Comparison of the potential of secondary and tertiary methods of influence on the formation for the production of hydrocarbon compounds from oil source rocks with high oil-generating potential

V.V. Levkina1*, A.G. Kalmykov1, T.N. Henarova2, M.S. Tikhonova1, A.V. Pirogov1, O.A. Shpigun1, A.Yu. Bychkov1
1Lomonosov Moscow State University, Moscow, Russian Federation
2A.V. Luikov Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus, Minsk, Belarus

Abstract. The work presents the comparison results of the quantitative and qualitative composition of hydrocarbon compounds that can be obtained as a result of secondary and tertiary methods of influence on organic-rich rocks (on the example of the Bazhenov Formation rocks) with a high oil-generating potential. It is shown that as a result of extraction of bitumoids presented in open pores, realisation the generation potential and the production of synthetic oil, it is possible to produce hydrocarbon compounds, the amount of which reaches 35 kg and 20 kg per 1 m³ of rock, respectively. Products possess high maturity and are identical in composition to the oil extracted from these rocks by standard technology of development. It was found that with the development of appropriate technologies of subsequent influence on the formation by secondary and tertiary methods, oil production can be significantly increased in the future.

Keywords: oil source rock, oil-generating potential, hydrocarbon compounds, synthetic oil, gas chromatography with mass spectrometry detection


Introduction

High-carbon formations are one of the key objects in the study of deposits and forecasting of hydrocarbon reserves and resources (Kontorovich et al., 1975; Prishchepa et al., 2014; Stupakova et al., 2015). They are the oil source strata, in which oil and gas are formed from the kerogen in the process of geological evolution. As a result of subsequent migration along the section, these hydrocarbons fill the conventional reservoirs. An assessment of the characteristics of the source rocks allows to determine how much oil was generated during the catagenetic transformation of sediments, how much hydrocarbon compounds (HCC) remained in the reservoir, and how much migrated to the overlying strata (Sannikova et al., 2019).

At the same time, high-carbon formations are subject to secondary transformations, changes in the mineral composition as a result of dissolution, the formation of new minerals, hydrothermal processes, and kerogen transformations, as a result of which a pore space is formed in the rocks that contains oil (Kalmykov, Balushkina, 2017). The development of fields with unconventional reservoirs in the oil source strata currently allows to increase the country’s resource potential and compensate the decrease in oil production from conventional reservoirs.

Conducted researches have shown that the amount of oil varies significantly in high-carbon formations, it depends on the maturity of organic matter and the conditions of its formation, as well as on the occurred secondary processes. At the same time, in the case of low maturity (stage of catagenesis PK3-MK2), most of the hydrocarbons in the rock are not in the form of oil, but in the form of physically connected or blocked hydrocarbons (Kalmykov, 2016). At the same time, kerogen is poorly transformed and in the future can generate a large volume of HCC as a result of further catagenetic transformations.

At low maturity, in most cases, the development of wells by drilling without additional technological work is inefficient and economically unprofitable. Therefore, companies are trying to develop various technologies to increase oil production. There are secondary and tertiary
Comparison of the potential of secondary and tertiary methods...  

V.V. Levkina, A.G. Kalmykov, T.N. Henarova et al.

Secondary methods of stimulation of a reservoir mean the injection of water, gas or reagents, allowing to extract already formed hydrocarbons. Tertiary methods involve exposure to the formation in order to convert organic matter, in fact, cracking in the formation. The use of these intensification methods will make it possible to extract fixed hydrocarbons from the rocks and partially realize the kerogen generation potential.

The characteristics of already formed HCC were previously considered in literature (Mueller, Philp, 1998; Tikhonova et al., 2019). These bitumen can have a sufficiently high maturity and be used as hydrocarbon feedstocks. In this case, it is important to understand where these or other bitumen are located in the rock and in which case they will be involved in the development. There are also a fairly large number of publications evaluating the prospects for tertiary methods of stimulating the formation (Popov et al., 2017). Assessment of the prospects for the formation of hydrocarbons from kerogen on the main high-carbon formations of Russia – the Bazhenov and Domanik suites – is usually based on experiments on rock hydro-pyrolysis (Bushnev et al., 2004; Bychkov et al., 2015; Popov et al., 2017; Kalmykov et al., 2017). The authors showed that under temperature exposure it is possible to partially realize the generation potential of kerogen and to obtain hydrocarbon systems of different compositions.

At the same time, the prospects for complex impact on the reservoir have not been previously evaluated. It is important to compare the capabilities of different development methods for oil-saturated high-carbon rocks; as well as to find out how the resulting products will vary in composition and how the amount of emitted HCC will vary. The aim of this work is to study the potential of secondary and tertiary methods of influencing on oil source rocks with high oil generation potential (for example, rocks of one deposit of the Bazhenov formation), and to compare the characteristics of the resulting products with oil obtained in the development of these rocks without special exposure technologies.

Experimental part
Materials and Reagents

To assess the prospects of secondary and tertiary methods of stimulating the formation, we used rock samples of the Bazhenov formation from one well located on the eastern side of the Frolovsky mega-basin. For the study, 3 samples were selected located in different parts of the section and differing in composition, previously determined by X-ray phase and X-ray fluorescence analysis methods (Table 1).

The following reagents were used in the work: n-hexane (Panreac, Spain), toluene (Panreac, Spain), methylene chloride (Component Reagent, Russia, for spectroscopy), chloroform (Himmed, Russia), KSKG silica gel 0.04-0.1 mm (Chromresurs, Russia) and silver nitrate (Labsintez, Russia), benzene (Component Reagent, Russia), ethyl alcohol (Flora of the Caucasus, Russia).

Research Methods

Pyrolysis. To determine the content of organic matter in the samples, its type and maturity, as well as the content of physically bound hydrocarbon compounds and to assess the generation potential, the samples were pyrolyzed before and after various actions on the Rock-Eval-6 device (France). The measurements on the device are described in detail in (Tissot, Welt, 1981; Espitalie, 1984).

Extraction. The extraction of bitumen from the rocks of the Bazhenov formation was carried out by the method of stepwise extraction using various solvents. Hot extraction by each solvent was carried out in a Soxhlet apparatus according to the international standard D5369-93. Chloroform, n-hexane and a mixture of ethyl alcohol and benzene in a ratio of 1:1 were used as solvents. To extract hydrocarbon compounds from open pores, the extraction was carried out on cylindrical samples 30×30 mm in size, to obtain bitumen from closed pores, the cylindrical samples were grind after extraction with all three solvents, and subsequent extraction was performed on the obtained powders. The extraction technique is described in detail in the article (Tikhonova et al., 2019).

Hydrothermal exposure. The obtaining of “synthetic” oil from the rocks of the Bazhenov formation was carried out by the method of hydrothermal exposure to samples in autoclaves in the presence of water. A sample weighing ~ 50 g is placed in an autoclave. Water is added to the sample in such a volume that, at the temperature of the experiment, the pressure of water vapor creates a reservoir pressure of 300 atm in the autoclave. The temperature of the experiments was 300 °C and 350 °C. The duration of the experiment was 7 days at a temperature of 300 °C and 12 hours at 350°C. The methodology and temperature selection are described in more detail in (Kalmykov et al., 2017).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth</th>
<th>Silicon</th>
<th>Clay minerals</th>
<th>Calcite</th>
<th>Dolomite</th>
<th>Pyrite</th>
<th>Albite</th>
<th>OM</th>
</tr>
</thead>
<tbody>
<tr>
<td>23-097</td>
<td>2924.0</td>
<td>53.3</td>
<td>12.8</td>
<td>0.6</td>
<td>2.9</td>
<td>3.2</td>
<td>11.1</td>
<td>15.8</td>
</tr>
<tr>
<td>30-032</td>
<td>2911.1</td>
<td>32.6</td>
<td>23.1</td>
<td>2.6</td>
<td>0.0</td>
<td>5.4</td>
<td>11.7</td>
<td>24.7</td>
</tr>
<tr>
<td>32-116</td>
<td>2905.8</td>
<td>43.9</td>
<td>15.0</td>
<td>6.4</td>
<td>0.0</td>
<td>8.2</td>
<td>9.3</td>
<td>16.6</td>
</tr>
</tbody>
</table>

Table 1. The mineral component composition of the samples
Separation of hydrocarbon compounds. Separation of maltenes from tar-asphaltenes substances in the obtained extracts and synthetic oils was carried out by adding to the sample a 40-fold excess of n-hexane, keeping the solution for a day in a dark place and following filtering. The separation of samples into saturated and aromatic fractions was carried out by liquid chromatography. A glass chromatographic column with an adsorbent (about 1-2 g of a mixture of silica gel and silver nitrate in a 9:1 ratio) was washed with n-hexane, 5 drops of oil/bitumen were transferred into it, and washed 3 times with n-hexane to collect the saturated fraction. The aromatic fraction was washed off with toluene.

Chromatographic analysis. An Agilent 7890B gas chromatograph equipped with an Agilent 7693 Autosampler automatic sampling device and an Agilent 5977A MSD mass spectrometer (Agilent Technologies, USA) was used to determine oil hydrocarbons. Data collection and chromatogram processing was performed using MassHunter software (Agilent Technologies, USA). HP-5MS capillary column (30 m × 0.25 mm, 0.25 μm) with a stationary phase based on methyl (95 %) – phenyl (5 %) – polysiloxane was used. Carrier gas was helium; carrier gas flow rate through the column was 1 cm³/min. The volume of the introduced sample was 1 mm³. Evaporator temperature – 290 °C, interface temperature – 300 °C; temperature gradient for the separation of the components of the saturated and aromatic fractions of oils, extracts and pyrolysis products was used.

Calculation of geochemical parameters. For all samples studied, the geochemical indices CPI (Carbon preference index) and OEP (odd to even predominance) were calculated, which are reduced to a numerical representation of the prevalence of even n-alkanes over odd ones in a specific range of the carbon chain. The CPI and OEP indices are calculated using the following formulas:

\[
\text{CPI} = 0.5 \times \left( \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} \right)
\]

\[
\text{OEP} = 0.5 \times \frac{C_{21} + 6C_{23} + C_{25}}{4(C_{22} + C_{24})}
\]

Results and discussion

The potential assessment of the studied samples of the Bazhenov formation can be obtained by analyzing the pyrolysis results of the samples. The results of the pyrolysis of the samples before extraction are shown in Table 2.

As can be seen from the pyrolysis results, the samples contain a large amount of organic matter (TOC value is more than 12 wt.%). Moreover, the samples have a high oil generation potential (the sum of parameters S1 and S2), ranging from 75 mg HC/g of rock to 105 mg HC/g of rock. Accordingly, the rocks from which the samples were selected can serve in the future as a source of a large number of hydrocarbon compounds. At the same time, the oil-generating potential characterizes both the already generated hydrocarbon compounds and the kerogen generation potential, which shows the amount of hydrocarbons that can be obtained in the future as a result of catagenetic maturation of rocks.

It is important to note that organic matter has high values of the HI hydrogen index, corresponding to ~ 500 mg HC/g TOC, and the parameter Tmax is 440 °C. This indicates a low degree of maturity of rocks, corresponding to the catagenesis stage MK1-2. Usually, for such stages of maturity, parameter S1 has lower values, rarely exceeding 10 mg HC/g of rock. These rocks can be attributed to rocks with a high saturation of hydrocarbons.

As mentioned earlier, secondary methods of stimulating the formation are aimed at extracting the hydrocarbon residues remaining after the traditional development of rocks, including compounds that are stationary due to their physical properties (for example, having a high molecular weight), as well as light compounds located in closed pores or physically associated with organic matter. To assess the prospects of secondary methods of stimulation on the studied rocks of the Bazhenov formation, it is necessary to assess the number of potentially recoverable compounds and their composition.

Estimation of the amount of HCC in the rock can be carried out based on the results of pyrolysis after extraction. It is worth noting that, according to the ideas about the structure of the rocks of the Bazhenov formation (Kalmykov, 2016), the pore space is divided into open and closed pores. To determine the amount of hydrocarbons in open pores, pyrolysis was performed after extraction of cylindrical samples. The amount of HCC in closed pores was estimated by the difference in parameters S1 and S2 after extraction of cylinders and powders. According to the results of pyrolysis, it was found that more than 90 % of light HCC (parameter S1) is in open pores and is about 12-15 mg HC/g of rock, while HCC with a high molecular weight (parameter S2) are distributed in open and closed pores approximately.

As mentioned earlier, secondary methods of stimulating the formation are aimed at extracting the hydrocarbon residues remaining after the traditional development of rocks, including compounds that are stationary due to their physical properties (for example, having a high molecular weight), as well as light compounds located in closed pores or physically associated with organic matter. To assess the prospects of secondary methods of stimulation on the studied rocks of the Bazhenov formation, it is necessary to assess the number of potentially recoverable compounds and their composition.

As can be seen from the pyrolysis results, the samples contain a large amount of organic matter (TOC value is more than 12 wt.%). Moreover, the samples have a high oil generation potential (the sum of parameters S1 and S2), ranging from 75 mg HC/g of rock to 105 mg HC/g of rock. Accordingly, the rocks from which the samples were selected can serve in the future as a source of a large number of hydrocarbon compounds. At the same time, the oil-generating potential characterizes both the already generated hydrocarbon compounds and the kerogen generation potential, which shows the amount of hydrocarbons that can be obtained in the future as a result of catagenetic maturation of rocks.

It is important to note that organic matter has high values of the HI hydrogen index, corresponding to ~ 500 mg HC/g TOC, and the parameter Tmax is 440 °C. This indicates a low degree of maturity of rocks, corresponding to the catagenesis stage MK1-2. Usually, for such stages of maturity, parameter S1 has lower values, rarely exceeding 10 mg HC/g of rock. These rocks can be attributed to rocks with a high saturation of hydrocarbons.

As mentioned earlier, secondary methods of stimulating the formation are aimed at extracting the hydrocarbon residues remaining after the traditional development of rocks, including compounds that are stationary due to their physical properties (for example, having a high molecular weight), as well as light compounds located in closed pores or physically associated with organic matter. To assess the prospects of secondary methods of stimulation on the studied rocks of the Bazhenov formation, it is necessary to assess the number of potentially recoverable compounds and their composition.

Estimation of the amount of HCC in the rock can be carried out based on the results of pyrolysis after extraction. It is worth noting that, according to the ideas about the structure of the rocks of the Bazhenov formation (Kalmykov, 2016), the pore space is divided into open and closed pores. To determine the amount of hydrocarbons in open pores, pyrolysis was performed after extraction of cylindrical samples. The amount of HCC in closed pores was estimated by the difference in parameters S1 and S2 after extraction of cylinders and powders. According to the results of pyrolysis, it was found that more than 90 % of light HCC (parameter S1) is in open pores and is about 12-15 mg HC/g of rock, while HCC with a high molecular weight (parameter S2) are distributed in open and closed pores approximately.

As can be seen from the pyrolysis results, the samples contain a large amount of organic matter (TOC value is more than 12 wt.%). Moreover, the samples have a high oil generation potential (the sum of parameters S1 and S2), ranging from 75 mg HC/g of rock to 105 mg HC/g of rock. Accordingly, the rocks from which the samples were selected can serve in the future as a source of a large number of hydrocarbon compounds. At the same time, the oil-generating potential characterizes both the already generated hydrocarbon compounds and the kerogen generation potential, which shows the amount of hydrocarbons that can be obtained in the future as a result of catagenetic maturation of rocks.

It is important to note that organic matter has high values of the HI hydrogen index, corresponding to ~ 500 mg HC/g TOC, and the parameter Tmax is 440 °C. This indicates a low degree of maturity of rocks, corresponding to the catagenesis stage MK1-2. Usually, for such stages of maturity, parameter S1 has lower values, rarely exceeding 10 mg HC/g of rock. These rocks can be attributed to rocks with a high saturation of hydrocarbons.

As mentioned earlier, secondary methods of stimulating the formation are aimed at extracting the hydrocarbon residues remaining after the traditional development of rocks, including compounds that are stationary due to their physical properties (for example, having a high molecular weight), as well as light compounds located in closed pores or physically associated with organic matter. To assess the prospects of secondary methods of stimulation on the studied rocks of the Bazhenov formation, it is necessary to assess the number of potentially recoverable compounds and their composition.

Estimation of the amount of HCC in the rock can be carried out based on the results of pyrolysis after extraction. It is worth noting that, according to the ideas about the structure of the rocks of the Bazhenov formation (Kalmykov, 2016), the pore space is divided into open and closed pores. To determine the amount of hydrocarbons in open pores, pyrolysis was performed after extraction of cylindrical samples. The amount of HCC in closed pores was estimated by the difference in parameters S1 and S2 after extraction of cylinders and powders. According to the results of pyrolysis, it was found that more than 90 % of light HCC (parameter S1) is in open pores and is about 12-15 mg HC/g of rock, while HCC with a high molecular weight (parameter S2) are distributed in open and closed pores approximately.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S1, mg HC/g of rock</th>
<th>S2, mg HC/g of rock</th>
<th>Tmax, °C</th>
<th>TOC wt.%</th>
<th>PI</th>
<th>HI, mg HC/g TOC</th>
<th>OSI, mg HC/g TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>23-097</td>
<td>13.2</td>
<td>61.4</td>
<td>441</td>
<td>12.1</td>
<td>0.18</td>
<td>508</td>
<td>108.9</td>
</tr>
<tr>
<td>30-032</td>
<td>16.6</td>
<td>89.0</td>
<td>440</td>
<td>18.5</td>
<td>0.16</td>
<td>480</td>
<td>89.8</td>
</tr>
<tr>
<td>32-116</td>
<td>12.9</td>
<td>63.3</td>
<td>443</td>
<td>12.3</td>
<td>0.17</td>
<td>516</td>
<td>105.1</td>
</tr>
</tbody>
</table>

Table 2. The results of the pyrolysis of the studied samples
Comparison of the potential of secondary and tertiary methods... V.V. Levkina, A.G. Kalmykov, T.N. Henarova et al.

The results show that for the extraction of light bitumen, which by their characteristics will be closest to oil, it is possible not to involve HCC located in closed pores. In this case, the total amount of hydrocarbon that can be extracted as a result of secondary methods of stimulating the formation for the studied rocks is about 35 mg HC/g of rock, which is a very high value for the rocks of the Bazhenov formation. It is also important to note that the proportion of light hydrocarbon in these rocks is about 40%, which will allow to produce about 35 kg of light hydrocarbon from 1 m³ of rock. Taking into account all the available hydrocarbons in the rock, the total value is about 90 kg.

The values of parameter $S_2$ after extraction characterize the generation potential of kerogen. This parameter varies from 40 to 70 mg HC/g of rock, which is a very high value for the rocks of the Bazhenov formation. It is also important to note that the proportion of light hydrocarbon in these rocks is about 40%, which will allow to produce about 35 kg of light hydrocarbon from 1 m³ of rock. Taking into account all the available hydrocarbons in the rock, the total value is about 90 kg.

The values of parameter $S_2$ after extraction show that the rocks selected for research have high potential for the application of secondary and tertiary methods of stimulating the formation. In this case, the maximum amount of hydrocarbon produced by each of the methods can be considered commensurate. However, in order to assess the potential of using various technologies, it is necessary to determine how much the composition of the HCC obtained by different methods is comparable with the composition of oil extracted from the field.

To compare the composition of recoverable hydrocarbons, a GC-MS analysis of the saturated and aromatic fractions of oil maltenes extracted from the rocks of the Bazhenov formation of this field, hexane and chloroform extracts from open pores, hexane extract from closed pores, and “synthetic” oil was performed. In order to evaluate the potential of secondary methods of exposure, only hexane and chloroform extracts from open pores (cylindrical samples) were studied, and to compare the potential of closed pores hexane extracts from closed pores were studied. This choice of extracts is due to the low content of light HCC in closed pores, as well as the high proportion of asphaltenes (up to 95%) in alcohol-benzene extracts from open pores.

At the first stage, a comparative analysis of the distribution of $n$-alkanes in hexane (Fig. 1) and chloroform (Fig. 2) extracts from open pores of rock samples located in different parts of the section was performed. As it was established earlier (Tikhonova et al., 2019), a comparison of the distribution of $n$-alkanes in the samples along the section allows to assess whether there is a migration of hydrocarbons in the reservoir, as well as to reveal differences in the generation of hydrocarbons in rocks of different compositions. As can be seen from Figure 1, the hexane extracts of the samples are completely identical. At the same time, the distribution of $n$-alkanes in chloroform extracts is somewhat different, although this difference can be considered insignificant, secondary minima and maxima on the curves are repeated, and the general appearance of the curves in the open pores is similar.

For hexane extracts from closed pores (Fig. 3), a local peak is observed for all samples, corresponding to an increased content of $n$-alkanes with a C22 chain length. Moreover, in general, the shape of the distribution curves is identical. At the same time, the presence of individual maxima and the absence of a pronounced peak for low molecular weight compounds (C16-C20) indicate a lower maturity of hexane extracts from closed pores.

According to the results of the study of the variability of the distribution of $n$-alkanes in different samples, it is possible to note the absence of perceptible differences in extracts along the section. Such an identity indicates that, in the whole section, the process of substance generation was the same. Moreover, extracts from open and closed pores are significantly different from each other. The hexane extract in all samples has a maximum for light $n$-alkanes with a chain length of C14-C18, in the chloroform extract, the maximum shifts toward C17-C21, and a single peak is characteristic for the hexane extract in C22 (Fig. 4). Such differences show that, in closed pores, the maturity of HCC is significantly lower. Presumably, HCC from closed pores will require additional processing after extraction, which is associated with high costs. It is likely that the extraction of bitumen from closed pores in such deposits is less promising.

To assess the prospects of tertiary methods of stimulating the formation, these samples were subjected to hydropyrolysis at the following parameters: 300 °C for 7 days and 350 °C for 12 hours. The amount of maltenes and asphaltenes in the resulting “synthetic” oil is shown in Table 4. As can be seen from the Table, the number

<table>
<thead>
<tr>
<th>Sample</th>
<th>S1, mg HC/g of rock</th>
<th>S2, mg HC/g of rock</th>
<th>Tmax, °C</th>
<th>TOC, wt.%</th>
<th>PI</th>
<th>HI, mg HC/g TOC</th>
<th>OSI, mg HC/g TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>23-097</td>
<td>0.1</td>
<td>39.1</td>
<td>442</td>
<td>8.5</td>
<td>0.00</td>
<td>462</td>
<td>1.4</td>
</tr>
<tr>
<td>30-032</td>
<td>0.4</td>
<td>70.2</td>
<td>440</td>
<td>15.5</td>
<td>0.01</td>
<td>452</td>
<td>2.8</td>
</tr>
<tr>
<td>32-116</td>
<td>0.3</td>
<td>39.3</td>
<td>439</td>
<td>9.6</td>
<td>0.01</td>
<td>412</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Table 3. The results of pyrolysis of the studied samples after complete extraction
of maltenes and asphaltenes with a mild exposure is comparable, and the total yield is 1-1.5 mg of HCC/g of rock. With increasing temperature, the majority of the resulting “synthetic” oil are maltenes (80-95 %). The total yield increases significantly, reaching 5-10 mg HC/g of rock. It is important to note that in both cases the realization of the generation potential amounted to about 5-10 mg HCC/g of rock, which indicates a high yield of liquid HCC and a small percentage of the generated at high temperatures gas. Probably, the selection of optimal conditions will increase the yield of “synthetic” oil from these rocks.

The distribution analysis of n-alkanes in the resulting “synthetic” oils showed that the primary rather narrow maximum occurring in C14-C19 is present in the obtained HCC. At the same time, at elevated experimental temperatures, for all samples of “synthetic” oil, a second maximum is observed corresponding to the C25-C30 chain length, which is especially pronounced for sample 32-116 (Fig. 5). This indicates that under mild conditions of hydrothermal exposure (300 °C, 7 days), only weak bonds break, while at elevated temperatures not only hydrocarbons can detach from kerogen, but also secondary cracking of asphaltenes and other compounds with high molecular weight can occur, resulting in the formation of new n-alkanes. Most likely, the secondary peak is explained by non-optimal conditions for the production of “synthetic” oil, the selection of other conditions, as it was shown by previous experiments (Bychkov et al., 2015, Kalmykov et al., 2017), should lead to a monomodal distribution. At the same time, the varying of conditions can lead to secondary cracking of light compounds and the formation of gaseous hydrocarbons.

Since the first peak in the distribution of n-alkanes of “synthetic” oils obtained under different conditions is

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fraction</th>
<th>Weight of “synthetic” oil at 300°C, g</th>
<th>Weight of “synthetic” oil at 350°C, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>23-097</td>
<td>maltenes</td>
<td>0.0137</td>
<td>0.2826</td>
</tr>
<tr>
<td></td>
<td>asphaltene</td>
<td>0.0355</td>
<td>0.0376</td>
</tr>
<tr>
<td>30-032</td>
<td>maltenes</td>
<td>0.0338</td>
<td>0.3348</td>
</tr>
<tr>
<td></td>
<td>asphaltene</td>
<td>0.0158</td>
<td>0.0145</td>
</tr>
<tr>
<td>32-116</td>
<td>maltenes</td>
<td>0.0495</td>
<td>0.4190</td>
</tr>
<tr>
<td></td>
<td>asphaltene</td>
<td>0.0245</td>
<td>0.0971</td>
</tr>
</tbody>
</table>

Table 4. The amount of synthetic oil obtained as a result of hydrothermal exposure under various conditions

Fig. 1. Distribution of n-alkanes in open pore hexane extracts

Fig. 2. Distribution of n-alkanes in chloroform extracts from open pores

Fig. 3. Comparison of hexane extracts from closed pores

Fig. 4. Distribution of n-alkanes in various extracts of sample 23-097

Fig. 5. Comparison of n-alkanes distribution in synthetic oils obtained from sample 32-116 under various conditions of pyrolysis
Comparison of the potential of secondary and tertiary methods...

V.V. Levkina, A.G. Kalmykov, T.N. Henarova et al.

Fig. 7. Overlaying chromatograms of the aromatic fraction obtained for sample 32-116 in the study of “synthetic” oil at 300 °C, 7 days – the violet line; “synthetic” oil at 350 °C, 12 hours – the blue line; and hexane extract from open pores – green line. The registration mode of the selected ion is m/z 192.

Table 5. Geochemical parameters of CPI and OEP calculated for the studied samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>CPI</th>
<th>OEP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane, o/p</td>
<td>0.97</td>
<td>0.90</td>
</tr>
<tr>
<td>Hexane, c/p</td>
<td>1.23</td>
<td>0.83</td>
</tr>
<tr>
<td>Chloroform, o/p</td>
<td>1.03</td>
<td>0.88</td>
</tr>
<tr>
<td>“Synthetic” oil, 300°C, 7 days</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>“Synthetic” oil, 350°C, 12 hours</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>Natural oil</td>
<td>0.99</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Fig. 6. Comparison of n-alkanes distribution in oil, hexane extract from open pores and “synthetic” oil (300 °C, 7 days) for sample 32-116.
for “synthetic” oils are also close to the indicated systems and are about 0.7. Thus, we can say that for this parameter, the indicated air-blast units are close.

Another parameter characterizing the maturity of HCC is determined by the ratio of 4-methyldibenzothiophene parameter, the indicated air-blast units are close. Thus, we can say that for “synthetic” oils are also close to the indicated systems and are about 0.7. Thus, we can say that for this parameter, the indicated air-blast units are close.

Table 6. The ratio Pr/Ph for the studied samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hexane,</th>
<th>Hexane,</th>
<th>Chloroform,</th>
<th>“Synthetic” oil, 300°C, 7 days</th>
<th>“Synthetic” oil, 350°C, 12 hours</th>
<th>Natural oil 7076</th>
</tr>
</thead>
<tbody>
<tr>
<td>23-097</td>
<td>0.59</td>
<td>0.27</td>
<td>0.43</td>
<td>0.66</td>
<td>0.72</td>
<td>0.59</td>
</tr>
<tr>
<td>30-032</td>
<td>0.63</td>
<td>0.25</td>
<td>0.48</td>
<td>0.70</td>
<td>0.65</td>
<td>0.71</td>
</tr>
<tr>
<td>32-116</td>
<td>0.57</td>
<td>0.30</td>
<td>0.26</td>
<td>0.69</td>
<td>0.71</td>
<td>1.56</td>
</tr>
</tbody>
</table>

Table 7. Geochemical parameter 4 MDBT/1 MDBT for the studied samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hexane,</th>
<th>Hexane,</th>
<th>Chloroform,</th>
<th>“Synthetic” oil, 300°C, 7 days</th>
<th>“Synthetic” oil, 350°C, 12 hours</th>
<th>Natural oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>23-097</td>
<td>1.67</td>
<td>1.69</td>
<td>1.45</td>
<td>1.69</td>
<td>1.53</td>
<td>1.56</td>
</tr>
<tr>
<td>30-032</td>
<td>1.66</td>
<td>1.56</td>
<td>1.46</td>
<td>1.59</td>
<td>1.58</td>
<td></td>
</tr>
<tr>
<td>32-116</td>
<td>1.65</td>
<td>1.97</td>
<td>1.3</td>
<td>1.55</td>
<td>1.51</td>
<td></td>
</tr>
</tbody>
</table>

for “synthetic” oils are also close to the indicated systems and are about 0.7. Thus, we can say that for this parameter, the indicated air-blast units are close.

Another parameter characterizing the maturity of HCC is determined by the ratio of 4-methyldibenzothiophene to 1-methyl dibenzothiophene (Table 7) and for all systems lies within the error. This also indicates a high degree of thermal maturity of OM in all cases.

**Conclusion**

As a result of the work done, it was found that samples of the Bazhenov formation with high oil generation potential are promising for development by secondary and tertiary methods of stimulating the formation. In case of secondary methods of stimulating the formation, hydrocarbon compounds should be removed that are in the well in a physically bound state or fixed with bitumen plugs. For development it is not necessary to carry out rock destruction, for example, by hydraulic fracturing, to extract hydrocarbons from closed pores, since their maturity is lower, the composition is different from natural oil, and probably product recycling will be required. When extracting bitumen from open pores, their composition is close to the composition of natural oils extracted from the Bazhenov formation of this field, and the number of light hydrocarbons can reach 35 kg from 1 m³ of rock.

At the same time these rocks are promising for tertiary methods of stimulation. The composition of the obtained “synthetic” oils is also close to the composition of natural oil. Moreover, when the rock is exposed to a temperature of 350 °C for 12 hours in the presence of water, it is possible to extract 15-20 kg of HCC from 1 m³ of rock. At the same time, sorbed HCC will remain in the rock after thermal exposure. Selection of optimal conditions for stimulating the formation will increase the production of “synthetic” oil by this method. Additional research is necessary to evaluate whether adsorbed HCC will remain in the strata after the extraction of “synthetic” oil.

Thus, secondary and tertiary methods of stimulating the formation will allow for the future, when developing appropriate technologies, to significantly increase oil production from rocks of high-carbon formations with high oil generation potential, will not require secondary processing of the product, and can be used sequentially by summing the amount of hydrocarbons produced.

**References**


Comparison of the potential of secondary and tertiary methods...


About the Authors

Valentina V. Levkina – Leading Engineer of the Analytical center, Lomonosov Moscow State University
1/3, Leninskie gory, Moscow, 119234, Russian Federation
Phone: +7(999)905-51-20
E-mail: jugora@mail.ru

Anton G. Kalmykov – Senior Researcher of the Petroleum Geology Department, Lomonosov Moscow State University
1, Leninskie gory, Moscow, 119234, Russian Federation

Tatsiana N. Henarava – Research Assistant of the Laboratory of Physico-Chemical Hydrodynamics, A.V. Luikov Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus
15, P. Brovka Street, Minsk, Belarus

Margarita S. Tikhonova – Engineer of the Petroleum Geology Department, Lomonosov Moscow State University
27, build. 1, Lomonosovsky ave., Moscow, 119234, Russian Federation

Andrey V. Pirogov – Professor of the Analytical Chemistry Department, Lomonosov Moscow State University
1/3, Leninskie gory, Moscow, 119234, Russian Federation

Oleg A. Shpigun – Professor of the Analytical Chemistry Department, Lomonosov Moscow State University
1/3, Leninskie gory, Moscow, 119234, Russian Federation

Andrei Yu. Bychkov – Professor of the Geochemistry Department, Lomonosov Moscow State University
1/3, Leninskie gory, Moscow, 119234, Russian Federation

Manuscript received 1 August 2019; Accepted 18 September 2019; Published 1 December 2019