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THERMAL ANALYSIS OF OIL SHALE IN THE BAYGUSHLU AND IYIMISH FIELDS

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Abstract: *The paper presents the results of thermal analysis of oil shale from the Baigushlu and Iyimish deposits (Azerbaijan). It was been established that in the shale of the Baygushlu deposit, the content of organic matter is 11%, while in the shale of the Iyimish deposit it is 40% higher - 15.3% (for dry shale). The absence of moisture and their high calorific value make it possible to consider the possibility of using combustible shale from the Iyimish and Baygushlu deposits as an alternative energy fuel. The results obtained indicate the prospects of their use both in the technological and fuel and energy areas.*

Keywords: *oil shale; thermal analysis; content of organic substances; heat of combustion; prospects for use.*
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Introduction

The depletion of traditional readily available sources of hydrocarbon raw materials was marked by the fact that more and more attention is paid to unconventional sources such as shale, shale gas, combustible natural bitumen, coalfield gases, gas hydrates, etc. Among them, slates are notable for the most ancient history of practical use (late 17th century). During this period, extensive material has been accumulated on their reserves, production and use. However, this notwithstanding, interest in this energy source is not falling; research is deepened and supplemented with new information [1-4].

According to the data of the Institute of Geology of ANAS [5-7], to date, more than 60 oil shale deposits associated with Cretaceous-Miocene geological formations have been discovered in Azerbaijan. The authors studied slates from outcrops of mud volcanoes; revealed patterns of their spatial distribution within oil and gas regions, geochemical features in terms of the genetic relationship of shale with the formation of hydrocarbons; performed a comparative analysis of the studied oil shale with those of foreign countries and found that Azerbaijani shale from the main indices standpoint (organic matter, sulfur, ash content, calorific value) are superior to shale in most countries with the developed oil shale industry [7].

The main part of oil shale is located on the territory of Ismayilly and Guba regions, in the Shamakhi-Gobustan zone and on the Absheron peninsula. Previously, we studied the physicochemical properties of oil shale from the Jangichai, Bolshoy and Maliy Siyaki deposits [8]. The results obtained indicated that the use of shale from these deposits as an energy fuel by direct combustion would be inefficient, and obtaining sulfur-free motor fuels from shale oils is possible only after a rather expensive desulfurization process. Therefore, the processing of this oil shale in combination with the production of petrochemical synthesis products was proposed as the main direction.

The recently discovered oil shale deposits requiring comprehensive exploration include

Baygushlu and Iyimish. The Baygushlu deposit is located 48 km west of Baku in the region of Central Gobustan, the thickness of the Paleogene-Miocene deposits here is 2.5-4.5 km [7]. The Iyimish oil shale deposit is new, so it is under exploration.

Despite the availability of general information about the prospects for shale use, the selection of a method for their processing should be considered for specific deposits based on the results of comprehensive studies. Express method, which is highly sensitive and informative, is considered to be thermal analysis. Besides, given that oil shale processing is based on thermal transformations of organic compounds, obtaining the results of complex thermal analysis makes it possible to obtain data on the nature of the components, their yield, and possible transformations even before performing labor-intensive and complex research work [9–13].

The purpose of this study was to assess the qualitative and quantitative organic component of oil shale from the Baygushlu and Iyimish deposits for the purpose of their possible processing.

Research method

Oil shale samples from the Baygushlu and Iyimish deposits were taken from a depth of 0.5–1 m. The shale was studied by the simultaneous thermal analysis (STA) method (combined use of differential scanning calorimetry and thermogravimetry) on a NETZSCH STA 409 PC/PG instrument with a heating rate of 10 °C/min in air atmosphere in corundum crucibles within the temperature range of 20-1000 ºC.

Results and its discussion

Thermogravimetric analysis of a sample of oil shale from the Iyimish deposit (Fig. 1) showed that the change in the mass of the sample occurs in two main stages: the first stage occurs within the range from 62 to 355 °C, the second stage - from 425 to 860 °C. The absence of an endothermic effect is noteworthy, and the marked ones are exothermic.

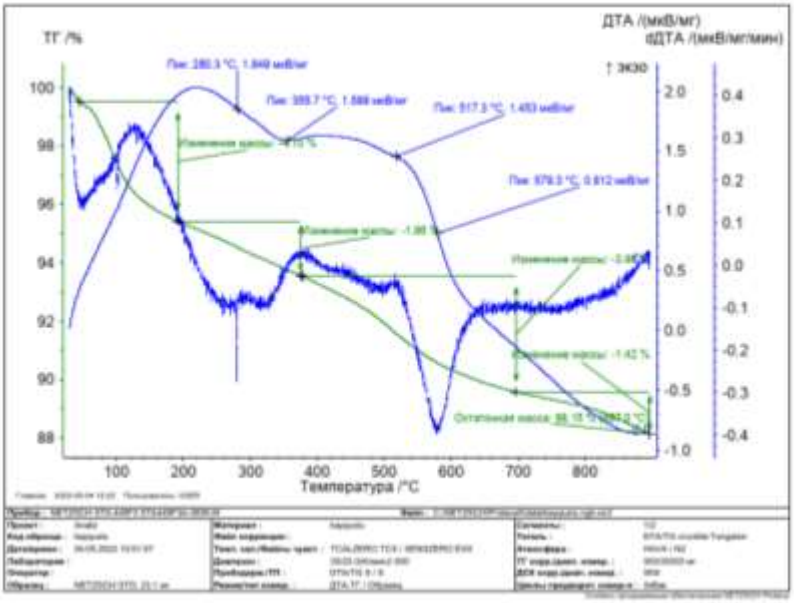

Fig.1. Thermogram of oil shale from the Baigushlu deposit

The DTA curve of the Baygushlu shale sample (Fig. 1) has a double overlapping exothermic effect within the range of 42-822°. The temperatures of the beginning, end, and maximum of the first exothermic peak were 42, 821, and 222°C, respectively, while those for the second were 71, 683, and 422°C. Significant overlap of the two effects is recorded on the DTA curve by a minimum point at a temperature of 355°C. The fact that both exothermic effects were recorded in a wide temperature range, had an extended, flat shape and asymmetry, indicated a slow process. Since the noted exoeffects have no form of intense pointed and symmetrical peaks that could be attributed to the formation of new crystalline phases from the decomposition products of the mineral, then, given the presence of an organic component, the nature of exothermic transformations in this process is associated with the occurrence of oxidation reactions.

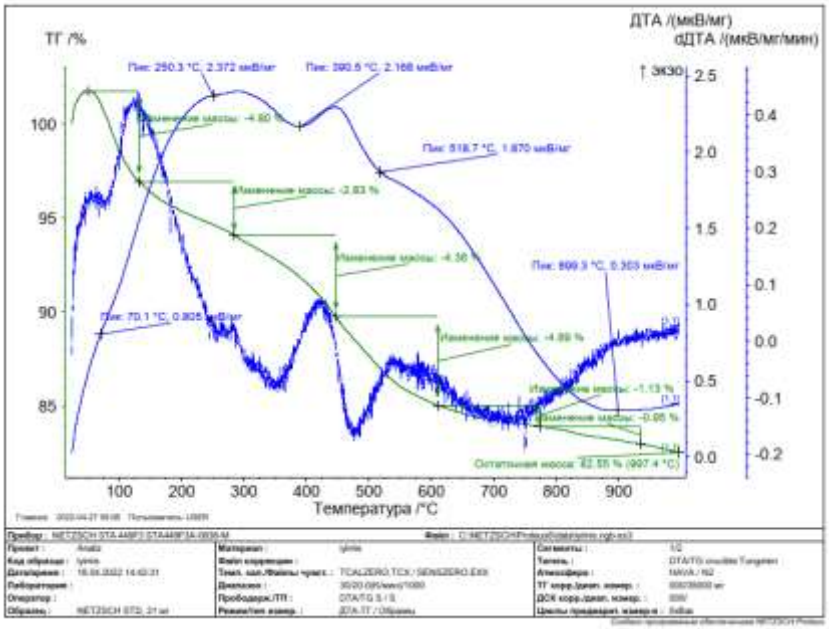

Fig.2. Thermogram of oil shale of the Iyimish deposit

The TG data made it possible to establish the mass loss (for dry shale): it was 5.9% for the first and 5.1% for the second temperature effect. The total weight loss is 11.0. The absence of endothermic effects within the range up to 250° C indicates that there is no water in the Baygushlu shale sample. Endothermic effects in the high-temperature region were not observed either, which is associated with the absence of polymorphic transformations within the temperature range up to 850°C.

The DTA of the Iyimish shale sample (Fig. 2) shows three exothermic effects within the range from 35 to 837°C. Here, as well as the sample considered above, there is no relatively low-temperature endothermic effect due to the release of water from the clay component. The first exoeffect occurs within the range of 35-837°C with a maximum at 294°C. The weight loss of the sample is 8.3%. The second exoeffect takes place at temperatures from 42 to 658°C with a weight loss of 7.1%. The first and second thermal effects following each other overlap at the minimum point, which falls at a temperature of 398°C. The third exoeffect overlaps significantly with the second one, as a result of which the minimum point is transformed into an inflection point, which falls on the DTA curve at 520°C. The nature and shape of the geometric elements of the thermogram of the Iyimish shale sample, as well as the

Baygushlu, indicate that the exothermic transformations are due to the oxidative rearrangement of organic matter. The total weight loss of the Iyimish shale sample was 15.3%.

A comparative analysis of the obtained data was indicative that in the shale of the Iyimish field, the content of both light and medium fractions of hydrocarbons (150-400°C), and heavy fractions and kerogen (400-650°C) is 40% higher than the content of the Baygushlu shale. The fact that the resin content in both shale samples exceeds 10% makes it possible to classify them as medium resin and confirm that their extraction is of undoubted interest for being used as a valuable chemical raw material.

To assess the efficiency of their fuel and energy use, their calorific value was estimated. For this purpose, the areas of exoeffects noted in both shale samples were determined. Thus, their calorific value was 3824 J/g and 2458 J/g for the indices of shale from the Iyimish and Baigushlu deposits, respectively. These figures are in good agreement with literature data 8, according to which Azerbaijani oil shale is the best among low-calorie oil shale in view of organic matter content (15-29%), sulfur (low content - 0.3-1.2%), ash content (65 -84%) and calorific value (6-12 MJ/kg). These indices make it possible to consider the possibility of using oil shale from the Iyimish and Baygushlu shale deposits as an alternative energy fuel. The absence of moisture in both shales is an undoubted advantage for using them as an energy fuel, because this raw material does not require additional heat to evaporate water.

Conclusions

The conducted thermal studies made it possible to provide a positive predictive assessment of the technical parameters of oil shale as a technological raw material and energy fuel. It was found that the content of organic matter in the shale of the Baygushlu deposit was 11%, and in Iyimish - 15.3%, which shows the prospects for their use as a valuable chemical raw material. The data on the calorific value of shale from the Iyimish and Baygushlu deposits allow us to consider them as a source of alternative energy fuel.

Referenses

1. Parfenova T.M., Kontorovich A.E., Borisov L.S., Melenevsky V.N. Kerogen of the Cambrian Kuonam Formation (northeast of the Siberian Platform*). Geology and Geophysics*, 2010, vol. 51, no. 3, pp. 353-363. (In Russian).
2. Zyuba O.A., Glushchenko O.N. Review of modern thermal methods of oil shale processing and environmental aspects of their application. *Oil and gas geology. Theory and practice*. 2012, vol. 7, no. 4, pp.1-10. (In Russian).
3. Nazarenko M.Yu., Kondrasheva N.K., Saltykova S.N. Efficiency of using combustible shale and shale-ash waste for water purification from organic pollutants. *Bulletin of the Tomsk Polytechnic University. Engineering of georesource*s. 2016, vol. 327, no. 9, pp. 95–103. (In Russian).
4. Nazarenko M.Yu., Saltykova S.N. Influence of parameters of the semi-coking process of combustible shale on the quality of shale semi-coke. *Bulletin of the Tomsk Polytechnic University. Engineering of georesources.* 2021, vol. 332, no. 9, pp. 109–118. (In Russian).
5. Aliyev Ad.A., Abbasov O.R. Mineralogical and geochemical proxies for the Middle Eocene oil shale from the foothills of the Greater Caucasus, Azerbaijan: Implications for depositional environments and paleoclimate. *Mineralia Slovaca*, 2019, vol. 51, pp. 157 – 174.
6. Aliyev Ad.A., Abbasov O.R., Ibadzade A.J., Mammadova A.N. Genesis and organic geochemical characteristics of oil shale in East-

ern Azerbaijan. *SOCAR Proceedings*. 2018, no.3, 004-015.
7. Abbasov O.R. Patterns of distribution and geochemistry of oil shale of Azerbaijan. *Mineral Resources of Ukraine.* 2017, no. 2, pp. 22-30.
8. Adjamov K. Yu., Rasulov S.R., Guseinova E.A. and others. Physical and chemical characteristics of oil shale deposits Dzhangichay, Big and Small Siyaki (Republic of Azerbaijan) *News of the Ural State Mining University*. 2019, issue. 3(55). pp. 39-45.
9. Fedorova N.I., Pavlusha E.S. Thermogravimetric study of oil shale kerogen and boghead of the Olenek region of the Lena basin. *Bulletin of the Kuzbass State Technical University*, 2009, no. 2, pp. 178-181.
10. Nazarenko M. Yu., Kondrasheva N. K., Saltykova S. N. Influence of thermal transformations in oil shale on their properties. *Tsvetnye metally*. 2017, no. 7, pp.15-22. (In Russian).
11. Yahya H.Khraisha, Ihsan M.Shabi. Thermal analysis of shale oil using thermogravimetry and differential scanning calorimetry. *Energy Conversion and Management*. 2002, vol. 43, issue 2, pp. 229-239.
12. Bayasgalan K., Bayanmunkh M., Baatar U., Bayarkhuu B., Murneren T. Characterization and thermogravimetric analysis of oil shale from Uvurjargalant deposit. *Mongolian Journal of Chemistry*, 2018, vol.19(45), pp.19-23.
13. Farouji M.S., Amir M.J., Gentzis S.Th., Kouqi B.L., Shokouhimehr L.M., Ostadhassan M. TGA and elemental analysis of type II kerogen from the Bakken supported by HRTEM. *Journal of Natural Gas Science and Engineering*. 2022, vol. 103, 104606.

BAYQUŞLU VƏ İYİMİŞ YATAQLARINDA YANAR NEFT ŞİSTLƏRİNİN TERMİKİ ANALİZİ

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Xülasə: Məqalədə Bayquşlu və İyimiş (Azərbaycan) yataqlarının neft şistlərinin termiki analizinin nəticələri təqdim olunur. Müəyyən edilmişdir ki, Bayquşlu yatağının şistində üzvi maddələrin miqdarı 11%, İyimiş yatağının şistində isə 15.3%-dir (quru şist üçün). Yüksək yanma istiliyi və nəmliyin olmaması İyimmiş və Bayquşlu yataqlarının yanar şistlərindən alternativ enerji yanacağı kimi istifadə imkanlarını nəzərdən keçirməyə imkan verir. Əldə edilmiş nəticələr onların həm texnoloji, həm də yanacaq-energetika sahələrində istifadəsinin perspektivlərindən xəbər verir.

Açar sözlər: *neft şisti, termal analiz, üzvi maddələrin tərkibi, yanma istiliyi, istifadə perspektivləri.*

ТЕРМИЧЕСКИЙ АНАЛИЗ ГОРЮЧИХ СЛАНЦЕВ МЕСТОРОЖДЕНИЙ БАЙГУШЛУ И ИЙИМИШ

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Аннотация: В работе представлены результаты термического анализа горючих сланцев месторождений Байгушлу и Ийимиш (Азербайджан). Установлено, что в сланце месторождения Байгушлу содержание органических веществ составляет 11%, а в сланцах месторождения Ийимиш - 15.3% (на сухой сланец). Отсутствие влаги и высокая теплота сгорания позволяют считать перспективным возможность использования горючих сланцев месторождения Ийимиш и Байгушлу в качестве альтернативного энергетического топлива. Полученные результаты свидетельствуют о перспективности их использования как по технологическому, так и топливно-энергетическому направлению.

Ключевые слова: *горючие сланцы, термический анализ, содержание органических веществ, теплота сгорания, перспективы использования.*