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THE EFFECT OF CLAY MINERALS ON CONVERSION OF YAREGA HEAVY OIL DURING CATALYTIC AQUATHERMOLYSIS PROCESS

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Abstract

In this study we present the results of physical stimulation of in-situ aquathermolysis process carried out on heavy crude oil sample from Yarega (Russia) oil field in the presence of nickel/iron tallates and clay minerals. The experimental results revealed that clay minerals as the co-catalyst show the best performance at 300°C in case of nickel tallates, where the viscosity of aquathermolysis products reduces by 4 times in contrast to the initial crude oil. Moreover, the content of saturated fraction isolated from the catalytic aquathermolysis products increased from 36.8 to 50.2 in contrast to the saturated fraction of initial crude oil, while the amount of resins decreased by two times after hydrothermal treatment in the presence of nickel catalyst and clay minerals. Thus, the obtained results justify the involvement of clay minerals to the aquathermolysis process and demonstrate catalytic performance in terms of enhancing group composition and viscosity reduction.

Keywords:
Heavy oil;
Upgrading;
Catalysts;
Aquathermolysis;
Clay minerals;
Transition metals; SARA;
Rheology.

Introduction

The supply of crude oil will be able to keep up with demand by developing unconventional oil resources such as heavy oil and natural bitumen [1]. Such resources are generally more difficult and costly to produce, transport and process due to high viscosity, density and significant amount of heteroatom compounds [2]. Therefore, unconventional crude oils have to be upgraded by cracking bonds and adding hydrogen prior to be a feedstock to traditional refinery. One of the promising techniques of heavy oil upgrading is aquathermolysis process [3–5]. This term was introduced by Hyne et.al in 1982 to describe the chemical reactions carried out during steam treatment of heavy oil or oil-saturated rocks. Since then there is a vast amount of literature on the catalytic effect of rock minerals on the chemical reactions [6–9]. Particularly, clay minerals significantly affect the hydrothermal conversion of hydrocarbon components [10–12]. On the other hand, aquathermolysis process can be accelerated by introduction of various transition metal nano-catalysts [13]. Currently, nanomaterials are very attractive and widely applied in upstream industry [14]. The nano-catalysts are difficult to deliver into the pay zone of reservoir formations due to the dispersity. Therefore, usually catalyst precursors, which are easily dissolves in organic solvents, are injected into the reservoir formations and after the distribution of catalyst precursors, the active form of them - nanoparticles are achieved in-place under high temperature and pressure.

However, the catalytic role of the clay minerals and the hydrothermal conversion mechanism of hydrocarbons in the presence of reservoir rock minerals nor the synergic effect of minerals and injected catalysts are not properly studied. In this paper, we present the laboratory results of comparison study of catalytic aquathermolysis process in the presence and absence of rock minerals extracted from Yarega oil field. The aim of the given study is to select the most efficient catalyst considering the composition of rock minerals for further field applications of catalytic complex.

Experimental part

The object of this study was a heavy oil sample from Yarega oil field, the density of which is 0.948 g/cm^2. The oil field is located in North Russian Lowlands. The reservoir rock minerals were isolated from the composition of drill cuttings and were

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analyzed in X-ray diffraction pattern, the result of which is presented in table 1.

The laboratory modeling of heavy oil hydrothermal treatment in the presence of clay minerals and synthesized catalyst precursors (Fe and Ni tallates) was carried out in a high-pressure reactor (Parr Instruments, USA), the volume of which was 300 mL. The temperature of steam chamber of Yarega reservoir formations reaches 250-300 °C, while the reservoir pressure is 9 MPa. Therefore, in laboratory conditions we heated up the model bulk up to 300 °C at constant pressure – 9 MPa. The pressure in reactor was supported by inert pure gas – nitrogen. The proposed catalytic complex is composed of synthesized nickel and iron tallates dissolved in hydrogen donor with the mass ratio of 1:1, while the share of catalytic complex in oil bulk is 2 wt.%. The scheme of modeling hydrothermal treating experiments is presented in figure 1.

The viscosity of crude oil and catalytic aquathermolysis products were measured in rotational viscometer «Alpha L» from Fungilab (Spain). The group composition of crude oil before and after catalytic aquathermolysis processes is determined by SARA analysis according to the ASTM D4124-09. Then the light fractions of heavy crude oil were analyzed in GC-MS (Chromatec Crystall, Russia).

Table 1

Composition of reservoir rock minerals before and after aquathermolysis process

Compound name	Before aquathermolysis, wt.%	After aquathermolysis, wt.%
Pyrite	<1	0
Dolomite	<1	0
Calcite	2	0
Kaolinite	4	0
Chlorite	5	0
Clinochlore	0	3.5
Laumontite	9	5.5
Mica	8	7.0
Microcline	15	21.5
Quartz	21	26.5
Albite	36	36.0

Results and discussions

The group composition of heavy crude oil before and after the catalytic treatment is summarized in table 2.

The hydrothermal treatment of heavy crude oil without any additive at 250°C provides increase in saturates fraction and decrease in resins content. However, introduction of clay minerals into the oil bulk under the hydrothermal impact accelerated the destructive hydrogenation reactions mostly in high molecular components of oil such as resins and asphaltenes. In its turn, the destructive products increased the amount of saturates and aromatics in contrast to the control sample (only hydrothermal treatment without any additives). Increasing the temperature of steam from 250 to 300 °C increases the intensity of destructive processes mostly in resinous compounds. However, the amount of asphaltenes raises due to polymerization of detached radicals. Among two synthesized metal tallates – iron and nickel, the significant performance in terms of group composition shows the combination of clay minerals with nickel tallates under the hydrothermal treatment at 300°C. From table 1 we see that the content of resins decreases twice, while the amount

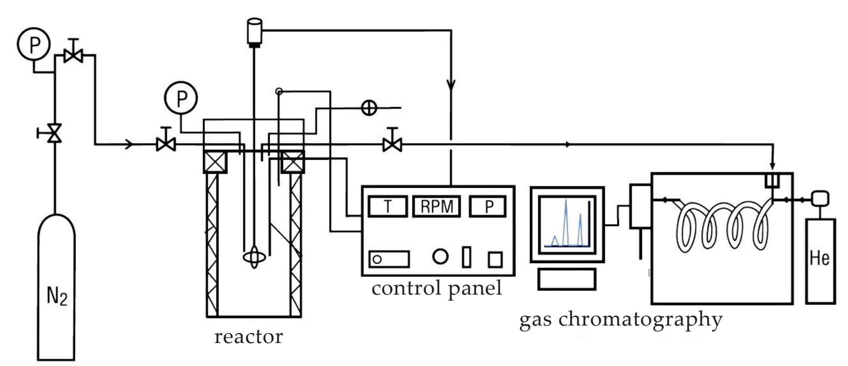

Fig.1. Scheme of high-pressure reactor combined with a gas chromatography used for carrying out the hydrothermal treatments under stirring and static conditions

of saturates increases more than 36 %. This shows the compatibility of nickel tallate with clay minerals on hydrothermal upgrading of heavy oil.

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Table 2

Comparative analysis of group-composition of heavy crude oil before and after the catalytic aquathermolysis

Samples	SARA fractions, wt.%				
	Temperature °C	Saturates	Aromatics	Resins	Asphaltenes
Crude oil		36.8	22.2	38.4	2.5
Crude oil after hydrothermal treatment	250	46.8	23.7	25.9	3.7
Crude oil after hydrothermal treatment in the presence of clay minerals	250	46.8	31.9	18.6	2.8
	300	52.9	26.8	17.3	3.1
Crude oil after hydrothermal treatment in the presence of clay minerals and Fe-catalyst	250	46.2	28.9	21.9	3.1
	300	50.1	26.0	20.4	3.5
Crude oil after hydrothermal treatment in the presence of clay minerals and Ni-catalyst	250	48.0	26.4	22.2	3.4
	300	50.2	29.8	16.7	3.4

It is believed that decrease in viscosity is due to the temperature rise and this phenomenon is temporary. This is true unless there are no chemical changes in the structure of crude oil. The hydrothermal treatment of heavy oil in addition to the physical consequences has a chemical consequence as well. Introduction of chemical additives speeds up such interactions and are able to permanently decrease the viscosity of crude oil by destructing the high-molecular components and reduction of their molecular weights. In figure 2, we present the results of viscosity measurements of heavy crude oil before and after hydrothermal treatment in the presence and absence of catalytic complex. The influence of hydrothermal treatment in the presence of clay minerals is noticeable at 300 °C. Addition of both catalysts provide significant viscosity reduction in contrast to

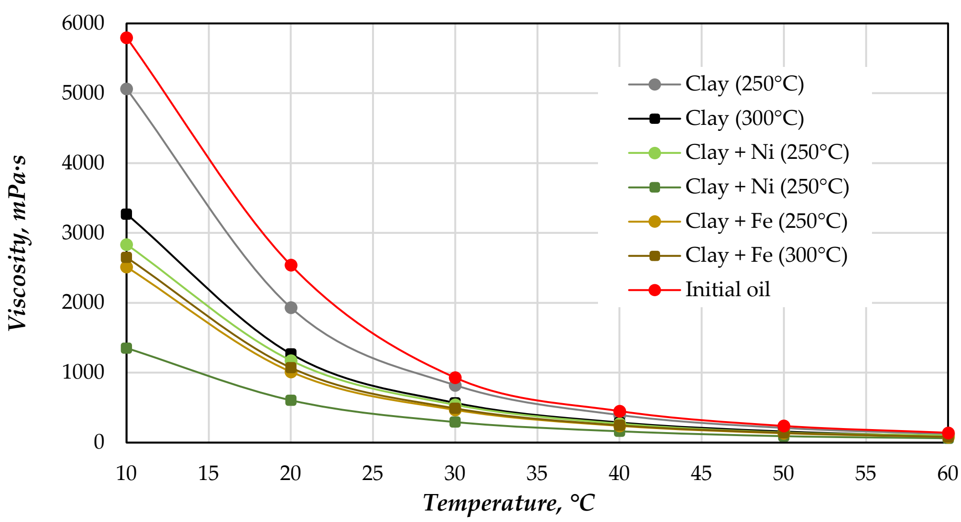

Fig.2. Dynamic viscosity of initial crude oil before and after various catalytic hydrothermal treatments

the initial crude oil. However, the viscosity of crude oil after hydrothermal treatment in the presence of nickel tallate and clay minerals is the lowest. It reduces from 5798 mPa·s at 10 °C to 1353 mPa·s, which makes the viscosity reduction more than 75%. This result is in accordance with SARA analysis results, where we can observe the dependency of viscosity from high molecular components of crude oil such as resins and asphaltenes. The increase in viscosity of crude oil after hydrothermal treatment at 300 °C in the presence of Fe-catalyst and clay minerals can be reasoned by polymerization of cracking products due to lack of hydrogen sources.

After the hydrothermal upgrading processes, the changes in the mineral parts of reservoir rocks were analyzed by using X-ray diffraction (XRD) spectroscopy. The minerals particles were isolated from the upgraded oil bulk by centrifuging at high speed – 5000 rpm at room temperature for 30 minutes and washed with toluene. We repeated this cycle until the transparency of toluene solvent was achieved (approximately 8-10 cycles). The XRD patterns of reservoir rock minerals are presented in figure 3, while the interpretation of them are summarized in table 1. The rock sample is composed of various composition and characterized by 10 components. Particularly, some minerals such as iron disulfide or pyrite (FeS_2), minerals from carbonate class – dolomite ($CaCO_3 \cdot MgCO_3$) and calcite ($CaCO_3$), clay minerals of aqueous aluminum silicate group – kaolinite ($Al_4[Si_4O_{10}](OH)_8$), and chlorite ($((Mg,Fe)_3(Si,\ Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6)$ undergo transformation under hydrothermal impact, which is clearly observed from the results (table 1). The number of minerals were reduced to six after aquathermolysis process. However, the contents of laumontite and mica were decreased, while the contents of quartz, microcline, clinochlore were increased. The content of albite was constant. It is important to note the appearance of clinochlore ($((Mg,Al)_6[Si_{3.1–2},Al)_{0.9-1.2}O_{10}](OH)_8)$ after the aquathermolysis process. The formation of such mineral is probably due to hydrothermal transformation of silicate group minerals.

Once the heavy crude oil is separated into its fractions, the light components – saturates and aromatics were further analyzed in GC-MS. The spectra of saturated fractions were examined in terms of aliphatic compounds, where the base peak was m/z = 57, which shows the presence of alkyl chains and a saturated aliphatic. From the spectra (fig. 4) we see that the products of catalytic

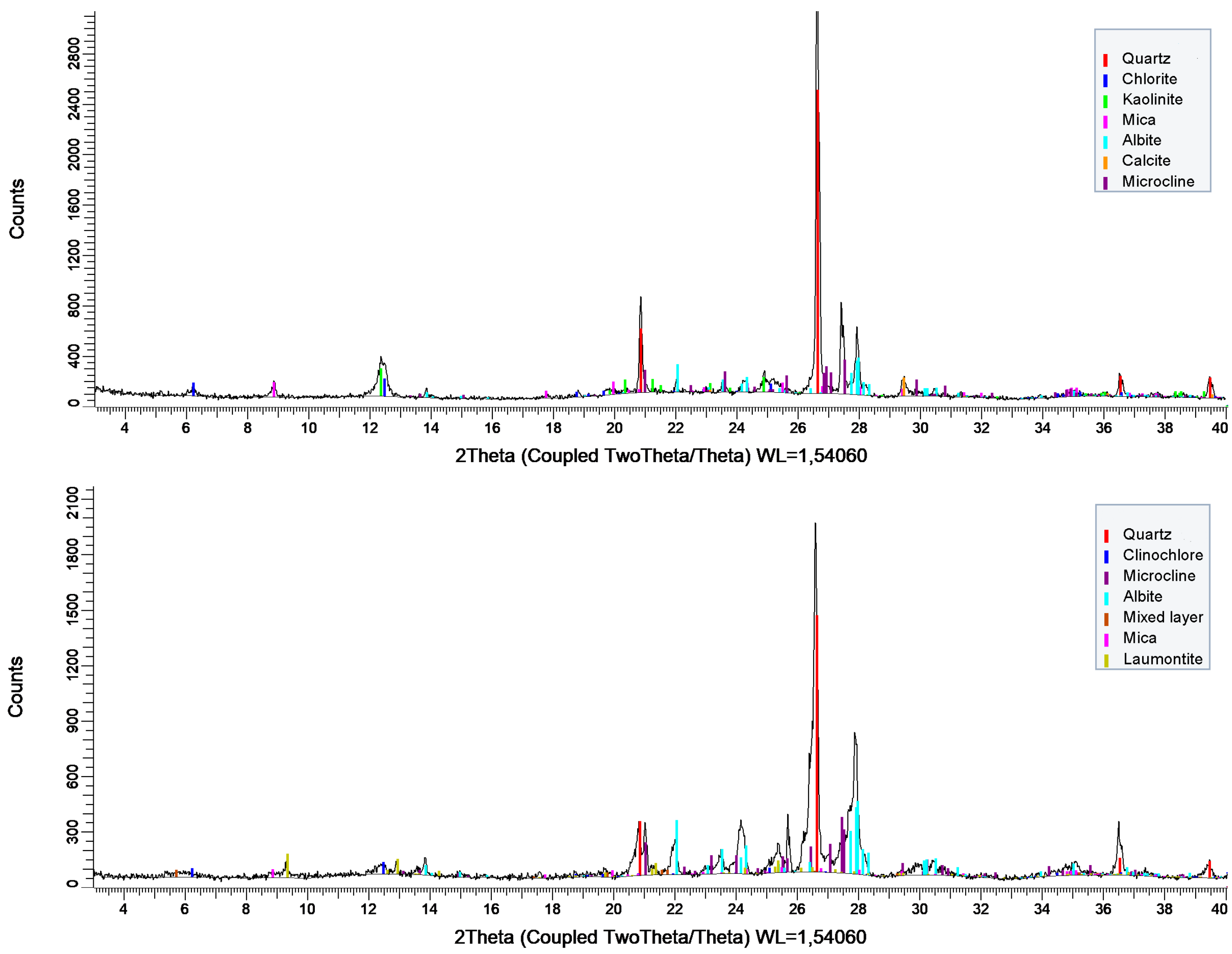

Fig.3. XRD pattern of the mineralogical composition of reservoir rocks before (left) and after (right) catalytic aquathermolysis process

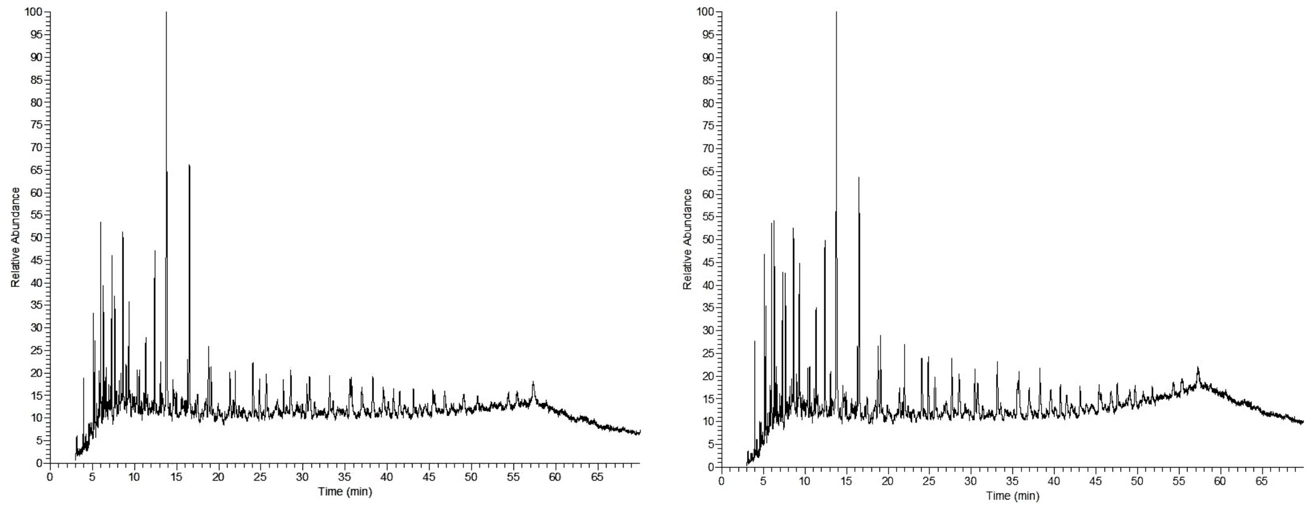

Fig.4. The spectra of saturates before (left) and after (right) catalytic aquathermolysis of crude oil at 300 °C in the presence of nickel based catalytic complex and clay minerals in the mass range of m/z = 56.5-57.5

aquathermolysis provide less increase in intensity of saturated aliphatic hydrocarbons. However, the significant changes are observed in spectra of aromatic fractions (fig. 5). The cracking products of resins are probably joined the aromatic hydrocarbons increasing the relative abundance of mono aromatic compounds in the composition of aromatic fractions, which were examined in the mass range of m/z=132.5-133.5. In our previous works we already justified the transition of tetramethyl phenanthrene and its derivatives from asphaltenes to aromatics due to destructive hydrogenation processes.

Clay minerals intensify the cracking and hydrogenolysis reactions resulting to the redistribution of oil fractions toward increasing the content of light components, particularly aromatic hydrocarbons. The yield of light components depends on the temperature of reactions (table 2). The intensity of heavier compounds, which were eluted from the column in the retention time range of 18-30 minutes were decreased after the catalytic hydrothermal treatment in the presence of clay minerals. Moreover, the relative abundance in the time range of 5-11 minutes was significantly increased after the catalytic hydrothermal treatment of heavy oil in the presence of clay minerals. This is due to the acceleration of cracking reactions of the least strong bonds C-S, C-N and C-O and detachment of alkyl substitutes in the composition of heavy molecules.

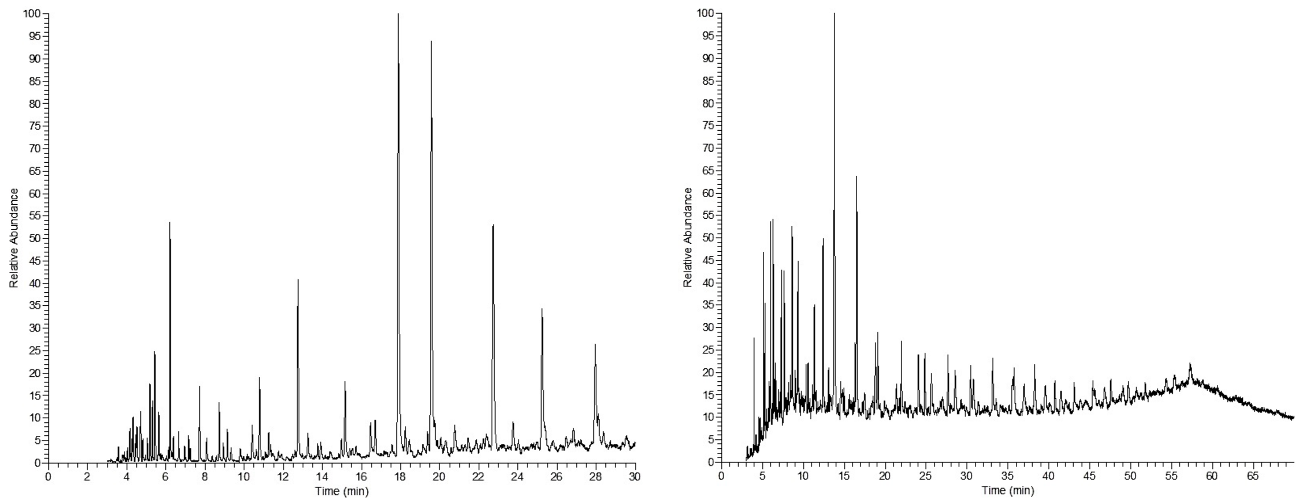

Fig. 5. The spectra of monoaromatic hydrocarbons before (left) and after (right) catalytic aquathermolysis of crude oil at 300 °C in the presence of nickel based catalytic complex and clay minerals in the mass range of m/z = 132.5-133.5

Conclusions

The most remarkable result to emerge from the data is a catalytic performance of clay minerals, which are in good compatibility with synthesized nickel-based nano-catalysts. The presence of the clay minerals promotes a number of chemical processes, which leads to the destruction of high-molecular compounds and an increase in the content of light fractions in the final products. The development of catalytic aquathermolysis technology for a given field and the selection of the most active catalyst for further field application show that a system consisting of a nickel-based catalyst in the presence of clay minerals shows the best effect at a temperature of 300 °C, reducing the viscosity by more than half. The results obtained confirm that the mineral part of the rocks participates in the process of aquathermolysis and demonstrates a good catalytic effect, improving the group composition, reducing the oil viscosity, thereby increasing the mobility of heavy crude oil in the porous media.

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Влияние глинистых породообразующих минералов на состав высоковязкой нефти ярегского месторождения в процессе каталитического акватермолиза

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Реферат

В статье освещаются результаты экспериментальных исследований процесса внутрипластового акватермолиза высоковязкой нефти ярегского месторождения в присутствии таллатов никеля и железа, и глинистых породообразующих минералов. Установлено, что глины как со-катализатор обуславливают синергетический эффект с каталитическим комплексом на основе никеля при 300°С. В результате вязкость нефти после акватермолиза снижается в 4 раза по сравнению с исходной нефтью. Более того, содержание насыщенной фракции продуктов каталитического акватермолиза увеличивается с 36,8 до 50,2 мас.% по сравнению с исходной нефтью, тогда как содержания смол после гидротермальной обработки в присутствии таллата никеля и породообразующего минерала снижается в два раза. Таким образом, полученные результаты подтверждают каталитическую роль глинистых минералов в ускорении реакций деструктивного гидрирования смолисто-асфальтеновых веществ, что приводит к улучшению группового состава и снижению вязкости.

Ключевые слова: высоковязкая нефть; upgrading; катализаторы; акватермолиз; глинистые минералы; переходные металлы; SARA-анализ; вязкость.

Katalitik akvatermoliz prosesində Yareqa yatağının yüksək özlülüklü neftinin tərkibinə süxur əmələ gətirən gil minerallarının təsiri

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Xülasə

Məqalədə nikel və dəmir tallatlarının və gilli süxurəmələgətirən mineralların iştirakı ilə Yareqa yatağının yüksək özlülüklü neftinin laydaxili akvatermoliz prosesinin eksperimental tədqiqatlarının nəticələrinə baxılır. Müəyyən edilmişdir ki, gillər so-katalizator kimi 300°C-də nikel əsaslı katalitik komplekslə sinergetik effektə səbəb olur. Nəticədə akvatermolizdən sonra neftin özlülüyü ilkin neftlə müqayisədə 4 dəfə aşağı düşür. Bundan başqa, nikel tallatı və süxurəmələgətirən mineralın iştirakı ilə hidrotermiki emaldan sonra qatranın miqdarı iki dəfə azaldığı halda, katalitik akvatermoliz məhsullarının doymuş fraksiyasının miqdarı ilkin neftlə müqayisədə 36.8 kütlə %-dən 50.2 -dək artır. Beləliklə, əldə edilmiş nəticələr qatran-asfalten maddələrinin destruktiv hidrogenləşmə reaksiyalarının sürətlənməsində gil minerallarının katalitik rolunu təsdiqləyir ki, bu da qrup tərkibinin yaxşılaşmasına və özlülüyün aşağı düşməsinə gətirib çıxarır.

Açar sözlər: : yüksək özlülüklü neft; upgrading; katalizatorlar; akvatermoliz; gilli minerallar; keçid metalları; SARA-analiz; özlülük.