When biosorbents are introduced to a petrochemical spill, it initially maintains its shape and then proceeds to break into separate patches as oil gets absorbed by the sorbent granules and forms into separate fragments. The fragments are removed mechanically or are left afloat. After a couple of weeks, depending on the temperature of water, the oil-degrading bacteria of the sorbent oxidize oil's hydrocarbon into carbon dioxide and water.

During oil spill response operations, use of biotechnologies is considered the best way of accident recovery and oil collection. The issue of their efficiency remains open due to the abundance of factors that influence the use of biosorbents in the open sea. The mechanism of the "water-oil-ice" interaction is currently not understood and studied well enough, as is the "ice-oil-water-biosorbent" interaction.

There exists a large number of microorganisms that are able to process hydrocarbons of various classes.

Among the decomposers there are 45 strains of bacteria belonging to Pseudomonas, Bacillus, Mycobacterium, Micrococcus, Achrobacter, and 4 strains of Candida and Cryptococcus yeasts. A technique has been developed to select the most active strains that are able to decompose different fractions of oil.

These are the microorganisms that serve as a basis for producing various bio-products and developing new techniques for selecting the most active strains that are able to decompose different fractions of oil and petrochemicals in order to remediate contaminated soils, natural bodies of water, aquatic areas, industrial wastewater, and rehabilitate contaminated territories. The best known products are Lenoil and Devoroil.

During biotechnological remediation of oil-contaminated soil, the decomposer organisms selected from the natural biocenosis exclude the unpredictable ecological effects that are possible when using foreign microorganisms. Other advantages include the low cost of decomposer bacteria cultures and the ability to use them for cleaning up pollution with oil and petrochemicals (petrol, kerosene, diesel fuel, etc.) in all parts of the Earth [2].

This way, development of technologies for reclamation of soil and water contaminated by oil and petrochemicals using decomposer microorganism cultures derived from native microflora becomes a priority trend in petrochemical waste disposal.

In order to select the correct method of using biotechnology and oil-contaminated waste disposal technique, it is necessary to carry out preliminary biological assessment and chemical analysis of the waste.

The advantage of biotechnologies over conventional methods of petroleum industry waste disposal lies in their mild effect on the natural environment. Biological processing of toxic oil compounds and their byproducts can not only cause the transition of waste from one class into another, but also result in non-hazardous substances and recyclable materials. Zero waste production is a new step in environmental education, and many countries all over the world already understand the importance of this trend for preservation of our planet and well-being of the population.

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RHEOLOGICAL PROPERTIES OF CRUDE OILS IN YAREGSKOYE AND YARAKTINSKOYE OIL FIELDS

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For the extraction and the pipeline transport of oil with anomalous properties, detailed information about the features of its rheological behavior at different shear stresses in a predetermined temperature range is required. Non-Newtonian properties are typically discovered in high-viscosity oils with a high content of asphaltene, resin and paraffin. As study objects, oil with a high content of resin and asphaltene (Yaregskoye oil field) and oil with high paraffin content (Yaraktinskoye oil field) were used.

After carrying out experimental researches on a rotary viscometer and producing typical rheology curves of shear stress (τ) versus shear rate (γ), it was found that oil with a high content of resin and asphaltene has pseudoplastic properties and can analytically be described by Ostwald De Waele equation: $\tau = K \cdot \gamma^{n}$, and its effective viscosity decreases with the increase of shear rate $\eta_{эфф} = K \cdot \gamma^{n-1}$. Unlike asphaltic oil, paraffinic oil is a viscous-plastic fluid, which has a yield point (τ_0) at temperature below 263 K. The rheological properties of paraffinic oil are described by equations, which result from the rheological Bingham – Shvedov model $\tau = \tau_0 + K \cdot \gamma^n$ and $\eta_{эфф} = \frac{\tau - \tau_0}{\gamma} = K \cdot \gamma^{n-1}$ from which it follows that oil viscosity also decreases with increasing shear rate [1].

The formal rheological equations above, describe the dependence of viscosity on the shear rate only, but does not explicitly consider the temperature effect, which, in turn, makes it difficult to understand the physical nature of the processes occurring at the molecular level. Therefore, under these conditions the search for other ways of analytical interpretation of the rheological properties of oil is reasonable. Using Arrhenius – Eyring $\eta = A \cdot e^{\frac{E_a}{RT}}$ equation for analytical description of the properties of liquids in a wide temperature range can determine the energy and geometric parameters of oil particles for different shear stresses. By analyzing the results of viscometric experiments with the coordinates lnη - 1/T (Figures 1 and 2), the values of viscous flow activation energy (Ea), pre-exponential factor (A) and average particle size (r), in different hydrodynamic conditions can be identified (Table 1 and 2).

As follows from Figures 1 and 2, the tangents of the angles of inclination are proportional to the activation energy of viscous flow (Ea), and they increase with increasing shear rate in case of Yaregskoye (asphaltene) oil, whereas they

remain practically constant considering Yaraktinskoye (paraffin) oil. Average radii of colloidal dispersed associates shown in Tables 1 and 2 were calculated according to the formula $r = \left[\frac{A}{\tau \cdot (16\pi\rho / 3kT)^{1/2}}\right]^{2/5}$ after experimental determination of the numerical values of the pre-exponential factor (A), which according to Frenkel-Eyring equation is dependent on the geometric dimensions of complex structural units (CSU), which may vary in structure due to oil composition.

According to modern concepts, crude oil is not a simple mixture of a large number of organic compounds dispersed to the molecular state, but it is a colloidal dispersion system [2]. The intermolecular forces in this system can form supramolecular associates, composed of many individual molecules which are arranged in ordered structures. The composition and size of CSU depend on relative content of paraffin molecules in the oil or the total amount of resin and asphaltene molecules. The dominance of a certain class of chemical compounds results in particular rheological behavior of oil.

The central nucleus of a complex structural unit (CSU) formed in asphaltic oil is composed of a large number of high and polycyclic asphaltenes which are bound together in an aggregate due to weak intermolecular interaction. Resin molecules are less connected to each other at the periphery of the nucleus in the solvate-adsorption layer. CSU nucleus, formed in paraffinic oil contains high molecular chain alkanes (paraffins), which are tightly packed together. Resin molecules in the solvate-adsorption membrane being weakly bound to the nucleus, diffusive scattering of the membrane occurs with a shift of particles due to movement which results in the decrease in CSU size to a constant value characteristic of a competent paraffin nucleus.

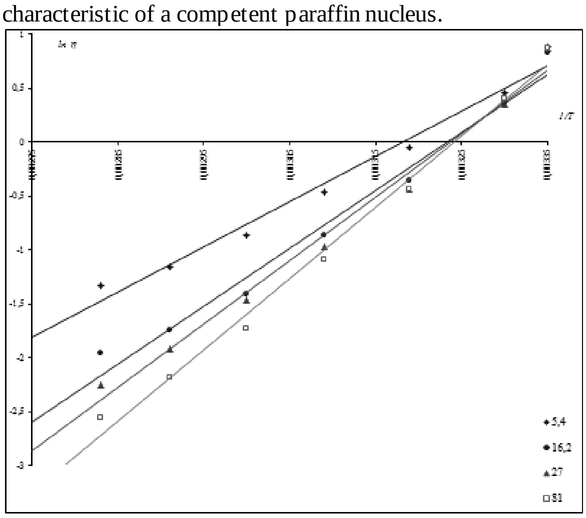

Fig. 1. lnη viscosity-inverse temperature (1/T) dependence, asphaltic oil

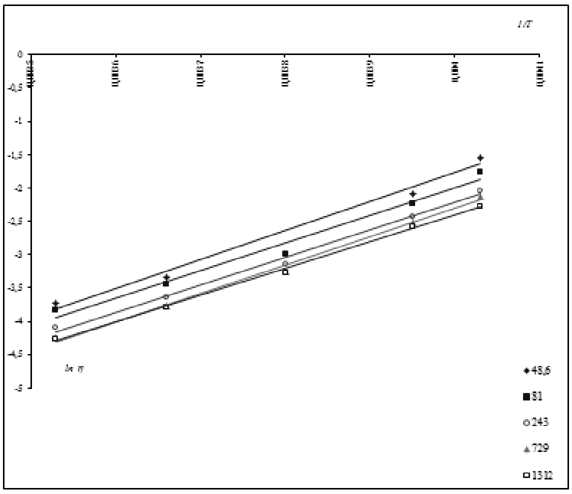

Fig. 2. lnη viscosity-inverse temperature (1/T) dependence, paraffinic oil

The results in Table 1 indicate that asphaltic oil associates in Yaregskoye field are highly susceptible to the destructive influence of the shear flow. Their mean radii in low shear rate area decrease from the colloidal particle size (~ 50 nm) to values close to the molecular size (~ 1 nm). Stronger particles (microcrystals paraffin) of oil in Yaraktinskoye field (Table 2) practically do not reduce their dimensions in the wide range of shear rates.

Table 1

Activation energy (E_a), pre-exponential value (A) and average particle radius (r) of asphaltic oil at various shearrates (γ).

Parameters	Shear rates γ, c^{-1}			
	5,4	16,2	48,6	145,8
E_a, kJ/mol·K	30,6	37,2	45,1	51,3
$A \cdot 10^8$, Pa.c	715	41,4	1,8	0,2
r, nm	47,8	10,9	1,9	1,1

Table 2

Activation energy (E_a), pre-exponential value (A) and average particle radius (r) of paraffinic oil at various shear rates (γ).

Parameters	Shear rates γ, c^{-1}			
	48,6	81,0	146	243
E_a, kJ/mol·K	36,2	34,3	33,6	34,3
$A \cdot 10^8$, Pa·c	0,47	0,9	1,1	0,73
r, nm	4,5	4,9	4,4	3,1

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IMPACT OF SLOPS FLOW ON THE PROCESS EFIICIENCY IN THE CATALYTIC CRACKING REACTOR

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The properties of raw materials and catalyst, process conditions, type of reaction system and also the quantity and quality of recycled fractions are determined the conversion of the feedstock, the yield of target products and their quality. Reinjection of sludge's portion (not more than 20 m^3/h) from the separation column to the central portion of the riser reactor is implemented on the KT-1/1 unit, on C-200 section. The slops contain a high proportion of polycyclic aromatic hydrocarbons, which leads to loss the catalyst activity and reduced the rate of secondary cracking reactions [1]. In this case the slops recycle allows optimize thermal mode of "riser-reactor-regenerator" system in processing of raw materials rich in saturated hydrocarbons by increasing the load on thecoke.

The quantity of generated coke determines the quantity of heat generated by burning the coke from the catalyst surface, and it effects on the temperature conditions of "lift reactor - regenerator" system. The connection of reactor and regenerator production conditions provides the regulation of this process by changing the catalyst circulation ratio.

Furthermore, during the processing of raw materials rich on paraffinic and naphthenic hydrocarbons, favorable for obtaining a high yield of gasoline fraction and gas, the coke yield is significantly lower than in case of converting materials with a high content of aromatic hydrocarbons.

The software-based mathematical model of catalytic cracking was used for the process parameters calculation. Figure 1 shows the main working window of this program. Using the mathematical model allows to predict the composition of the stream after the reactor, output of wet gas, gasoline fractions, light and heavy gas oil depending on the composition of the feedstock and also allows to optimize process conditions depending on the production objectives (increase in the yield of wet gas, gasoline and diesel fraction). Besides is possible the process conditions correction depending on the feedstock composition and on the amount of coke on the catalyst, that formed in the riser reactor.