Stages of thermal transformation of oil shales organic-mineral substance of the Middle Volga region during combustion

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Abstract. The study of the staging of the thermal conversion of oil shale, common in the Middle Volga region, was carried out. It is established that the organic matter of rocks due to the polycomponent composition undergoes multi-stage pyrolysis in the temperature range 200–600°C. The most favorable temperature of pyrolysis, when up to 80% of the potential heat of shale is released, falls within the interval of 460–480°C. The main thermal transformations of the ash component are carried out at temperatures above 480°C. They are due to the release from the structure of clay minerals of the OH group, the oxidation of pyrite, the decomposition of calcite and the formation of spinels.

Summing up the obtained results, we can draw to the following conclusions:
1. Oil shale of the Middle Volga region is characterized by significant variations in the content of organic matter from 9 to 40%. The light isotopes C12 predominance in the composition of organic carbon indicates the predominantly biochemical origin of the organic matter.
2. The configuration of the DSC curve in the temperature range of 200–600°C indicates both the multicomponent composition of the organic compounds of oil shale and their multi-stage pyrolysis.
3. The most favorable pyrolysis temperature, when up to 80% of the potential heat of shale is released, is in the range of 460–480°C.
4. In the process of burning oil shale, the ash component of the rock also subjected to thermal transformation. The composition of rock-forming minerals determined the main temperature ranges of transformation in the areas of 480–600°C (extraction of hydroxyl water from clays, oxidation of pyrite with the formation of hematite), 680–800°C (destruction of calcite), 880–900°C (formation of spinels).

1. Introduction
The global trend of increasing energy consumption stimulates the development of research on the introduction of additional, local energy raw materials sources into the technology of the thermal electricity production. In the territory of the Middle Volga region one of such promising objects for energy needs is oil shale [1, 2, 3]. Shale strata confined to terrigenous-clayey complexes of Late Jurassic age can be traced in the Ulyanovsk and Saratov regions, as well as in the western part of the Republic of Tatarstan. The shale rocks are deposited at an insignificant depth and formed layers with a thickness of up to 7.0 m sustained along the strike [4].
Such geological conditions make the development of oil shale profitable by the cheapest open-pit (quarry) method. Despite the fact that oil shale is a low-grade energy resource, they have several advantages compared to higher-quality but imported coal. These are proximity to consumers, a well-established infrastructure in their areas of occurrence, the possibility of utilizing ash waste in the production of building materials in nearby factories. In this regard, the issue of considering the possibility of using the Volga oil shale in the energy sector becomes urgent.

2. Methodology
Taking into account the prospects for the industrial use of oil shale, in this work we studied the peculiarities of rocks organic component pyrolysis and their mineral substances transformation. Optical microscopic analysis of thin sections was carried out on an optical polarization microscope the Axio Imager research class (Carl Zeiss, Germany). The main research method was thermal analysis performed on an NETZSCH STA 449 Jupiter F3 instrument. The heating ranged from 30 to 1000 °C, the heating step – 10 deg. / min. with constant air blowing. SEM, X-ray, and isotope analysis methods were used as auxiliary methods.

X-ray phase analysis. The X-ray phase analysis was performed on the diffractometer D2 Phaser (Bruker, Germany) used for measuring the powder products in the Bragg-Brentano geometry, with the use of monochromatic CuKα-radiation (λ = 1.54178 Å), in the step-scan mode. Measuring and recording modes: X-ray tube voltage-30 kV, current-30 mA. Scanning step – 0.02°; speed – 1 deg/min. The range of scanning angles in the Bragg-Brentano geometry 3-40°. Mineral types are determined by comparing experimentally obtained values of interplanar distance (d, Å) and relative intensity (Irel) of reflections to the standard XRD data from the International Database PDF-2 ICDD.

In order to establish the morphological appearance of minerals and their interrelations with each other, the samples were studied using a scanning electron microscope XL-30 ESEM, which equipped with an energy-dispersive analyzer (EDAR). From the most interesting areas were made small fragments, which were covered with carbon coating. After this, the objects were scanned and a selective survey of their surface was made.

The ratio of stable isotopes of light elements 13C / 12C and 18O / 16O was determined on a Delta V Plus isotope mass spectrometer (Thermo Fisher Scientific, Germany). The analysis of the substance was carried out in the gas phase.

3. Results and Discussion
In the outcrops, oil shales are characterized by a dark gray color, with black areas, cryptomerous structure, poorly-defined layered texture and well-pronounced foliation. According to optical microscopic and X-ray analysis data the shales are composed mainly of mixed-layer clay minerals illite-montmorillonite composition. The chlorite and muscovite flakes, as well as allothigenic grains of quartz, albite and microcline up to 0.1 mm in size are present as impurities [2]. Shales are enriched with limestone fragments of marine animals and pyrite aggregates. Coal shales are split by numerous sub-vertical cracks, some of which are filled with black organic matter. The latter indicates that in the process of lithogenesis, an active redistribution of the organic component took place. At the lithification time there were mobile carbonaceous compounds in shale, capable to migration and secondary concentration. To determine the genesis of carbon on some samples were analysis for the ratio of the C12 and C13 isotopes in them, as well as the content of the total amount of organic and inorganic carbon. Negative values indicate about less C13 contain in sample than the standard (lighter than the standard), positive values are heavier than the standard. PDB1 - the belemnite rostrum Belemnitella americana served as a standard (Table 1).

| Table 1. The isotopic composition of organic and inorganic carbon oil shales. |
The results showed that the content of organic carbon in oil shale reaches 40%. The light isotopes of C12 predominate, indicating it’s predominantly biochemogenic origin. Considering the anoxide geochemical environment during the sedimentation and lithification period of carbonaceous-clay sediments, it can be assumed that the formation of organic matter was carried out with the active participation of anaerobic microbial communities. The latter, in the course of their vital activity, processing plant and animal biomass, could easily enrich the rocks with light C12 isotopes. The content of “heavy” inorganic carbon in the shells of marine animals is conditioned on the one hand by the forced extraction of C13 by floating organisms directly from sea water; on the other hand, by the ability of skeletal forms for a long time remain buried without significant changes. Due to the outer protective layer of organic-mineral matter, the shells retain the original ratio of light and heavy carbon isotopes, acquired during the life of mollusks.

On the basis of the data obtained, it can be assumed that the scattered dispersed organic matter of combustible shale is represented mainly by the products of biochemical transformation of plant-plankton residues by colonies of anaerobic microorganisms. Indirectly, this is confirmed by a significant amount of pyrite (2-3%), common in the rocks.

In order to detail the fractional composition of carbonaceous compounds and the ash component transformation stages, a study of oil shale was carried out using thermal analysis. The thermograms data showed that, with a consistent increase in the firing temperature, very diverse thermal transformations occur in the rocks, due to their multicomponent composition (Fig. 1).
The first changes occur already in the range of 60-150°C. Here on the thermogravimetric curve (TG) there is a two-step mass loss of the sample by 2-3%, accompanied by the appearance on the curve of differential scanning calorimetry (DSC) of two consecutive endo-effects. Considering the presence of montmorillonite, muscovite and chlorite in combustible shales, these effects can be attributed to the successive release of capillary-condensed and then molecular (interlayer) water from clay minerals of the shale.

The following changes are noted in the temperature range of 260-600°C. In this range occurs organic matter thermo-oxidative destruction. The complex configuration of the DSC curve indicates that the thermal decomposition of organic compounds proceeds in several stages. At the first stage, in the range of 260-320°C, boiling up of light hydrocarbon fractions occurs [5]. Considering the high content of methane components in the oil shales composition (up to 49.6% according to [4]), we can assume that the first exothermic effect is due to the release of CH4 from rocks. At the same time, at temperatures above 300°C, resinous substances condense with their transition to a semi-liquid state, that is, the bituminization process takes place. The main mass of shale resin is formed in the temperature range 320-450°C. Under conditions of rapid temperature increase in the heating chamber, the resulting resin evaporates and leaves in the form of steam. The mass restructuring process of kerogen carbon skeleton during its transition to a plastic state takes place at 380-400°C and fully ends at 450°C. The boiling up of shale resin is accompanied by the release of heat and, as a result, by the appearance of the following exo-effects on DSC in the interval of thermo-oxidative destruction of medium fractions hydrocarbons [5]. At temperatures above 400°C, along with resin, heavy hydrocarbons start to be released from shale, the amount of which in rocks according to [4] reaches 1.3%. The peak of their boiling is at 450-480°C, which is noted by the following exo-effect on DSC. Starting at 500 °C, the pyrolysis of organic matter enters its final phase. Beginning processes of semi-coking the heavy resin and other relics of thermal bitumen. Due to the low content of hydrogen and oxygen in the products of carbonaceous clay shale pyrolysis, the subsequent increase in the firing temperature of rocks above 500 °C does not lead to the significant gaseous substance formation. As a result, on the general decline of the DSC curve, only two small-

![Figure 1. Synchronous thermal analysis data of the Middle Volga region oil shale deposit. The solid line is the differential scanning calorimetry (DSC) curve; the dotted line is the mass loss curve (TG).](image-url)
intensity exo-effect in the region of 510–520 °C and 560–580 °C are distinguished, accompanied by a loss of mass. Their appearance is caused by the formation of coke and the decomposition of kerite.

Thus, the complex configuration of the DSC curve in the temperature range of 150-600 °C indicates both the multicomponent composition of carbonaceous compounds in coal shale and organic matter multistage pyrolysis. The predominant primary components are the lipid constituents in kerogen, as indicated by the carbon isotope composition, as well as light and heavy oil-like fractions; the secondary ones are shale resins, which are the main constituents of the thermal bitumen; coke and kerite. The yield of volatile substances during the combustion of shales is 8-12%. Of these, light hydrocarbons - up to 49.6%, shale resin - up to 10%, heavy hydrocarbons - up to 1.3%. The significant yield of oil-like fractions in the process of burning coal shale is due to the presence high hydrogen content (up to 10.6% according to [4]) in the organic mass of rocks. It is his presence that contributes to the liquefaction of organic carbon compounds with the formation of various by compositions and boiling points of shale resins. Successively formed hydrocarbons, boiling in different, albeit overlapping, temperature ranges, create conditions for the continuous formation processes of the vapor-gas mixture, which determines the energy value of the carbonaceous-clay shale of the Middle Volga region. The vapors of hydrocarbons and non-condensable gases (CO₂, CO, H₂, N₂, H₂S) generated during the pyrolysis of organic matter, make conditions a relatively high heat of combustion of the rocks (2.5-6.8 MJ / kg). The most favorable pyrolysis temperature, when up to 80% of the potential heat of shale is released, is in the range of 460-480°C.

Further mass change on the TG curve to a temperature of 680°C is associated with lost hydroxyl water (OH-) from clay minerals structure. The implicitly pronounced nature of the endo-effect on the DSC curve appears to be due to the superimposed exo-effect caused by the oxidation of pyrite to form hematite. Mass loss in the temperature range of 680–800°C, accompanied by endo-effect, corresponds to the thermal destruction of calcite to CaO. The exo-effect on the DSC curve with a maximum at 880–900°C, which passes without a change in mass, corresponds to the recrystallization of amorphous products of destruction of clay minerals, accompanied by the formation of new mineral phases of the spinel type [5].

4. Conclusions
Given the above, we can draw the following conclusions:
1. Oil shale of the Middle Volga region is characterized by significant variations in the content of organic matter from 9 to 40%. The light isotopes C12 predominance in the composition of organic carbon indicates the predominantly biochemical origin of the organic matter.
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