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Experimental Study of the Effect of Composite Solvent and Asphaltenes Contents on Efficiency of Heavy Oil Recovery Processes at Injection of Light Hydrocarbons

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Additional information is available at the end of the chapter

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Abstract

The current state of research in the field of solvent injection techniques for increase of heavy oil production efficiency is discussed in the chapter. As a result of a series of experiments on the physical modeling of oil displacement processes in a porous medium in large-sized model, features of asphaltene precipitation and the formation of fixed residual oil upon injection of solvent based on light alkanes are revealed. The oil displacement by n-hexane was studied and the difference in the composition of residual oil in the zones of dispersion and diffusion has been shown. The influence of the composition of asphaltenes peculiarities on the dynamics of oil recovery and on the accumulated oil recovery during the injection of n-hexane, as well as the composition and quantity of asphaltenes precipitated in the porous medium, has been estimated. The effect of toluene and nonylphenol additives on the proportion of asphaltenes in the residual oil and cumulative oil recovery has been evaluated using the Ashalchinskoye field oil as an example of heavy oil in the physical modeling of injection of n-hexane as the base solvent.

Keywords: heavy oil, composition of asphaltenes, injection of solvent, reservoir modeling, enhanced oil recovery

1. Introduction

The results of the pilot projects on combined steam and solvent injection for increasing heavy oil (HO) and bitumen recovery [1] have confirmed the viability of their use. The main volume of heavy oil recovery by downhole methods is provided by using steam; for example, in

Canada, these are mainly cyclic steam stimulation (CSS) and steam assisted gravity drainage (SAGD). The main problems of thermal steam effect are mainly associated with energy costs and requirement of deep water purification for steam generators. The main criterion in thermal steam methods is the availability of fuel resources used for a steam generation: in order to recover 1 ton of heavy oil one is required to burn averagely about 300 kg fuel, and natural gas is often used as fuel. The combined use of solvents and steam significantly increases energy efficiency due to the decrease in the amount of heat required in order to decrease the bitumen viscosity. As a result of this, the operational costs are reduced as well as carbon dioxide emissions which are important from the ecological point of view. Since 2000, various projects have been realized in Canada for combined steam and solvent injection [2–8]: Solvent aided process (SAP), solvent-assisted SAGD (SA SAGD), liquid addition to steam to enhance recovery (LASER), expanding solvent SAGD (ES SAGD), and steam alternating solvent (SAS). Mostly light alkanes or their mixtures (propane, butane, pentane and hexane) and gas condensate were used as a hydrocarbon solvent, which were injected into paired horizontal, single horizontal and vertical wells.

Currently, increased attention is paid to providing methods of recovering heavy oil from thin reservoirs, where the variants of using SAGD are not applicable. For example, in western Canada (Saskatchewan province), where about 2/3 of all Canadian heavy oil resources are located (5.4 billion m³ of proven and probable ones), 55% of the deposits are contained in the reservoirs of less than 5 m thick. In Russia, the Tatneft Company has such reservoirs [9]. In this connection, several variants of heavy oil recovery are considered using pure solvent: the cyclic solvent process (CSP) and cyclic solvent injection (CSI) technologies, which are designed for single wells. It has been experimentally established that the main technical limitations of common CSI process are the untimely restoration of the oil viscosity due to solvent release and loss of oil mobility during recovery associated with it. In order to overcome the said technical drawbacks in the recent years some non-thermal process variants are proposed: enhanced CSP (ECSP) [10], cyclic production with continuous solvent injection (CP-CSI) [11] and gas flooding-assisted cyclic solvent injection (GA-CSI) [12]. For example, in the ECSP method two components are used as a solvent: methane and propane. Methane provides for enveloping the reservoir by the effect and propane reduces the oil viscosity. Analysis of the obtained results indicates limitations of the propane use for maintaining the required oil viscosity which implies a necessity of using hydrocarbons and oil fractions with higher boiling points. In this connection in the pilot CSP project, the propane–butane mixture is used as a solvent and other solvents are further assessed.

The Nsolv process involves the injection of a pure, heated solvent vapor into a bitumen reservoir. Its main advantage is a possibility of realization in the reservoirs of small thickness. Moreover, the capital investments have been reduced by more than 40% compared to the SAGD technology, mainly due to the absence of necessity of using steam generators and water treatment plants. It is also stated [13] that the oil viscosity, coking ability and metal contents are decreased in the Nsolv process due to partial upgrading of oil in reservoir. The technology enhanced solvent extraction incorporated electromagnetic heating (ESEIEH) it comprises solvent injection with preliminary electromagnetic heating of the reservoir using low-frequency radio waves is carried out. The emitters in the wellbores generate electromagnetic waves and

after the heating the solvent is introduced. At use of the pure solvent, the development of productive deposits of small thickness is possible. No water is required in this case, and capital investments, operational costs and total energy costs are significantly reduced (up to 85%). The experience shows that the dissolving mixtures injected into the deposits should be mostly gaseous in order to fill the free pore volume formed as a result of development using primary methods. Moreover, the dissolving mixtures should have good oil solubility and should be readily available and relatively not expensive.

At use of light alkane hydrocarbons as solvents one must take into the account the data about asphaltenes precipitated in the oil-saturated reservoir and should develop methods of inhibiting the precipitation [14]. The possible methods of preventing asphaltene precipitation are the addition of aromatic compounds or use of asphaltene stabilizers (inhibitors). In various periods many investigators have analyzed the *in vitro* effect of the various chemical compounds on precipitation of asphaltenes in oils and model asphaltene systems [15–20]. For example, in the paper [21] the effect of three groups of additives on asphaltene precipitation was studied: aromatic compounds, heteroatom compounds (O, S, N) and hydrogen donor solvents (tetraline, decaline). It was established that all additives except nitrogen-containing compounds have a trend to inhibit asphaltene precipitation. In the toluene-naphthalene-phenanthrene the molecular weight increases additive efficiency. The isomers of toluene and xylene dissolve asphaltenes, xylene being more effective than toluene. Nonylphenol is more effective than toluene and xylene isomers due to its alkyl chain and polar hydroxyl group. The paper [22] demonstrates that asphaltenes do not precipitate when the ratio of alkanes to aromatic compounds is below 7 and if this value exceeds 8 there is a possibility of asphaltene precipitation.

Depending on chemical and structural characteristics of asphaltene precipitation inhibitors and oil characteristics (resin, asphaltenes and aromatics contents) their efficiency may be different [23]. It is suggested to use both natural inhibitors such as oil resins and deasphalted oils [24], and synthetic amphiphiles based on alkyl phenols, alkyl benzene and alkyl sulfonic acids [21, 25, 26] as asphaltene inhibitors.

Apart from the contents of the solvent and collector properties, these processes should take into the account various factors such as a ratio of resins and asphaltenes in the oil [27–29], contents of the asphaltenes themselves [30], the presence of water, clay, etc. [31–35].

In order to understand the asphaltene precipitation processes in the reservoir upon injection of light alkane-based solvents, it is necessary to carry out physical modeling using specifically selected methodological approaches [36–38].

In this chapter, we used a special stand for physical modeling of the heavy oil displacement process from the reservoir. An experimental evaluation of light alkanes solvents injection options in a reservoir model for heavy oil extraction has been carried out. We compared amount and composition of displaced and residual oil and investigated the distribution of precipitated asphaltenes in the sandstone after oil displacement. Additives to prevent asphaltene precipitation in a porous medium were selected and their minimum required amount in the composition of the displacement solvent was determined. Using the increased size model of reservoir allows to obtain more accurate data on the dynamics of oil production during the experiment.

2. Materials and methods

2.1. Physical modeling of heavy oil displacement from the porous medium using the large oil reservoir model

To model oil displacement processes, we used Ashalchinskoye field HOs. Density, viscosity and composition are presented in **Table 1**. Asphaltenes were precipitated from petroleum by 20-fold volume excess of n-hexane. After 24 h, the obtained precipitate was filtered and washed with boiling n-hexane in Soxhlet apparatus up to decolorization of flowing solvent to remove as much maltenes as possible. Solvent from maltenes solution was removed up to a constant weight using rotary evaporator. Maltenes were separated into Saturates, Aromatics and Resins through the adsorption method on silica using n-hexane for Saturates, Aromatics and isopropanol:benzene (1:1 v/v) for Resins according to the known procedure (ASTM, 1993) [39].

The physical modeling of the oil displacement processes by hydrocarbon solvents was carried out using a laboratory model which was a transparent cell made out of an acrylic glass with the inner chamber dimensions of 450 × 450 × 20 mm [40, 41].

A mixture of heavy oil (**Table 1**) and sand (fraction 0.250–0.315 mm) was prepared prior to each experiment. The displacement process was carried out at 20°C by injecting the solvent into the cell via the upper opening at the constant excess pressure of 1563.1 Pa (0.0154 atm) provided by stable liquid level in the metering vessel. n-Hexane as a model basic solvent (one of the main component of distillate fractions, use of which is possible in oil refineries) and also additives of toluene and nonylphenol (product of PJSC “Nizhnekamskneftekhim”) were used. The samples of the displaced HO mixed with solvent were sampled via the bottom opening. The test samples (HO and solvent mixtures) were sampled starting from ≈5.5 hours after the solvent was injected into the reservoir model; further, the fluid sampling was carried out with 1-hour intervals. Duration of each experiment was 16 hours. For all of the solvents the accumulated oil recovery, oil percentage in the recovered HO + solvent mixture, amount of residual oil in the reservoir model after displacement and asphaltenes contents in it were assessed. After each of the experiments, the residual oil was removed from the model and separated into nine identical sectors (**Figure 3**). In order to remove the residual oil the sand from each of the sectors was separately washed by benzene several times with subsequent solvent evaporation till constant weight. The asphaltenes were precipitated from the oil by the 20-fold excess volume of n-hexane according to the aforesaid technique.

| Density, g/cm ³ , 20°C | Viscosity, mm ² /s, 20°C | Composition, wt% | | | |
|-----------------------------------|-------------------------------------|------------------|-----------------------|--------|------------------------|
| | | Asphaltenes | Saturates + Aromatics | Resins | Light fractions <200°C |
| 0.9540 | 3083 | 6.3 | 61.1 | 3.8 | 1.8 |

Table 1. Density, viscosity and composition of Ashalchinskoye field HOs.

2.2. Preparation of model oils with various asphaltene contents and physical modeling of their displacement by solvents from a porous medium

Asphaltenes (A0) of the Ashalchinskoye field HOs obtained at the separation of deasphalted oil were fractionated into two fractions, A1 and A2, by selected toluene/hexane mixture at a ratio of 35/65% v/v [30, 42]. After this, the “common” asphaltenes A0, and asphaltenes of the A1 and A2 fractions were mixed with deasphalted oil in the same ratio they were present in the natural oil. Therefore, three artificial model oils were obtained differing only in contents and structure of asphaltenes (Table 2).

The comparative analysis of chemical contents and structure of A0, A1 and A2 isolated from the HO was carried out using various investigation methods.

Investigation of the molecular weights of the asphaltenes was carried out using the UltraFlex III mass spectrometer (Bruker, Germany) with time-of-flight (TOF) detector using the Matrix-activated laser desorption and ionization (MALDI) method, using 1,8,9-trihydroxyanthracene as a matrix.

IT spectra of the asphaltenes were recorded in the 4000–400 cm^{-1} range using the Tensor-27 Fourier IT spectrometer (Bruker, Germany) with the optical resolution of 4 cm^{-1} . The asphaltenes were first ground in a mortar with KBr powder, and a pellet was made from the obtained mixture using a hand press. The obtained values of the intensities allowed for calculating the aromaticity spectral coefficients (Arom = $D_{1600}/D_{720} + 1380$ – reflects the percentage of C=C bonds in aromatic fragments relative to the C-H bonds in the aliphatic structures), aliphaticity (Al = D_{1450}/D_{1600} – reflects the percentage of C-H bonds in aliphatic fragments relative to the aromatic C=C bonds); condensation (Cond = $D_{1600}/D_{740} + 860$ – reflects the percentage of C-H bonds in the aromatic structures); oxidation (Ox = D_{1700}/D_{1600} reflects the personage of carbonyl groups R-C=O at the presence of OH group) [43].

Thermal stability and possible phase transitions of the starting asphaltenes A0 and also of the isolated A1 and A2 fractions were assessed using combined thermogravimetry (TG) and differential scanning calorimetry (DSC) methods using the STA 449 CJupiter thermal analyzer (Netzsch, Germany) in the argon atmosphere with total flow of 50 ml/min in the temperature range of 30–800°C. The heating rate was 10°C/min. The weight of the sample was 6–7 mg.

Measurements of the stable free radical (SFR) and vanadyl complexes (VC) contents were carried out using the SE/X-2544 EPR spectrometer (RadioPan, Poland) under the same conditions at room temperature. At determination of SFR and VC contents in the studied samples

| Sample | Composition | Viscosity, mm^2/s , 50°C |
|--------------|----------------------------------|--|
| Model oil A0 | Deasphalted oil + asphaltenes A0 | 966.8 |
| Model oil A1 | Deasphalted oil + asphaltenes A1 | 1054.7 |
| Model oil A2 | Deasphalted oil + asphaltenes A2 | 647.6 |

Table 2. Composition and properties of model oils.

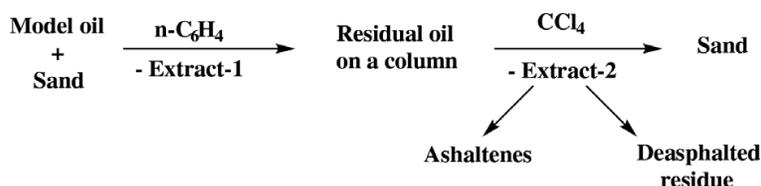


Figure 1. The general scheme of experiments on the displacement of model oils.

ampoules with 3 mm inner diameter out of molybdenum glass that did not produce a visible signal in the EPR spectrum were used. The ampoules were densely filled with asphaltenes 13–14 mm in height. The intensity of the stable free radical line was determined using the amplitude of the single line in the EPR spectrum center ($g = 2.003$). In order to calculate the intensity of the vanadyl complexes lines the amplitude of the +1/2 line that is near the SFR line in the weaker magnetic field area was determined. The intensity of the SFR and VC signals of the studied samples was discounted to the sample weights.

Vanadium and nickel concentrations in oils and asphaltenes were measured by means of direct flame atomic absorption spectrometry using AAS-1 N spectrophotometer (Carl Zeiss Jena, Germany), with approved standard samples of metal concentration in oil products used as blank solutions.

The experimental displacements of the model oils A0, A1 and A2 in the porous medium by n-hexane were carried out using a 3×100 cm glass column wherein the oil + sand mixture (fraction 0.25–0.35 mm, oil saturation 10%). Further, the 3 pore volumes of hexane at 20°C were passed by injecting the solvent through the upper opening of the tube at the constant excess pressure of 1563.1 Pa (0.0154 atm) provided by stable liquid level in the metering vessel, and 5 cm^3 samples were sampled. After 3 pore volumes of hexane were passed, additional displacement of the residual oil from the model was carried out by hexane until full disappearance of coloration of the solvent passing through the column (Extract 1). The asphaltene concentrates precipitated in the porous volume were extracted by washing (extraction) from the column by tetrachloromethane (Extract 2). Then the solvent was evaporated from Extract 2, the remainder was dried in vacuo until constant weight and was dissolved in small amount of toluene for further isolation of asphaltenes by 20-fold excess n-hexane. The general scheme of experiments on the displacement of model oils is outlined in **Figure 1**.

3. Results and discussion

3.1. Physical modeling of the process of HO displacement from the reservoir by n-hexane

At modeling the HO recovery processes from the reservoir using solvents, the experiment results were represented in the form of diagrams of plots of Cumulative oil recovery and oil percentage in the recovered HO + solvent mixture vs. time. The experiments were carried out under the 10% oil saturation of the sand (**Figure 2**).

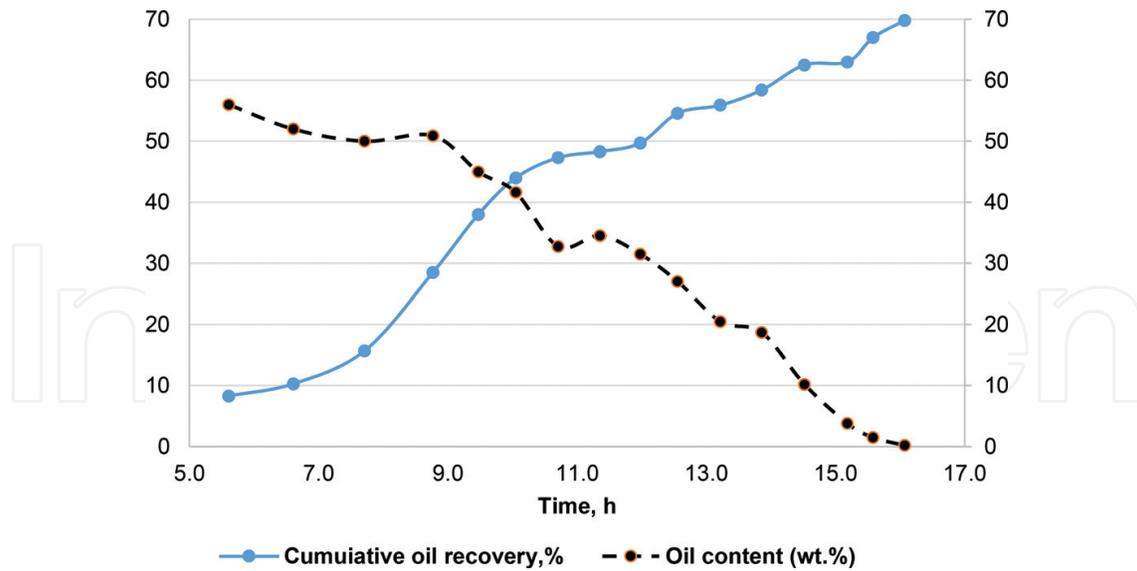


Figure 2. Cumulative oil recovery and oil content in the recovered HO + solvent mixture at carrying out the displacement experiments by hexane.

The results of experiments indicate the following supposed mechanism of the oil recovery by solvent based on n-hexane. At the first step, increased oil yield was noted from the model with a maximum rate which stabilizes over some time. The stabilization of the oil yield from the model occurs at the transition of the displacement mode from the dispersion (affected by gravity force) to diffusion (in a peripheral area). Regarding the content of asphaltenes in the residual oil, for all 9 samples from various model sectors higher values are indicated compared to the starting bitumen (**Figure 3, Table 1**).

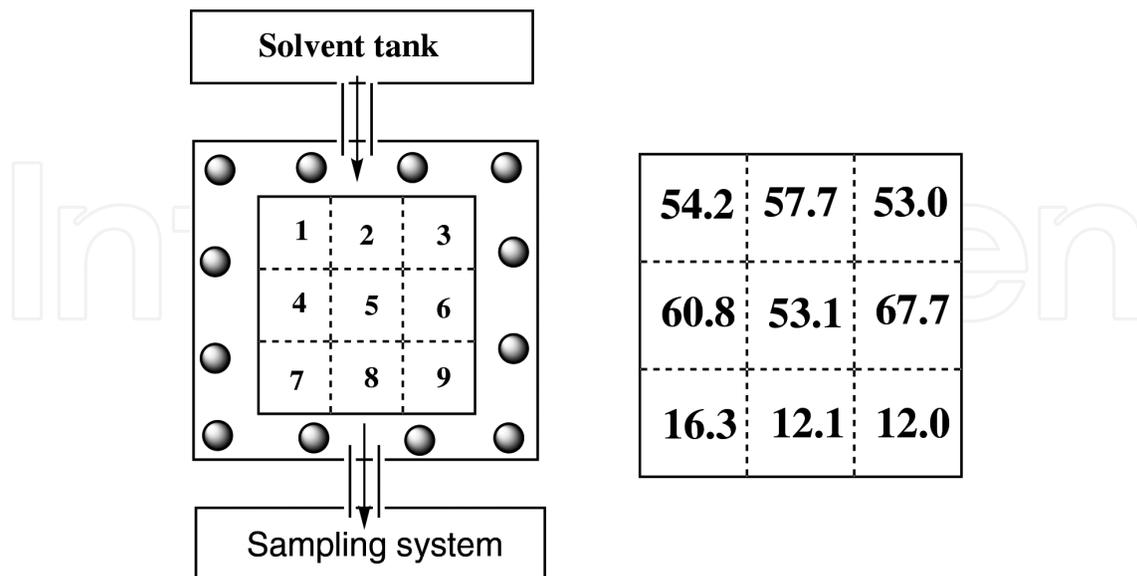


Figure 3. Scheme of an experimental setup of modeling the physical and chemical effect of solvents on the oil-saturated reservoir and the asphaltene amount (wt%) in the residual oil by cell sectors.

It was found that the highest asphaltene concentration in the residual oil is detected in upper sectors where the starting step of the oil displacement occurs and where the oil contacts the pure solvent (**Figure 3**). Hexane alters the solubility of asphaltenes in oil because light saturated hydrocarbons affect the interaction of asphaltenes and resins destabilizing the asphaltenes [28, 29]. Introduction of aromatic compounds in the system may positively affect the stability of asphaltenes in the system [20, 23–26] because the asphaltenes have a polyaromatic structure.

3.2. Investigation of the effect of fractional asphaltene contents in the HO on the recovery process by n-hexane

In order to identify the features of supermolecular structure formation in the porous medium depending on the fraction contents of the asphaltenes, the approach was used that allows discovering the content and a number of other oil components. The natural object, heavy oil of the Ashalchinskoye field, was separated into the deasphalted oil (maltenes) and A0 asphaltenes, from which by fractioning the two fractions were isolated, the so-called A1 fraction (“island” type), the part of the asphaltenes characterized by highest condensation, and the A2 fraction (“archipelago” type), which is regarded to be as less condensed, comprising larger number of heteroatoms and alkyl substituents [42, 44, 45]. Then the obtained “common” A0 asphaltenes, the A1 and A2 asphaltene fractions were mixed with deasphalted oil at the same ratio as they are present in the natural oil (**Table 2**).

In order to enable a possibility of quantitative production of the asphaltene fractions and their characterization by physical and chemical investigation methods and also in order to obtain a sufficient amount of model oils and carrying out modeling of the oil displacement from porous medium by n-hexane, it was necessary for the A0 asphaltenes to be separated into fractions in the ~ 50:50% ratio. Experimentally in the 25 to 40% range, the ratio of the solvent (toluene) to precipitant (hexane) was found equal to 35%. As a result of fractioning the A1 and A2 asphaltene fractions were obtained at the ratio of 51:49%. The A1 asphaltene fraction isolated at various toluene percentage in the precipitant was characterized by a number of physical and chemical methods: EPR with determination of SFR and VC contents, spectrophotometry with determination of specific light absorption coefficient (K_{1a}), atomic absorption spectroscopy with determination of vanadium and nickel contents (**Table 3**) and also IR spectroscopy (**Table 4**) and elemental analysis (**Table 5**).

In accordance with the obtained results, at increase in toluene percentage from 25 to 40% in the mixture with hexane the decrease in the A1 fraction yield occurs from 62 to 39.5 wt%, correspondingly (**Table 3**). Thereby, as the toluene percentage in the hexane mixture increases, the gradual increase of vanadium, nickel, SFR, VC and specific K_{1a} occurs in contents of the A1 asphaltenes. According to FTIR data (**Table 4**), the A1 asphaltenes at their precipitation from the mixture of hexane with toluene are characterized by the increase in the aromaticity and condensation coefficients, decrease in the aliphaticity and oxidation coefficients. Elemental contents data demonstrate that as the toluene percentage increases, the carbon content insignificantly increases in the asphaltenes while hydrogen content decreases. As a whole,

| Amount of toluene in the mixture, % vol | Yield A1, wt% | V, wt% | Ni, wt% | VC*, ×10 ¹⁸ rel.sp/g | SFR**, ×10 ¹⁸ rel.sp/g | SFR/VC | K _{1a} *** |
|---|---------------|--------|---------|---------------------------------|-----------------------------------|--------|---------------------|
| 25 | 62.0 | 0.220 | 0.0278 | 33.8 | 122 | 3.61 | 76.26 |
| 30 | 52.1 | 0.225 | 0.0278 | 34.4 | 126 | 3.66 | 77.20 |
| 35 | 51.0 | 0.235 | 0.0285 | 35.0 | 124 | 3.54 | 78.91 |
| 40 | 39.5 | 0.240 | 0.0291 | 35.1 | 132 | 3.76 | 79.30 |

*VC=Vanadyl complexes.
 **SFR = Stable free radicals.
 ***K_{1a} = light absorption coefficient.

Table 3. Fraction yield, contents of metals, paramagnetic centers, VC, K_{1a} value for A1 asphaltenes isolated at various toluene content in hexane.

| Amount of toluene in the mixture, % vol | Arom | Cond | Al | Ox |
|---|------|------|------|------|
| 25 | 0.43 | 1.15 | 2.39 | 0.18 |
| 30 | 0.46 | 1.19 | 2.37 | 0.17 |
| 35 | 0.47 | 1.25 | 2.33 | 0.17 |
| 40 | 0.50 | 1.26 | 2.34 | 0.15 |

Table 4. Structural-group composition of A1 according to FTIR data with different toluene content in hexane.

| Amount of toluene in the mixture, % vol | C, % | H, % | N, % | S, % | C/H |
|---|-------|------|------|------|-------|
| 25 | 72.69 | 7.24 | 2.46 | 5.28 | 10.04 |
| 30 | 75.44 | 7.45 | 2.66 | 5.16 | 10.13 |
| 35 | 75.86 | 7.46 | 2.92 | 5.01 | 10.16 |
| 40 | 77.58 | 7.61 | 3.11 | 5.63 | 10.19 |

Table 5. Elemental composition of A1 with different toluene content in hexane.

differences between the asphaltenes A1 obtained by using 25 and 40% toluene are quite significant in all elemental analysis parameters (**Table 5**).

In order to find out the main structural differences of the A0 asphaltenes and A1 and A2 fractions, the comparative analysis of data of some physical and chemical investigation methods was carried out (**Tables 6–9**).

Analysis of EPR, spectrophotometry and atomic absorption spectrometry data allowed for identifying a number of principal differences in the asphaltene fractions (**Table 6**). Thus, from the A1 fraction higher values of all parameters, K_{1a}, vanadium, nickel, SFR and VC contents were found. The least difference in the values is found in the VC content which does not exceed 10%. In all other parameters, the observed value difference is 1.6 to 1.9 fold.

| Sample | V, wt% | Ni, wt% | VC, $\times 10^{18}$ rel.sp./g | SFR, $\times 10^{18}$ rel.sp./g | SFR/VC | K_{ia} |
|--------|--------|---------|--------------------------------|---------------------------------|--------|----------|
| A0 | 0.185 | 0.0232 | 33.8 | 100 | 2.96 | 60.28 |
| A1 | 0.235 | 0.0285 | 35.0 | 124 | 3.54 | 78.91 |
| A2 | 0.120 | 0.0161 | 30.8 | 69 | 2.24 | 49.79 |

Table 6. Results of determining the contents of metals, SFR, VC and also K_{ia} for the asphaltenes.

At comparison of the molecular weight of the asphaltenes the value of the average molecular weight is used that, according to the MALDI mass spectra, is equal to 1600 and 1200 amu for the asphaltenes of the A1 and A2 fractions, correspondingly, and for the A0 asphaltenes the value of 1400 amu is found.

Thermal stability and possible phase transitions for A0 asphaltenes and isolated A1 and A2 fractions were assessed by the combined thermogravimetry (TG) and differential scanning calorimetry (DSC) methods (**Table 7**). The threshold temperature of the intimation of intensive thermal destruction of A1 and A2 fraction asphaltenes in significant degree are determined by their structural features: ratio of naphthene-aromatic and fused aromatic structures. For the A1 fraction, the higher condensation degree is characteristics than for the A2 fraction and contents of the alkyl substituents in the A2 asphaltene fraction molecules is higher than in the A1 asphaltene fraction molecules (**Table 8**). This factor mostly determines thermal stability of the asphaltenes. Intensive weight loss begins in the A1 asphaltene fraction at 436°C and in the A2 fraction at 360°C. The temperature of half weight loss for the A1 and A2 asphaltene fraction is 501.6 and 470.2°C, correspondingly, and for the A0 asphaltene fraction it has an intermediate value of 493.0°C. Also, the characteristic feature of the A1 asphaltene fraction compared to A2 is a higher yield of residue (coke) after heating to 800°C.

Most of the parameters allow for identifying the asphaltene fractions reflecting specifics of their structural features. Thus, from the A2 asphaltene fraction higher values of aliphaticity

| Sample | Loss of mass in the temperature range (°C),% | | | | | | | | The temperature of half weight loss, °C | Yield of residue, % |
|--------|--|---------|---------|---------|---------|---------|---------|---------|---|---------------------|
| | 30–100 | 100–200 | 200–300 | 300–400 | 400–500 | 500–600 | 600–700 | 700–800 | | |
| A0 | 0.36 | 1.12 | 1.94 | 5.99 | 41.98 | 4.92 | 4.96 | 4.99 | 493.0 | 33.74 |
| A1 | 1.15 | 3.86 | 0.98 | 4.74 | 39.03 | 4.17 | 1.59 | 1.02 | 501.6 | 43.46 |
| A2 | — | 2.79 | 6.25 | 9.57 | 40.58 | 3.62 | 1.10 | 0.63 | 470.2 | 35.46 |

Table 7. Results of thermal analysis for the asphaltenes and for their A1 and A2 fractions.

| Sample | Arom | Cond | Al | Ox |
|--------|------|------|------|------|
| A0 | 0.46 | 1.33 | 2.44 | 0.23 |
| A1 | 0.53 | 1.73 | 2.32 | 0.16 |
| A2 | 0.44 | 1.24 | 2.76 | 0.25 |

Table 8. Structural-group composition of samples according to FTIR data.

| Sample | C, % | H, % | N, % | S, % | C/H |
|--------|-------|------|------|------|------|
| A0 | 78.42 | 8.13 | 2.08 | 4.43 | 9.65 |
| A1 | 75.41 | 7.75 | 2.91 | 3.45 | 9.79 |
| A2 | 72.48 | 7.64 | 1.79 | 6.05 | 9.49 |

Table 9. Elemental analysis data for the asphaltenes and for their A1 and A2 fractions.

and oxidation are found. At the same time for the A1 asphaltene fraction higher condensation and aromaticity can be noted (**Tables 8 and 9**).

As a result of performed experiments, it was found that at the displacement of the A1 model oil with n-hexane the number of supermolecular asphaltene-resin structures formed in the porous medium is more than 2-fold higher compared to the A2 model oil. The asphaltene content in such asphaltene-resin concentrates differs insignificantly for the A1 and A2 oils, 74.5 and 61.1 wt% correspondingly. Thereby in the case with model A1 oil, the main weight (59%) of the asphaltenes present in the oil remains in contents of the asphaltene concentrates formed in the porous medium. For the A2 oil, this parameter is much lower, just 18.9% (**Table 10**).

The identified features of asphaltene precipitate formation in the porous medium affect dynamics and the oil recovery rate. Thus, for the A2 model oil maximum oil recovery rate is observed at displacement with hexane (**Figure 4**).

As a whole, at the comparison of the A1 and A2 asphaltenes obtained after oil displacement the analogous picture is observed as for the starting asphaltenes A1 and A2. For the A1 asphaltenes higher contents of vanadium, nickel, vanadyl complexes and also K_{1a} are observed; however, the SFR content in the A2 asphaltenes is significantly higher (**Table 11**). In most cases, the values of the analyzed parameters remarkably differ at the comparison of the starting asphaltene fractions and those formed after oil displacement. Therefore, contents and

| Sample | Asphaltenes in Extract-2, wt % | Asphaltenes percentage in the Extract-2 vs. potential content in the starting oil, wt% |
|--------------|--------------------------------|--|
| Model oil A0 | 70.9 | 45.7 |
| Model oil A1 | 74.5 | 59.0 |
| Model oil A2 | 61.1 | 18.9 |

Table 10. Results of displacement of model oils with n-hexane from the porous medium (asphaltenes percentage in the extract 2 vs. potential content in the starting oil, wt%).

| Sample | V, wt% | Ni, wt% | VC, $\times 10^{18}$ rel.sp./g | SFR, $\times 10^{18}$ rel.sp./g | K_{1a} |
|--------|-------------|--------------|--------------------------------|---------------------------------|-------------|
| A0 | 0.185/0.160 | 0.0232/0.020 | 33.8/22.5 | 100/116 | 60.28/56.04 |
| A1 | 0.235/0.175 | 0.0285/0.025 | 35.0/31.4 | 124/116 | 78.91/70.87 |
| A2 | 0.120/0.165 | 0.0161/0.021 | 30.8/30.9 | 69.0/163 | 49.79/60.38 |

Table 11. Contents of metals, paramagnetic centers, VC, K_{1a} values for the asphaltenes isolated from the starting model oils and sediments formed after the oil displacement process with hexane (model oil/extract 2).

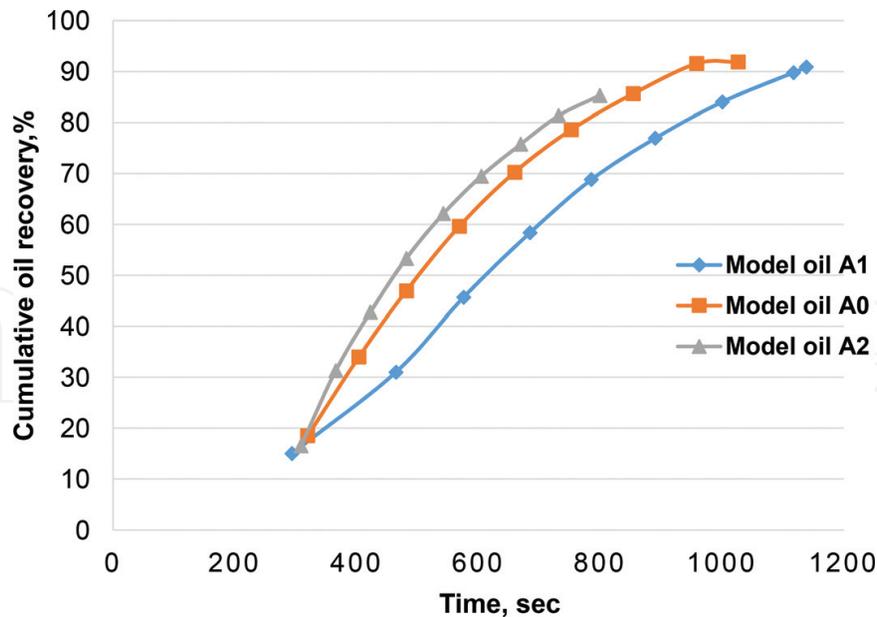


Figure 4. Cumulative oil recovery at the displacement of model oils with n-hexane from the porous medium.

properties of the asphaltenes formed during displacement of heavy oil in the porous medium by n-alkanes differ from the starting asphaltenes. Thereby, from the high molecular weight asphaltene fraction, A1, this trend has insignificant changes whereas for the A2 fraction significant increase is observed. This fact allows for supposing that during oil displacement process in case of the A2 asphaltenes their further fractioning occurs in the porous medium, as a result of which higher molecular weight asphaltene concentrates are formed compared to the starting asphaltenes.

3.3. Physical modeling of the HO displacement process with n-hexane with additives inhibiting precipitation of asphaltenes on a large oil reservoir model

The primary function of asphaltene stabilizers in the oils is played by resins forming solvate shells that prevent asphaltene precipitation. When the solvate shells are dissolved by saturated hydrocarbons, the asphaltenes precipitate. Therefore, in order to stabilize the oil + solvent mixtures one can use the additives of oil resins, synthetic alkyl phenols or aromatic compounds which are asphaltene solvents.

In order to increase the colloidal stability of the asphaltene components of the Ashalchinskoye HO field during its displacement with n-hexane, an experimental selection of chemical additives was carried out (sand fractions 0.250–0.35 mm, oil saturation 10%, temperature 20°C).

Originally, toluene and nonylphenol were used as an additive for the main solvent to decrease the amount of asphaltene residue. Moreover, the preliminary injection of free toluene was tested with subsequent injection of n-hexane. In this case, the toluene to n-hexane ratio was 5 and 95% correspondingly. As a result of experiments, the cumulative oil recovery was assessed (in percents to the oil contained in the model cell) over time (**Figure 5**).

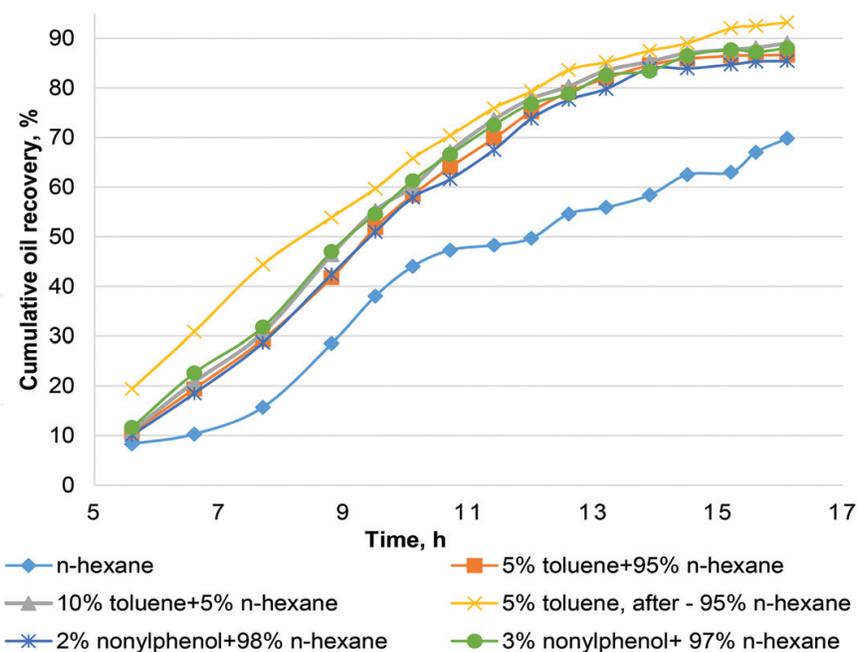


Figure 5. Cumulative oil recovery at carrying out the experiments on HO displacement with various solvents.

Use of toluene and nonylphenol mixed with n-hexane at displacement significantly affects alteration of total oil recovery and oil content in the extracted products. The cumulative oil recovery at HO displacement only with n-hexane is 69.8% whereas the addition of 5 and 10% toluene to n-hexane increases the accumulated oil recovery to 86.6 and 89.0% correspondingly. Use of nonylphenol gives the values of cumulative oil recovery comparable with those with toluene use of 85.4 and 88.0% for 2 and 3% nonylphenol in n-hexane, correspondingly. The highest oil recovery (93.2%) from the reservoir model is achieved when toluene is injected prior to n-hexane at 5:95 toluene–hexane ratio.

After each experiment, the residual oil was extracted from the model separately in each of the nine sectors by benzene extraction. An amount of asphaltenes in the residual oil samples was measured (**Figure 6**).

At use of n-hexane for the oil displacement, in the residual oil on average 50 to 60 wt% asphaltenes is contained. The asphaltene content is significantly lower in the lower part of the model cell, which is on average about 12 to 16 wt%. The results show that use of the compositions based on n-hexane with toluene and nonylphenol allows for significantly decreasing the asphaltene contents in the residual oil compared to the using of n-hexane only. For the 10 wt% toluene or 3 wt% nonylphenol in the mixture with n-hexane the asphaltene contents in the residual oil in the lower part of the model cell is on average less than 10 wt% what insignificantly exceeds their contents in the starting oil. Use of such method as pre-injection of toluene prior to injecting the base solvent allows for achieving even higher inhibition of asphaltenes in the residual oil. In this case, the amount of toluene used is only 5% of the total solvent amounts, which finally allows for significantly decreasing its consumption and, as a consequence, improves the project economy.

| | | | | | | | | |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| 54.2 | 57.7 | 53.0 | 30.7 | 37.7 | 33.0 | 29.5 | 34.9 | 28.4 |
| 60.8 | 53.1 | 67.7 | 30.6 | 44.6 | 43.7 | 29.0 | 26.3 | 19.6 |
| 16.3 | 12.1 | 12.0 | 8.9 | 10.5 | 8.6 | 7.9 | 11.3 | 7.3 |
| a | | | b | | | c | | |
| 10.4 | 11.6 | 14.0 | 38.7 | 43.7 | 43.0 | 26.9 | 33.3 | 27.4 |
| 14.1 | 14.0 | 15.4 | 36.6 | 49.6 | 48.7 | 25.2 | 28.1 | 26.5 |
| 7.0 | 8.7 | 7.4 | 10.9 | 12.5 | 12.6 | 8.9 | 10.3 | 8.6 |
| d | | | e | | | f | | |

Figure 6. Changes in the amount of asphaltenes in residual oil for different solvent used. (a) n-hexane, (b) 5% toluene +95% n-hexane, (c) 10% toluene +90% n-hexane, (d) 5% toluene, after – 95% n-hexane, (e) 2% nonylphenol +98% n-hexane, (f) 3% nonylphenol +97% n-hexane.

The increased asphaltene contents observed in all of the performed experiments at transition from the upper part of the model to the lower ones can be explained by the fact that at the beginning of each experiment upon the oil contact with solvent asphaltene precipitation occurs and then the solvent is enriched by deasphalted oil that facilitates decrease in the precipitate amount in the residual oil.

If one refers to the distribution of the asphaltene contents in horizontal, at the use of pure n-hexane, in the side parts of the model, where the slow diffusion process occurs, an elevated content of asphaltenes is observed compared to the central part of the model where the contact of the oil with n-hexane occurs faster. Upon addition of nonylphenol and toluene to n-hexane aligning of asphaltene contents in the residual oil in the neighboring model segments is observed and achievement of better encompassing of the model porous medium by a solvent.

Natural inhibitors acting as solvating agents are also effective; they, in contrast to the aromatic solvents are compliant with ecological safety regulations. These are oil resins and deasphalted oil [23, 46, 47].

Earlier in our paper [48] we have carried out a comparative analysis of various methods for assessing the efficiency of asphaltene precipitation stabilizers for Ashalchinskoye field HOs. According to the results of performed studies, it was established that the deasphalted oil of Ashalchinskoye field HOs is quite an effective stabilizer of asphaltene precipitation, which is not inferior to the aromatic hydrocarbons. The oil resins as asphaltene precipitation inhibitors differ insignificantly in efficiency from expensive synthetic products. It was established that the percentage of benzene resins of not above 6.5% per hexane volume allows for fully

providing asphaltene stabilization during heavy oil displacement process. Also, it was found that alcohol-benzene resins at normal conditions are not the effective asphaltene precipitation inhibitors.

4. Conclusions

In modeling, the oil displacement process by injecting n-hexane, the influence of the molecular weight and condensation of asphaltenes on parameters of their deposition in a porous medium is shown. It was revealed that features of structural and group composition of heavy oil asphaltenes affect the dynamics and completeness of oil extraction. Under the same conditions, the process of displacement of model oil with low molecular weight asphaltenes makes it possible to achieve almost 5% more accumulated oil recovery than that for high molecular weight asphaltenes.

In a separate series of experiments, it was shown that the composition and properties of asphaltenes formed during the displacement of heavy oil in a porous medium by n-alkanes differ from that of the initial condition of asphaltenes. Herewith for the fraction of high-molecular-weight asphaltenes A1 this trend is weak, while for fraction A2 it is pronounced significantly. This fact suggests that in the process of oil displacement the less condensed asphaltenes A2 undergo additional fractionation in a porous medium, resulting in higher molecular weight asphaltene concentrates in comparison with the initial asphaltenes.

As a result of several experiments for the physical modeling of heavy oil displacement in porous medium in a large-sized model, the opportunities of using various composite solvents based on n-hexane with toluene and nonylphenol additives were assessed.

By taking the example of the Ashalchinskoye field heavy oil, we have shown that accumulated oil recovery by n-hexane only appears at the level of 69.8%, whereas adding the toluene in 5–10 or 2–3% nonylphenol amount rises the recovery to 85–89%. The largest oil recovery (93.2%) from the reservoir model is achieved when toluene is injected prior to n-hexane (5% of toluene relative to the volume of n-hexane).

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References

- [1] Rassenfoss S. A tricky Tradeoff - can adding a little solvent yield a lot more heavy crude? *Journal of Petroleum Technology*. 2012;6:58-64. DOI: 10.2118/0612-0058-JPT

- [2] Orr B. ES-SAGD: Past, Present, and Future. SPE 129518. 2009. DOI: 10.2118/129518-STU
- [3] Boone T. An Integrated Technology Development Plan for Solvent-Based Recovery of Heavy Oil. SPE 150706. 2011. DOI: 10.2118/150706-MS
- [4] Stark S. Increasing Cold Lake Recovery by Adapting Steam flood Principles to a Bitumen Reservoir. SPE 145052. 2011. DOI: 10.2118/145052-MS
- [5] Gupta S, Gittins S. Semi analytical Approach for Estimating Optimal Solvent Use in Solvent Aided SAGD Process. SPE 146671. 2011. DOI: 10.2118/146671-MS
- [6] Edmunds N, Maini B, Peterson J. Advanced solvent-additive processes by genetic optimization. *Journal of Canadian Petroleum Technology*. 2010;**49**:34-41. DOI: 10.2118/140659-PA
- [7] Sharma J, Gates I. Dynamics of Steam-Solvent Coupling at the Edge of an ES-SAGD Chamber. SPE 128045. 2010. DOI: 10.2118/128045-MS
- [8] Gates I. Design of the Injection Strategy in Expanding-Solvent Steam Assisted Gravity Drainage. In: Paper at the Second CDEN International Conference on Design Education, Innovation, and Practice Kananaskis; 18–20 July; Alberta, Canada; 2005. DOI: 10.24908/pceea.v0i0.3888
- [9] Yakubov M, Amerkhanov M, Khisamov R, Khanipova Y. World experience of solvents injection for extraction of heavy oil and solvent-based processes potential in TATNEFT PJSC heavy oil fields. *Oil Industry*. 2017;**2**:78-81. DOI: 10.24887/0028-2448-2017-2-78-81.
- [10] Jamaloei B, Dong M, Mahinpey N, Maini B. Enhanced cyclic solvent process (ECSP) for heavy oil and bitumen recovery in thin reservoirs. *Energy and Fuels*. 2012;**26**(5):2865-2874. DOI: 10.1021/ef300152b
- [11] Jiang T, Zeng F, Jia X, Gu Y. A new solvent-based enhanced heavy oil recovery method: Cyclic production with continuous solvent injection. *Fuel*. 2014;**115**:426-433. DOI: 10.1016/j.fuel.2013.07.043
- [12] Jia X, Zeng F, Gu Y. Gasflooding-assisted cyclic solvent injection (GA-CSI) for enhancing heavy oil recovery. 2015;**140**:344-353 DOI: 10.1016/j.fuel.2014.09.066
- [13] Krawchuk P. Development and Operation of the Nsolv BEST Demonstration. Paper WHOC16–135 presented at the World Heavy Oil Congress 2016, Calgary, Alberta, 6–9 September, 2016
- [14] Yakubov M, Yakubova S, Borisov D, Gennady Romanov G, Yakubson K. Asphaltene Precipitation Inhibitors and Phase Behavior Control for Bitumen Recovery by Solvent Injection. Canada. Society of Petroleum Engineers; 2014. p. 1913-1918. DOI: 10.2118/170165-MS
- [15] Yarranton H, Masliyah J. Molar mass distribution and solubility modeling of asphaltenes. *Alche journal*. 1996;**42**(12):3533-3543. DOI: 10.1002/aic.690421222
- [16] Tojima M, Suhara S, Imamura M, Furuta A. Effect of heavy asphaltene on stability of residual oil. *Catalysis Today*. 1998;**43**(3–4):347-351. DOI: 10.1016/S0920-5861(98)00163-1

- [17] Rogel E. Theoretical approach to the stability of visbroken residues. *Energy and Fuels*. 1998;**12**(5):875-880. DOI: 10.1021/ef970222r
- [18] Schabron J. The solubility and three-dimensional structure of asphaltenes. *Petroleum Science and Technology*. 1998;**16**:361-375. DOI: 10.1080/10916469808949788
- [19] Koots J, Speight J. Relation of petroleum resins to asphaltenes. *Fuel*. 1975;**54**(3):179-184. DOI: 10.1016/0016-2361(75)90007-1
- [20] Miadonye A, Evans L. The solubility of asphaltenes in different hydrocarbon liquids. *Petroleum Science and Technology*. 2010;**28**(14):1407-1414. DOI: 10.1080/10916460902936960
- [21] Ghloum E, Al-Qahtani M, Al-Rashid A. Effect of inhibitors on asphaltene precipitation for Marrat Kuwaiti reservoirs. *Journal of Petroleum Science and Engineering*. 2010; **70**(1-2):99-106. DOI: 10.1016/j.petrol.2009.10.003
- [22] Rogel E. Effect of inhibitors on asphaltene aggregation: A theoretical framework. *Energy and Fuels*. 2011;**25**:472-481. DOI: 10.1021/ef100912b
- [23] Clarke P, Pruden B. Asphaltene precipitation: Detection using heat transfer analysis, and inhibition using chemical additives. *Fuel*. 1997;**76**(7):607-614. DOI: 10.1016/S0016-2361(97)00052-5
- [24] Chang C, Fogler H. Asphaltene stabilization in alkyl solvents using oil-soluble amphiphiles. In: SPE International symposium on Oilfield Chemistry; New Orleans, Louisiana. Society of Petroleum; 2-5 March, 1993. p. 339-345. DOI: 10.2118/25185-MS
- [25] González G, Middea A. Peptization of asphaltenes by various oil soluble amphiphiles. *Colloids and Surfaces*. 1991;**52**:207-217. DOI: 10.1007/s12182-0160098-1
- [26] Kyeongseok O, Milind D. Effect of organic additives on the onset of asphaltene precipitation. *Energy and Fuels*. 2002;**16**:694-699. DOI: 10.1021/ef010223q
- [27] Guzmán R, Ancheyt J, Trejo F, Rodríguez S. Methods for determining asphaltene stability in crude oils. *Fuel*. 2017;**188**:530-543. DOI: 10.1016/j.fuel.2016.10.012
- [28] Carnahan N, Salager J, Antón R, Dávila A. Properties of resins extracted from Boscan crude oil and their effect on the stability of asphaltenes in Boscan and Hamaca crude oils. *Energy and Fuels*. 1999;**13**(2):309-314. DOI: 10.1021/ef980218v
- [29] Khvostichenko D, Andersen S. Electrodeposition of asphaltenes. 2. Effect of resins and additives. *Energy and Fuels*. 2010;**24**(4):2327-2336. DOI: 10.1021/ef900970j
- [30] Petrova L, Abbakumova N, Borisov D, Yakubov M, Zaidullin I, Romanov G. Interrelation of flocculation, precipitation, and structure of asphaltene fractions. *Chemistry and Technology of Fuels and Oils*. 2013;**49**(1):25-31. DOI: 10.1007/s10553-013-0407-y
- [31] Mukhametshina A, Kar T, Hascakir B. Asphaltene precipitation during bitumen extraction with expanding solvent steam assisted gravity drainage (ES-SAGD): Effects on pore-scale displacement. *SPE Journal*. 2016;**21**(2):380-392. DOI: 10.2118/170013-PA

- [32] Mohammadzadeh O, Rezaei N, Chatzis I. Production characteristics of the steam-assisted gravity drainage (SAGD) and solvent-aided SAGD (SA-SAGD) processes using a 2-D macroscale physical model. *Energy and Fuels*. 2012;**26**(7):4346-4365. DOI: 10.1021/ef300354j
- [33] Kar T, Ovalle C, Rogel E, Vien J, Hascakir B. The residual oil saturation determination for steam assisted gravity drainage (SAGD) and solvent-SAGD. *Fuel*. 2016;**172**:187-195. DOI: 10.1016/j.fuel.2016.01.029
- [34] Kar T, Hascakir B. The role of resins, asphaltenes, and water in water-oil emulsion breaking with microwave heating. *Energy and Fuels*. 2015;**29**:3684-3690. DOI: 10.1021/acs.energyfuels.5b00662
- [35] Kar T, Mukhametshina A, Unal Y, Hascakir B. The effect of clay type on steam assisted gravity drainage performance. *Journal of Canadian Petroleum Technology*. 2015;**54**(6):412-423. DOI: 10.2118/173795-PA
- [36] Mohammadzadeh O, Rezaei N, Chatzis I. Pore-level investigation of heavy oil and bitumen recovery using solvent – aided steam assisted gravity drainage (SA-SAGD) process. *Energy and Fuels*. 2010;**24**:6327-6345. DOI: 10.1021/ef100621s
- [37] Ahmadloo F, Asghari K, Henni A, Freitag N. Experimental investigation of capillarity and drainage height roles in the vapor extraction process. *Petroleum Science and Technology*. 2013;**31**:204-214. DOI: 10.1080/10916466.2010.525580
- [38] Yazdani A, Maini B. Modeling of the VAPEX process in a very large physical model. *Energy and Fuels*. 2008;**22**:535-544. DOI: 10.1021/ef700429h
- [39] ASTM D2007–93. Standard test method for characteristic groups in rubber extender and processing oils by the clay-gel adsorption chromatographic method. ASTM, 1993
- [40] Yakubov M, Borisov D, Sinyashin K, Amerkhanov M, Khisamov R. Physical modeling of ultraviscous oil displacement by using solvent on a large model of oil reservoir. *Journal of Petroleum Science and Engineering*. 2017;**154**:457-461. DOI: 10.1016/j.petrol.2017.02.024
- [41] Yakubov M, Borisov D, Sh R, Amerkhanov M, Khisamov R. Effect of solvent composition on heavy oil displacement while modeling. *Oil Industry*. 2014;**10**:106-109
- [42] Trejo F, Centeno G, Ancheyta J. Precipitation, fractionation and characterization of asphaltenes from heavy and light crude oils. *Fuel*. 2004;**83**:2169-2217. DOI: 10.1016/j.fuel.2004.06.008
- [43] Petrova L, Abbakumova N, Zaidullin I, Borisov D. Polar-solvent fractionation of asphaltenes from heavy oil and their characterization. *Petroleum Chemistry*. 2013;**53**(2):81-86. DOI: 10.1134/S0965544113020084
- [44] Acevedo S, Castro A, Negrin J, Fernández A, Escobar G, Piscitelli V, Dessalces G. Relations between asphaltene structures and their physical and chemical properties: The rosary-type structure. *Energy and Fuels*. 2007;**21**(4):2165-2175. DOI: 10.1021/ef070089v

- [45] Ganeeva Y, Yusupova T, Romanov G. Asphaltenenano-aggregates: Structure, phase transitions and effect on petroleum systems. *Russian Chemical Reviews*. 2011;**80**(10):993-1008. DOI: 10.1070/RC2011v080n10ABEH004174
- [46] León O, Contreras E, Rogel E, Dambakli G, Acevedo S, Carbognani L, Espidel J. Adsorption of native resins on asphaltene particles: A correlation between adsorption and activity. *Langmuir*. 2002;**18**(13):5106-5112. DOI: 10.1021/la011394q
- [47] Al-Sahhaf T, Fahim M, Elkilani A. Retardation of asphaltene precipitation by addition of toluene, resins, deasphalted oil and surfactants. *Fluid Phase Equilibria*. 2002;**194-197**: 1045-1057. DOI: 10.1016/S0378-3812(01)00702-6
- [48] Yakubov M, Yakubova S, Borisov D, Milordov D, Usmanova G, Gryznov P, Romanov G. Change in the composition and properties of asphaltene for physical modeling of processes of replacement of heavy oil-based solvent of n-alkanes. *Herald of the Kazan Technological University*. 2013;**16**(22):277-280

