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EVALUATION OF THE AQUATHERMOLYSIS CATALYST EFFECT ON THE COMPOSITION AND PROPERTIES OF HIGH-VISCOSITY OIL FROM THE STRELOVSKOE FIELD

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Abstract

The article examines the aquathermolysis process of high viscosity oil from Strelovskoe field developed by RITEK LLC using steam injection. Laboratory modeling of non-catalytic and catalytic aquathermolysis in a high-pressure reactor was performed. Laboratory tests have demonstrated the high efficiency of the iron-based oil-soluble catalyst developed at Kazan Federal University in the destruction reactions of resinous asphaltene. Samples of the initial oil as well as products of non-catalytic and catalytic aquathermolysis in the presence of iron tallate and the solvent Asphalt-Resin-Paraffin Deposits were studied at temperatures of 200, 250 and 300°C for 24 hours. In addition, the gas composition of the oil aquathermolysis products and the viscosity-temperature characteristics of the oil samples were determined. The studies have shown that catalytic aquathermolysis has a significant effect on the changes in the composition and properties of oil from the Strelovskoe field. It was found that the presence of a catalyst contributes to decarboxylation reactions, increases the degree of desulfurization and decreases the viscosity of oil samples

Keywords:

High-viscosity oil;
Aquathermolysis;
Catalyst precursor;
Steam thermal treatment;
Viscosity.

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1. Introduction

In recent years, a decline in the growth rate of oil reserves has led to an increased interest in high-viscosity oils as the number of oil deposits has significantly increased in many countries around the world. Therefore, one of the most important tasks is to ensure their rational processing and meet the growing consumption of energy resources [1-4].

Heavy oils are considered as alternative sources of hydrocarbon feedstocks. The difference between heavy oils and light oils is the higher density and different complex composition. In addition to hydrocarbons, naphthenic acids, sulfonic acids, simple and complex esters, and rare non-ferrous metals are also present in conditioned concentrations [5-7].

Therefore, scientific research to develop new technologies for the conditioning of high viscosity oils and natural bitumen for processing and transportation plays an important role in the development of high viscosity oils [8-12].

In this work, the research objective is to develop

a catalyst for in situ refining of high viscosity oil from Strelovskoe field. In this context, we used the initial oil of Strelovskoe field in Samara region as a research object, as well as products of non-catalytic and catalytic aquathermolysis.

Research tasks:

- Synthesis of an oil-soluble iron-based catalyst precursor;
- Laboratory modeling of the aquathermolysis process in a high-pressure reactor;
- Determination of the composition of the gas phase after the thermal steam treatment;
- Measurement of the viscosity of non-catalytic and catalytic aquathermolysis products.

2. Experimental

The research experiments in this paper were conducted with the high viscosity oil from well 117G of the Strelovskoe field.

The oil of Strelovskoe field is a heavy oil (class I – $\rho = 934-966 \text{ kg/m}^3$ (14-20 °API)), with ultra-high-viscosity ($\eta = 1000 - 10000 \text{ MPa}\cdot\text{s}$).

In this study, iron tallate (a brown paste containing 9.5% iron) was used [13]. The resulting

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resinate dissolves easily in gasoline, oil, tetralin and toluene.

Laboratory modeling of the phenomenon of non-catalytic and catalytic aquathermolysis was carried out in a high-pressure reactor from Parr Instruments (Moline, Illinois, USA) with a loading of oil and water at a ratio of 70:30. Iron carboxylate and solvent were loaded in an amount of 0.2% by metal and 2% by oil, respectively. The emulsion was exposed to temperature at 200, 250 and 300 °C for 24 hours and the initial pressure was recorded at 8.5 atm.

Table Physical and chemical properties of the initial oil from the Strelovskoe field	
Parameters	Values
Density at 20 °C, kg/m ³	956.5847
Dynamic viscosity at 20 °C, MPa·s	4046.3
Group composition, wt. %:	
- saturated HC	23.5
- aromatic HC	44.1
- resins	23.5
- asphaltenes	8.9

The gascomposition was analysed by the method of gas chromatography. The analysis was carried out using a Chromatec-Crystal 5000 device (Chromatec Company) and computer data processing with a signal detector of thermal conductivity. The gas phase sample was carried out with a special water outlet in the autoclave lid into the tube leading to the gas chromatograph. The column of the chromatograph was purged with the aquathermolysis gases. The viscosity-temperature characteristics of the Strelovskoe field oil were determined using a FUNGILAB Alpha L rotary viscometer.

3. Results and discussions

Figures 1 and 2 show the content and composition of gases (individual gases, alcohols and other gases) and mixtures of isomers C₄-C₁₀, olefins+dienes and

cycloalkanes+aromatic hydrocarbons per 1 ton of oil, depending on the control experiment, in the presence of a catalyst and solvent in the oil during aquathermolysis at 300 °C.

The appearance of C₁-C₅ hydrocarbons obviously indicates the occurrence of radical thermal degradation processes. The catalyst precursor in the oil increases the methane and ethane content. The presence of a catalyst promotes decarboxylation reactions, as indicated by a significantly greater amount of carbon dioxide released. In addition, in the presence of a solvent, the hydrogen sulfide content increases, indicating an increase in the degree of desulfurization and a decrease in viscosity due to the breaking of C-S bonds in high molecular weight components.

As a result of cracking the alkyl substituents, the growth of olefins and dienes occurs (the formation of double bonds). An increase in C₄-C₁₀ isomers occurs as a result of the PABS decomposition (polyalkylbenzene resin).

Figures 3 and 4 show the content and composition of gases (individual gases, alcohols and other gases) and mixtures of C₄-C₁₀ isomers, olefins+dienes and cycloalkanes+aromatic hydrocarbons per 1 ton of oil, depending on the control experiment, in the presence of a catalyst and solvent in the oil during aquathermolysis at 250 °C.

The resulting hydrogen sulfide during catalytic conversion is the result of C-S bond breaking in resinous-asphaltene substances. The decrease in CO₂ content probably indicates the dissolution of carbon dioxide in the oil and a further decrease in its viscosity. The presence of the reagent confirms the catalytic effect in increasing the content of methane hydrocarbons.

The decrease in isomers in the case of catalytic thermal treatment may be due to redistribution of group composition and isomerization of saturated hydrocarbons. Figures 5 and 6 show the content and composition of gases (individual gases, alcohols and other gases) and mixtures of C₄-C₁₀ isomers, olefins+dienes and cycloalkanes+aromatic hydrocarbons per 1 ton of oil, depending on the

Fig. 2. Content and composition of gases (mixture of isomers C_4 - C_{10} , olefins+diene and cycloalkanes+aromatic hydrocarbons)

Fig.3. Content and composition of gases (individual gases, alcohols, and other gases)

Fig.4. Content and composition of gases (mixture of isomers C_4 - C_{10} , olefins+diene and cycloalkanes+aromatic hydrocarbons)

Fig. 5. Content and composition of gases (mixture of isomers C_4 - C_{10} , olefins+diene and cycloalkanes+aromatic hydrocarbons)

control experiment, in the presence of a catalyst and solvent in the oil during aquathermolysis at 200 °C.

Figure 5 shows a significant effect of the mixture of catalyst and solvent on the composition of aquathermolysis gases. In comparison with the control experiment, a large amount of hydrogen sulfide is emitted, confirming the assumption about the cleavage of carbon-sulfur bonds in the alkyl substituents of the heavy components. The emitted carbon dioxide results from decarboxylation reactions of oxygenated oil components.

Strelovskoe oil is a typically non-Newtonian fluid and a viscous-elastic fluid according to the rheological properties. In general, the fluids that have both liquid and solid properties and share both viscous and elastic behavior in response to an applied shear stress are viscoelastic. The viscosity value of the oil after hydrothermal treatment with and without catalyst at 300°C are shown in figure 7.

The viscosity of the initial oil and the product of

non-catalytic aquathermolysis at a temperature of 10 °C is more than 10000 mPa·s. The viscosity of the oil samples at 20 °C with a catalyst precursor and a solvent or with a solvent only decreases by about 2.5 and 2 times, respectively. It is likely that the catalyst is involved in the thermodestructive decomposition of the aliphatic side chains of the asphaltene molecules. Compact secondary asphaltenes with a lower molecular weight are formed. In addition, the decrease in viscosity of the oil is also influenced by the presence of a paraffin solvent, the mechanism of action of which is the adsorption of a dispersant on the wax crystals, hindering the processes of their aggregation and accumulation and reducing the temperature of fluidity of the oil [14].

Figure 8 shows the results of viscosity dependence on the temperature of the initial oil and the aquathermolysis products at 250 °C. The viscosity values show the same results as after aquathermolysis at a temperature of 300 °C. The

Fig.6. Content and composition of gases (mixture of isomers C_4 - C_{10} , olefins+diene and cycloalkanes+aromatic hydrocarbons)

Fig.7. Viscosity-temperature characteristics of the initial oil and oils after non-catalytic and catalytic aquathermolysis at 300 °C

viscosity of the initial oil and the product of non-catalytic aquathermolysis at a temperature of 10 °C is above 10000 mPa.s.

The viscosity of oil with iron tallate and solvent, measured at 20 °C, decreases by more than 1.5 times

compared to the control experiment. Moreover, the catalyst promotes the destruction of associated complexes of resin molecules, thereby affecting a decrease in the viscosity of the oil. The impact of the dispersant is that it dissolves directly in the oil, then alkane surfactant blocks are embedded in paraffin deposits at the moment of phase transition to a solid state and co-crystallize [15].

Figure 9 shows the results of viscosity dependence on the temperature of the initial oil and the aquathermolysis products at 200 °C. The viscosity values show the same results as after aquathermolysis at a temperature of 300 °C. The viscosity of the initial oil and the product of non-catalytic aquathermolysis at a temperature of 10 °C is above 10000 mPa.s.

Compared to the control experiment, the viscosity of oil with a solvent, measured at a temperature of 20 °C, decreases by more than 1.5 times. In this case, the decrease in viscosity was significantly influenced by the paraffin solvent. However, in the presence of a catalyst precursor, there was a slight increase in viscosity, probably due to coking of the surface of the catalyst particles. However, the viscosity is lower compared to the control test.

Fig.8. Viscosity-temperature characteristics of the initial oil and oils after non-catalytic and catalytic aquathermolysis at 250 °C

Fig.9. Viscosity-temperature characteristics of the initial oil and oils after non-catalytic and catalytic aquathermolysis at 200 °C

Conclusions

In summary, laboratory modeling of the steam-thermal treatment of high-viscosity oil from the Strelovskoe field was carried out without and with the addition of a catalyst (Oil-soluble iron tallate.). The appearance of C₁-C₅ hydrocarbons obviously indicates the occurrence of radical processes of thermal destruction. Also, the presence of a catalyst promotes the decarboxylation reactions, as can be seen from the significantly large amount of carbon dioxide emitted. Moreover, in the presence of a catalyst, the hydrogen sulfide content increases, indicating an increase in the degree of desulfurization and a decrease in viscosity due to the breaking of C-S bonds in high molecular weight components.

According to viscometry data, the viscosity of the oil samples at 20 °C with a catalyst precursor and a solvent or with only a solvent, decreases by 2.5 and 2 times, respectively, compared to the initial oil.

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Оценка влияния катализатора акватермолиза на состав и свойства высоковязкой нефти стреловского месторождения

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Реферат

В работе исследован процесс акватермолиза высоковязкой нефти Стреловского месторождения, осваиваемого ООО «РИТЭК» с использованием закачки пара. Было проведено лабораторное моделирование явления некаталитического и каталитического акватермолиза в реакторе высокого давления. По данным лабораторных испытаний установлена высокая эффективность разработанного в Казанском федеральном университете нефтерастворимого катализатора на основе железа в реакциях деструкции смолисто-асфальтеновых веществ.

Исследованы образцы исходной нефти, а также продуктов некаталитического и каталитического акватермолиза в присутствии таллата железа и растворителя АСПО при температурах 200, 250 и 300 °С в течение 24 часов. Определен газовый состав продуктов акватермолиза нефти, а также вязкостно-температурные характеристики образцов нефтей. Проведенные исследования выявили, что каталитический акватермолиз оказывает значительное влияние на изменение состава и свойств нефти Стреловского месторождения. Установлено, что наличие катализатора способствует реакциям декарбоксилирования, повышается степень обессеривания и снижается вязкость образцов нефтей.

Ключевые слова: высоковязкая нефть, акватермолиз, прекурсор катализатора, паротепловое воздействие, вязкость.

Akvatermoliz katalizatorunun Strelovsk yatağının yüksək özlülüklü neftinin tərkibinə və xassələrinə təsirinin qiymətləndirilməsi

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Xülasə

Məqalədə «RITEK» MMC tərəfindən mənimsənilən Strelovsk yatağının yüksək özlülüklü neftinin akvatermoliz prosesi buxarvurmanın istifadəsi ilə tədqiq edilmişdir. Yüksək təzyiq reaktorunda qeyri-katalitik və katalitik akvatermoliz təzahürünün laboratoriya modelləşdirilməsi aparılmışdır. Laborator sınaqlarının məlumatlarına əsasən Kazan Federal Universitetində işlənmiş dəmir əsaslı nefthəddici katalizatorun qatran-asfalten maddələrinin destruksiya reaksiyalarında yüksək effektivliyi müəyyən edilmişdir. İlkin neftin, həmçinin qeyri-katalitik və katalitik akvatermoliz məhsullarının nümunələri 24 saat ərzində dəmir tallatı və AQPÇ həlledicisinin iştirakı ilə 200, 250 və 300 °C temperaturalarda tədqiq edilmişdir. Neftin akvatermoliz məhsullarının qaz tərkibi, həmçinin neft nümunələrinin özlülük-temperatur xarakteristikaları müəyyən edilmişdir. Aparılan tədqiqatlar göstərmişdir ki, katalitik akvatermoliz Strelovsk yatağı neftinin tərkib və xassələrinin dəyişməsinə əhəmiyyətli təsir göstərir. Müəyyən edilmişdir ki, katalizatorun olması dekarboksilləşmə reaksiyalarına imkan yaradır, kükürtsüzləşmə dərəcəsini yüksədir və neft nümunələrinin özlülüynü aşağı salır.

Açar sözlər: yüksək özlülüklü neft; akvatermoliz; katalizator prekursoru; buxar-istilik ilə təsir; özlülük.