvents and in pellets with potassium bromide. The measurement range was 4000–400 cm^{-1}. The measurement temperature was 25°C. The results were represented in the form of the dependence of the intensity of absorption I_{abs} (%) on frequency (cm^{-1}) [6].

The C=C, C–H, S–H, S=O, S–O, S–H, N=O, and N–HS groups, H_2O, and aliphatic compounds were detected in the crude shale oil. The presence of these groups is responsible for the chemical activity of the shale oil. This means that the shale oil product is moderately active toward adsorption processes and oxidation reactions.

The crude shale oil formed upon the pyrolysis can be used in road building as a binding agent in asphalt concrete for increasing adhesive properties with respect to the base layer.

Thus, we established the process conditions of the pyrolysis of oil shale with an optimum yield of products. It is important to determine not only the composition of gaseous products but also the quantitative concentrations of hydrocarbons and sulfur and carbon oxides. This makes it possible to carry out the process of oil shale pyrolysis in a closed cycle; that is, the pyrolysis gas obtained is directed to the preheating of apparatuses in order to decrease the energy characteristics of the process.

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