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Studying group composition of natural bitumen of the Beke oil sands

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ABSTRACT

In the paper, group composition of the natural bitumen of the Beke oil sand were studied. During the experiment, the they separated by chromatographic method in a Soxhlet apparatus and determined the percentage of oil, resin and asphaltene fractions of natural bitumen. Natural bitumen was analyzed at a Fourier transform IR-spectroscopy Spectrum-65 with 450-4000 cm^{-1} range. Comparing the results of elemental analysis of resin and asphaltene, it was observed that asphaltene contains more elements except carbon and hydrogen than resin. Morphological structure of asphaltene samples were studied by the scanning electron microscope (SEM) at 20 KV voltage and 0.003 Pa pressure.

Keywords: natural bitumen, oil sand, oil, resin, asphaltene

1. Introduction

Resource base of oil sand natural bitumen and heavy oil is increasing as the unconventional sources of hydrocarbons. Natural bitumen is organic part of oil sands that close to bitumen by physical and chemical properties. In the near future, their role in the energy balance expected significantly increase regarding reduction in the reserves of conventional petroleum and consumption of their reproduction. Natural bitumen consists of higher content of resin-asphaltene compounds, petroleum acids, sulfur containing compounds and metals, also higher viscosity and density than conventional crude oil [1-4].

Crude oil is a complex mixture of a large number of diverse chemical compounds, predominantly hydrocarbons. Successful analysis of the chemical composition of oil is possible only when reliable methods are used to separate it into groups of chemically homogeneous compounds. One of the simple and widely used schemes for separating oil into components in laboratory conditions is SARA analysis. This method is based on dividing the oil into four analytical groups of compounds, namely, saturated hydrocarbons, aromatic compounds, resins, and asphaltenes (SARA). Saturated hydrocarbons: alkanes - nonpolar aliphatic compounds with straight and branched chains, as well as cycloalkanes, are typically eluted by aliphatic solvents, such as hexane, heptane, or iso-octane. Saturated hydrocarbons in crude oil may include gaseous alkanes C_1-C_4, liquid alkanes C_5-C_{16}, which constitute the main mass of liquid oil fractions, and solid alkanes, also called paraffins, whose molecules contain straight carbon chains C_{17} and above. Aromatic compounds: cyclic organic compounds including benzene and its structural derivatives. Most aromatic structures can contain alkyl chains, naphthenic rings, and aromatic rings. There are classification of aromatic hydrocarbons as mono-, di-, tri-, and poly-aromatics. Aromatic compounds are extracted from oil during liquid-adsorption separation using benzene or toluene. Resins: high-molecular-weight components of oil consisting of polar molecules containing heteroatoms such as N, O, and S. Main structural elements of resin molecules are condensed cyclic systems, including aromatic, cycloalkanic, and heterocyclic rings, which have several aliphatic and cyclic substituents within the ring. Asphaltenes defifined as insoluble compounds in aliphatic hydrocarbons (in n-pentane and/or n-heptane), soluble in aromatics (in toluene, benzene). Asphaltenes span consists wide range of

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molecular weights, actually they are from hundreds to millions that leading to speculation about self-aggregation [5-9].

Deposits of the oil sands have been investigating all over the world for the production of asphalt for road construction or for the extraction of bitumen for further production of synthetic oil [10-11]. In the paper the oil, asphaltene and resin fraction of natural bitumen separated from the Beke oil sands were investigated.

2. Materials and methods

Group composition of the natural bitumen of the Beke oil sand were used as the object of the study. They are separated by chromatographic method in a Soxhlet apparatus. On the precipitation of asphaltene, the natural bitumen was added in n-hexane in relation to the initial hitch of bitumen, then put it to the dark place for 24 h. Maltenes separation in resin and oil were used Soxhlet with activated silica gel. Silica gel activated at 350 °C for 4 h. Then it wetted with hexane and prepared maltenes transferred to activated silica gel in apparatus. Soxhlet was placed on water bath and extracted oil with hexane in the volume of 200 ml. Adsorbed resins on the activated silica gel desorbed by 1:1 ratio of alcohol-benzene mixture. Separated resins and oil samples were dried at the temperature of 60 ± 4 °C until a constant weight.

Chemical composition of oil, resin and asphaltenes were identified by infrared spectroscopy Spectrum-65 with spectra 450-4000 cm^{-1} range. Elemental composition of the asphaltene samples was studied at X-ray fluorescent spectrometer. Morphological structure of asphaltene samples were studied using a scanning electron microscope (SEM) with 20 KV accelerated voltage and 0.003 Pa pressure.

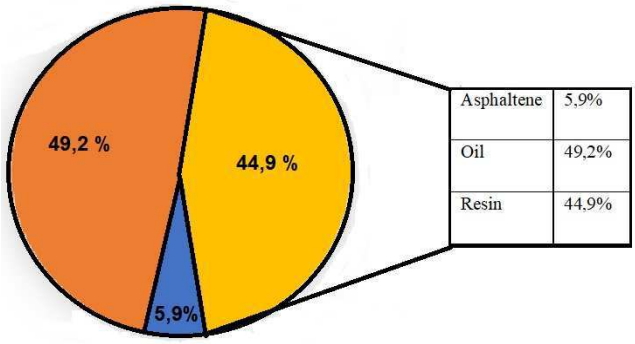

Fig. 1. Group composition of natural bitumen of the Beke oil sands.

3. Results and discussion

Crude oil fractionations are based on the solubility of components of hydrocarbon in various organic solvents used in analyses. Each fraction of the analyses consists of a solubility class containing the range of different of molecular-weight species. In the study, the natural bitumen of the Beke deposit was fractionated to three solubility classes, such as asphaltene, resin and oil. During the experiment, the percentage of separated component fractions were determined and them illustrated in the Fig. 1.

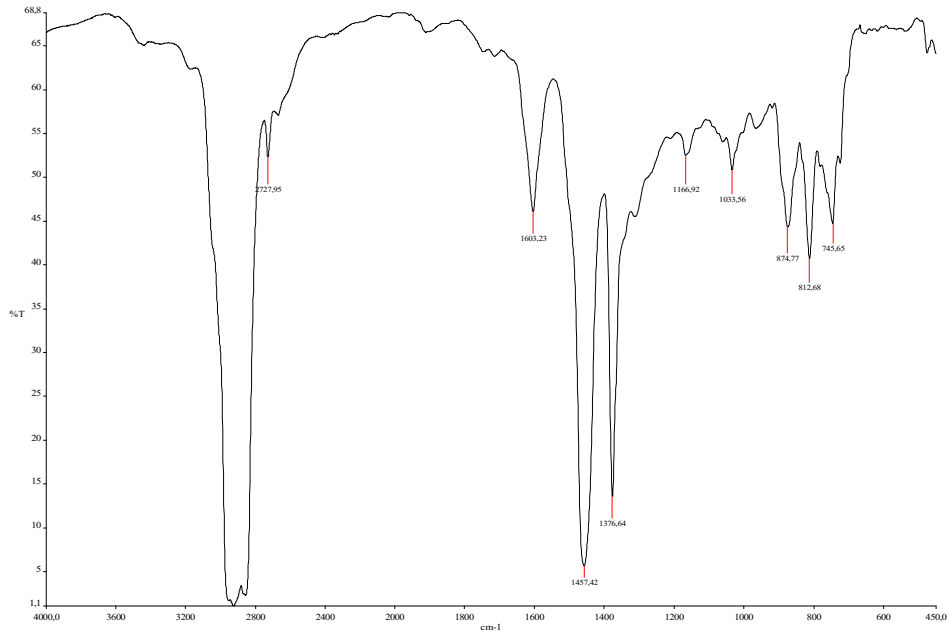

Fig. 2. IR spectrum of oil separated from natural bitumen of the Beke oil sands.

Table 1. Results of analysis of oil deposited from the Beke Field oil

Sample wavelength, cm	Functional group	Region of the corresponding component wavelength
745,65	δ-CH	Aromatic
812,68	δ-CH	Aromatic
1033,56	δ-CH	Aromatic
1166,92	ν C-O-	Oxygen compounds
1376,64	δ-CH_3	Alkanes
1457,42	ν-$C(CH_2)$	Aromatic
1603,23	ν=NH_2	Amines
2727,95	ν-NH_2	Alkanes
2915.05	ν-CH_2	Alkanes

As it can be seen in the Fig. 1, the amount of asphaltene in Beke natural bitumen is not much. Its amount was up to 6%, as shown in crude oil content. However, the content of resin in natural bitumen is high, it is 44.9%. Therefore, this oil sand natural bitumen belongs to the highly resin-asphaltene compounds.

The properties and characteristics of the group composition of the Beke bitumen were further studied by various methods in modern installations. The analysis of asphaltene, oil and resin were tested at infrared spectroscopy. This type of analysis makes it possible to determine the functional groups of samples and compare its composition. The result of IR spectroscopic analysis of oil fraction separated from the Beke bitumen is shown in the Fig. 2 and its numerical data are tabulated in Table 1.

Infra-red spectroscopical analysis provided to oil fraction of Beke natural bitumen with 450-4000 cm^{-1} range and its result is shown in Table 1. Oil fraction of natural bitumen containing planar and out-of-plane deformation vibrations C-H of aromatic compounds. Also seen stretching vibrations of the aromatic ring, actually, the band at 1450 cm^{-1} is overlapped by the band of bending vibrations of CH_2. The spectrum contains oxygen, sulfur and nitrogen organic compounds. According to the analysis results of the oil fraction, it should be said that there are many vibrational waves characteristic of alkanes.

Oil fraction of natural bitumen containing saturated hydrocarbons and aromatic compounds. The saturated hydrocarbons are non-polar aliphatic compounds with a straight and branched chain. The aromatic compounds cyclic organic compounds,

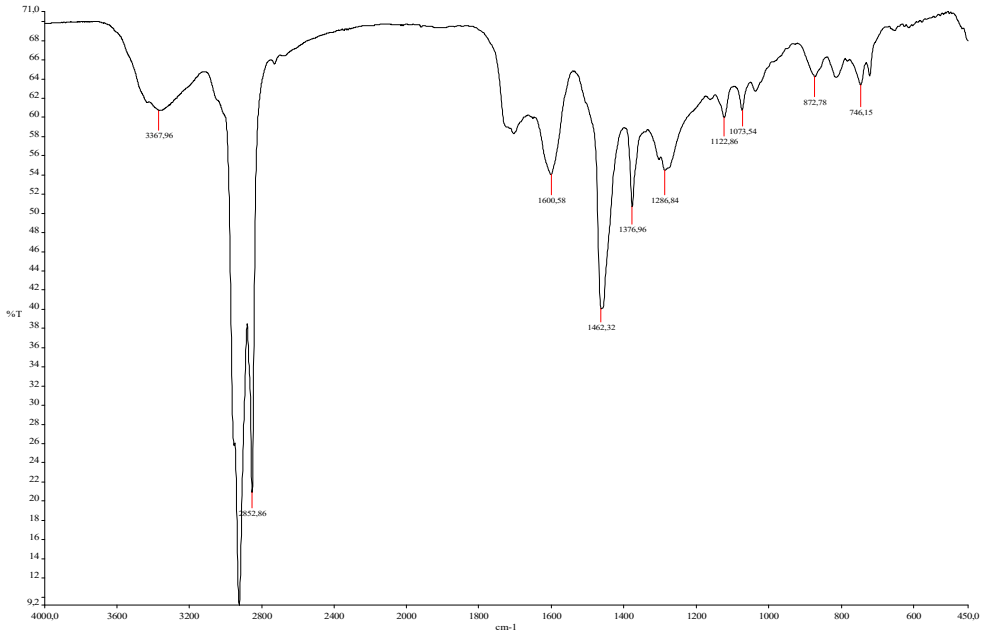

Fig. 3. IR spectrum of resin separated from natural bitumen of the Beke oil sands.

Table 2. Results of IR analysis of resin separated from the Beke natural bitumen

Sample wavelength, cm	Functional group	Region of the corresponding component wavelength
746,15	δ-CH	Aromatic
872,78	δ-CH	Aromatic
1073,54	ν C-O-	Oxygen compounds
1122,86	ν C-O-	Oxygen compounds
1286,84	δ-OH	Oxygen compounds
1376,96	δ-C(CH_3)	Alkanes
1462,32	δ-C(CH_3)	Alkanes
1600,58	ν-NH_2	Amines
2852,86	ν-CH_2	Alkanes
2923,93	ν-CH_2	Alkanes
3367,96	ν-OH	Oxygen compounds

including benzene and its structural derivatives. Most aromatic structures can contain alkyl chains, naphthenic rings, and additional aromatic rings. Therefore, oil is a much lighter hydrocarbon fraction than resin and asphaltene. The result of IR spectroscopic analysis of resin fraction of the Beke natural bitumen is presenting in Fig. 3.

Aromatic compounds and alkanes are evident in the resin separated from Beke natural bitumen. At the same time, an oxygen and hydroxy compound in bonding with carbon atoms were identified. Among these, amines can be seen in the composition of the resin. The list of wavelengths and functional groups characteristic of mentioned compounds is given in the Table 2.

Resins have higher concentrated aromatic carbon and higher heteroatoms, asphaltenes have the highest molar mass and they contain most of the polar compounds. Resins are components of an intermediate structure located between the oil and asphaltenes, they serve to keep the aggregates dispersed in the oil. The result of IR spectroscopic analysis of asphaltene deposited from the Beke bitumen is showing in Fig. 4 and its numerical data are presenting in Table 3.

In the spectrum, it was found that there are heterocyclic compounds with double bonds having oxygen, sulfur and nitrogen compounds (such as R-SO-OH and S-O st). Also, asphaltene contains alkenes with ν-CH_2, ν-CH_3, O-CH_3 bonds and amines with δ-NH_2 bonds.

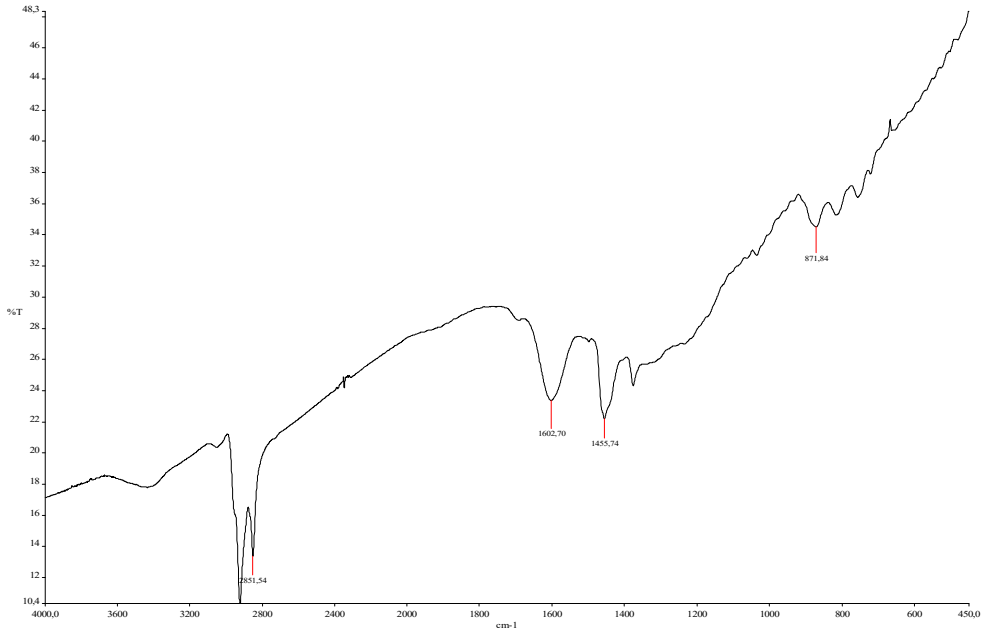

Fig. 4. IR spectrum of asphaltene precipitated from natural bitumen of the Beke oil sands.

Table 3. Results of the asphaltene analysis of the natural bitumen of the Beke oil sands.

Sample wavelength, cm	Functional group	Region of the corresponding component wavelength
871,84	ν_{C-H} vibration ring	Heterocyclic compounds
1455,74	O-CH_3	Alkanes
1602,70	δ-NH_2	Amines
2851,54	ν-CH_2	Alkanes
2922,43	ν-CH_3	Alkanes

Table 4. Results of elemental analysis of asphaltene and resin separated from natural bitumen of the Beke deposit.

Element	Asphaltene, mass %	Resin, mass %
C	77,30	79,70
H	7,590	9,766
S	1,004	0,556
N	1,070	0,720
O+ metals	13,036	9,258
Amount	100,00	100,00

Asphaltenes are the most refractory and the heaviest components that contains highly aromatic and polar of hydrocarbon. Table 4 compares the results of elemental analysis of asphaltene and resin deposited from natural bitumen of the Beke deposit. The amount of hydrogen and nitrogen and its elements was basically the same.

According to the data in the table, we know that resin contains more C and H than asphaltene, and the amount of S, N and O is lower than asphaltene. From this we can understand that asphaltene concentrate more metals in their composition than resins. Therefore, the X-ray fluorescent analysis was performed on it to see the metals containing in asphaltene precipitated from the Beke bitumen (Fig. 5).

As you can see in the table, the elemental composition of asphaltene deposited from oil from the Beke field was determined to have C, O, S, CI and

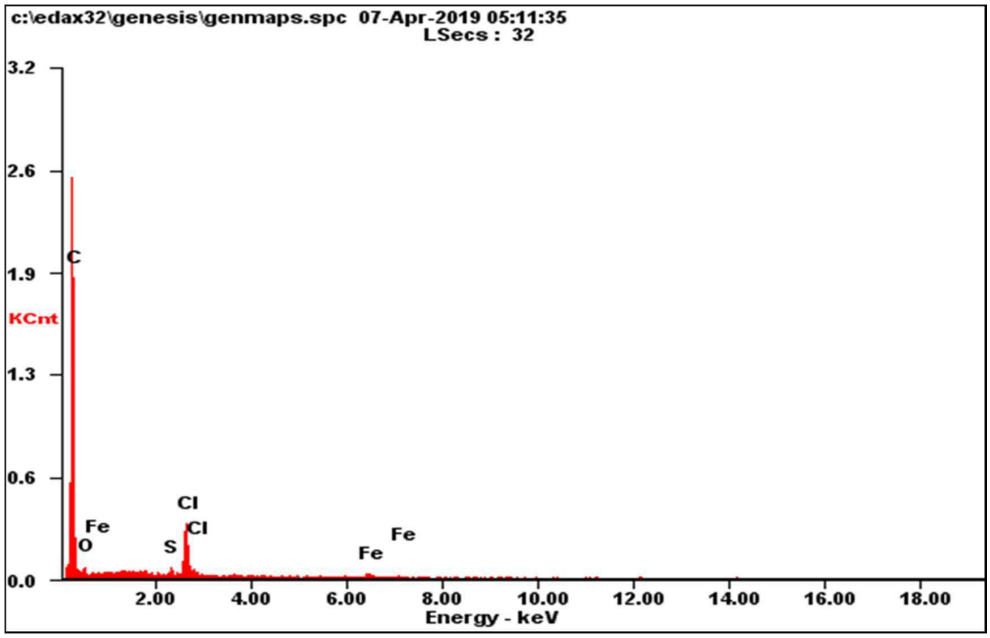

Fig. 5. Diagram of X-ray fluorescent analysis of asphaltene deposited from the oil of the Beke field.

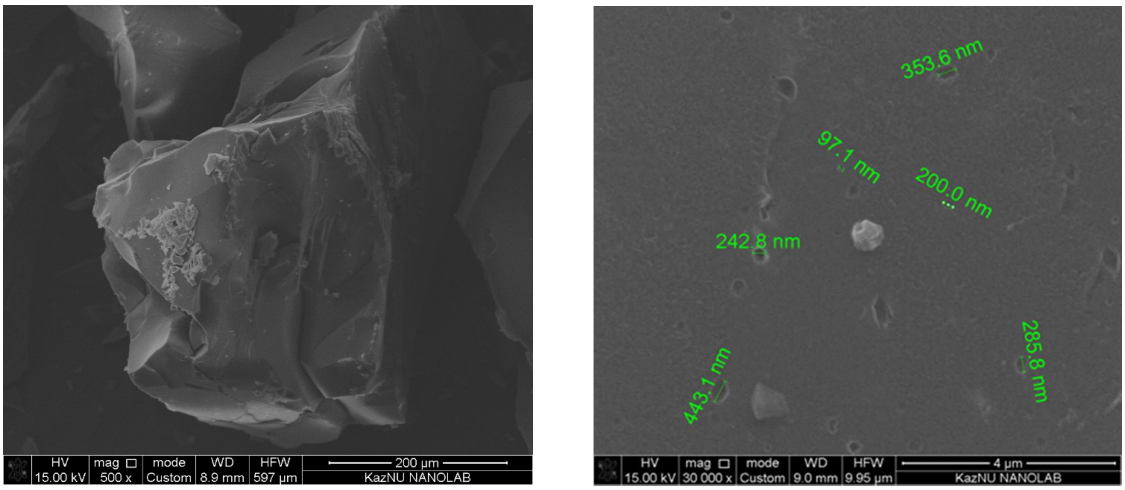

Fig. 6. Morphological structure of asphaltene deposited from oil from the Beke field.

Fe. In terms of the highest percentage, C is 91.89%. On the contrary, it contains a lower amount of sulfur (S-0.37%). The surface structure and morphology of asphaltene samples were studied using modern microscope devices. Electron microscopic images of asphaltene of Beke bitumen are shown in Fig. 6.

As can be seen from the SEM image of asphaltene precipitated Beke natural bitumen, we can see a homogeneous surface layer consisting of amorphous carbon in the structure of asphaltene. In the 4 micrometer-scale image is visible pores, or cracks, in the surface layer of the asphaltene measuring until 97.1 nanometers.

4. Conclusion

During the experiment, the percentage of asphaltene, resin and oil obtained from natural bitumen of the Beke deposit was determined. It concluded that natural bitumen belongs to the highly resin-asphaltene compounds. As a result of infrared spectroscopy, the oil fraction of natural bitumen containing planar and out-of-plane deformation vibrations C-H of aromatic compounds, stretching vibrations of the aromatic ring. The spectrum also contains oxygen, sulfur and nitrogen organic compounds. It should be noted that there are many vibrational waves characteristic of alkanes. In the spectrum of asphaltene, it was found that heterocyclic compounds with double bonds having oxygen, sulfur and nitrogen compounds (such as R-SO-OH and S-O st). Also, it contains alkenes with ν-CH_2, ν-CH_3, O-CH_3 bonds and amines with δ-NH_2 bonds. Whereas, the resins are components of an intermediate structure located between the oil and asphaltenes, they serve to keep the aggregates dispersed in the oil. According to the data in the elemental analysis, we know that resin contains more C and H than asphaltene, and the amount of S, N and O is lower than asphaltene. Structural study of solid fraction of natural bitumen showed that asphaltene homogeneous surface layer consisting of amorphous carbon and there are pores or cracks.

Acknowledgment

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Беке мұнайлы құмдарының табиғи битумдарының топтық құрамын зерттеу

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АННОТАЦИЯ

Жұмыста Беке мұнайлы құмының табиғи битумының топтық құрамы зерттелді. Тәжірибе барысында топтық құрам Сокслет аппаратында хроматографиялық әдіспен бөлініп, табиғи битумның май, шайыр және асфальтен фракцияларының пайыздық мөлшері анықталды. Табиғи битумның химиялық құрамы 450-4000 $см^{-1}$ диапазонда Фурье трансформациясының инфрақызыл спектроскопиялық Spectrum-65 апаратында зерттелді. Шайыр мен асфальтеннің элементтік талдау нәтижелерін салыстыра отырып, асфальтеннің құрамында шайырға қарағанда көміртегі мен сутектен басқа элементтердің көп екені анықталды. Асфальтен үлгілерінің беттік құрылымы мен морфологиясы сканерлеуші электронды микроскоптың көмегімен 20 КВ жеделдетілген кернеуде және 0,003 Па қысымда зерттелді.
Түйін сөздер: табиғи битум, мұнайлы құм, май, шайыр, асфальтен.

Изучение группового состава природных битумов нефтеносных песков беке

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АННОТАЦИЯ

В работе изучен групповой состав природных битумов нефтеносных песков Беке. В ходе эксперимента групповой состав битума был разделен хроматографическим методом в аппарате Сокслета, определено процентное содержание масла, смоляной и асфальтеновой фракции природного битума. Химический состав природных битумов идентифицирован методом инфракрасной Фурье-спектроскопии «Спектр-65» в диапазоне 450-4000 $см^{-1}$. Сравнивая результаты элементного анализа смолы и асфальтенов, было замечено, что в сравнении со смолой асфальтен кроме углерода и водорода содержит много других элементов. Структура поверхности и морфология образцов асфальтенов была изучена с помощью сканирующего электронного микроскопа при ускоренном напряжении 20 кВ и давлении 0,003 Па.

Ключевые слова: природный битум, нефтеносный песок, масла, смола, асфальтены