Features of the change in the composition heavy oils of various types and solid asphaltite in the hydrothermal-catalytic conditions

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Abstract. The paper reveals the distinctive features of the change in the composition heavy oils of various types and of natural bitumen - asphaltite from the sandstones of the Permian sediments of the Spiridonovsky field in the territory of Tatarstan, in model experiments at a temperature of 250°C, characteristic for steam-thermal impact on the formation, and the pressure in the system of not more than 2 MPa. The choice of low pressure is due to the fact that bituminous rocks in the Permian sediments occur at relatively shallow depths in the near-surface deposits of the sedimentary strata, which necessitates the development of special technologies for their extraction. The experiments used natural iron oxide - hematite. As a part of the products of asphaltite conversion under the influence of hydrothermal-catalytic factors, the content of hydrocarbons almost 4-fold, the content of alcohol-benzene resins and asphaltenes decreases. The content of benzene resins increases somewhat. The composition of asphaltite proved to be less stable than of heavy oils from age-old sediments, apparently due to special conditions for the formation of its composition in natural conditions under the influence of secondary low-temperature biochemical processes that led to the accumulation of thermally unstable resinous-asphaltene components. Compared with the original asphaltite, in the products of the experiment, the content of alkanes of composition C_{10}-C_{30} substantially increases with an obvious predominance of homologues with an even number of carbon atoms in the molecule. The product is characterized by a lesser degree of aromaticity and content of sulfoxide groups. The results of the studies showed the possibility of upgrading the composition of solid bitumen - asphaltite in in situ conversion by diluting its composition with lighter newly formed hydrocarbons, due to the destruction of its high molecular weight components.
1. Introduction

In Permian sediments of Tatarstan region there are many bituminous rock formations, containing high viscous and solid bitumen – asphalts and asphaltites [1-3]. According to many experts [4-5] bitumen reservoirs in that region represent disrupted oil formations and its formation process is related with generation of oil during ancient Paleozoic era. The fractured zones of bedding rocks and sedimentary cover assisted migration of hydrocarbon fluids from the deep of Paleozoic horizons to surface laydown of sedimentary formations. In the process of geological history under secondary recover techniques, the oil reservoirs are destroyed resulting formation of bitumen with various composition and phase conditions. This prevents their genetical relation with primary source generation and provides a reason to assume about their initial bedding in other sediments. Thereby, determination of natural factors and processes, which bring to formation of hydrocarbon accumulations on surface of sedimentary rocks in Tatarstan region is very important and relevant fundamental issue. The perspective of oil saturated sedimentary formations of given territory depends on solving upper mentioned problems. Apart depletion of light hydrocarbon resources alternative resources like heavy oil and natural bitumen have been already developing by many oil producing countries including Russia in industrial scale [1]. However, hydrocarbon resources concentrated in bituminous rocks are resting untouched underground. Concerning this potential, developing new upgrading technologies of heavy oil and natural bitumen is of big interest. The primary target of investigated technology is conversion of high molecular components to light components in situ by steam treating and introducing various conversion catalysts [6-7].

2. Materials and Methods

In the work [8] we have determined the absence of direct relation between technological properties of heavy oil and natural bitumen from sheshminskoye layers (Permian deposits, prepared by PJSC “Tatneft” for industrial exploitation) and formation depth, effective oil saturation and oil productive area of reservoirs, including flow properties. This stands for occurrence of Permian deposits in secondary bedding and their composition depends on intensive effect of secondary recover processes. To study the genesis of hydrocarbon accumulations in Permian deposits and seeking for possible exploitation ways, the heavy oil composition properties of Ekaterina, Ashalcha and Olimpiada oil fields are investigated [9], [10]. These reservoirs are characterized by geological-geochemical and physic-chemical properties. Also hydrocarbon compositions and their components are different before and after hydrothermal-catalytic influences. In this work for comparative analysis rock sample of bituminous sediments from Spiridonovsky reservoir was included. Extract from the given rocks contain 69.8 % asphaltenes and corresponds to solid asphaltite (Table 1). The influences of hydrothermal-catalytic processes to composition of investigated fluids are experimentally investigated at 250°C, peculiar to steam injection techniques. The pressure of steam mixture in system is not exceeded 2 MPa with 30 wt % of water content in reactive system. Natural
iron-oxide catalyst – hematite is applied in conversion of heavy oil as a heteroatom catalyst [11].

Oils before and after experiments were analyzed by the method of column-liquid-adsorption chromatography on ASK silica gel with separation of the hydrocarbon part and two groups of resins - benzene and alcohol-benzene. Before the adsorption separation according to the standard procedure, asphaltenes precipitated in 40 times the amount of petroleum ether (bp. 40–70°C).

The analysis of saturate fractions were carried out by highly effective gas chromatography method in Clarus 500 (PerkinElmer, Waltham, MA), which is equipped by auto dosing gas phase HS 40 (PerkinElmer). The capillary column with a length of 25 m, diamater of 0.2 mm and immobile phase PE-XLB (0.33 mm) was used. The temperature regime of chromatography procedure was in the range of 100°C – 300°C. From 50°C to 150°C, the rate of temperature increase was 10°C/min and starting from 150°C, the rate of temperature declines up to 3°C/min. The temperature in vaporizer was 300°C, while in detector it was 250°C and the gas-carrier was helium.

3. Results and Discussions

Based on relative distribution data (Fig. 1) of gas chromatography (GC), the normal and isoprenoid alkanes in heavy oil structure belong to different chemical types [12]. In common chromatogram of saturated hydrocarbons of Ekaterina oil field (Fig. 1a) the residue concentration of n-alkanes is clearly observed comparing to naphthenic “bunch”. This is corresponds to biodegraded type of oil in B1 stage, when the major quantity of n-alkanes are already oxidized, mainly prevailing triterpenes hopane lines of C27-C29. In B2 type oil from Ashalcha field (Fig. 1b) there are n-alkanes neither. However isoprenoid hydrocarbons C14-C20 prevail, among which prystane (C19) and phytane (C20) have a maximum concentration.
**Figure 1.** GC chromatograms saturated fractions of heavy oils: a – Ekaterina, b – Ashalcha.

**Table 1.** Heavy oil composition and Spiridonovsky asphaltite before and after hydrothermal-catalytic treatment.

| Reservoir, Well number | Sampling Interval, m | **Composition, wt %** | **HC** | **BR** | **ABR** | **Σ resins** | **Asph.** |
|------------------------|----------------------|------------------------|--------|--------|---------|-------------|-----------|
| **Heavy Oil**           |                      |                        |        |        |         |             |           |
| Ekaterinovo, 6072       | 315-325              |                        | 48.7   | 18.9   | 16.2    | 35.1        | 16.4      |
| Ekaterinovo, 6072*      |                      |                        | 56.0   | 17.3   | 9.9     | 27.2        | 16.8      |
| Ashalcha, 195           | 82                   |                        | 63.2   | 18.7   | 11.6    | 30.3        | 6.5       |
| Ashalcha, 195*          |                      |                        | 65.0   | 18.7   | 10.1    | 28.8        | 6.2       |
| Olimpiadov, 247         | 128-228              |                        | 64.0   | 15.9   | 15.4    | 31.3        | 4.7       |
| Olimpiadov, 247*        |                      |                        | 69.0   | 16.9   | 8.8     | 25.7        | 5.3       |
| **Asphaltite**          |                      |                        |        |        |         |             |           |
| Spiridonovsky rock outcrop |                  |                        | 5.4    | 2.2    | 22.6    | 24.8        | 69.8      |
| Spiridonovsky*          |                      |                        | 20.13  | 4.11   | 15.8    | 19.91       | 59.96     |

*Oil and asphaltite after experiments; **HC – Hydrocarbons; BR – Benzene resins; ABR – Alcohol-benzene resins; Asph. – asphaltenes

Oil from Olimpiadov field refers to paraffinic type A. N-alkanes of C_{12}-C_{35} and bigger molecules prevails among its components with a maximum concentration of C_{17} (Fig. 2). The given type corresponds to paraffinic oil from deep Devonian coal formations. Independent of oil type in hydrothermal-catalytic processes the same processes intensify the composition: the light components of hydrocarbons increase because of decreasing the resin content 1.5-2 times, especially thermally less stable – alcohol-benzene resins. The asphaltene content slightly increases.
The changes do not have a specific character (Tab. 1). But some distinctive features are revealed in changing composition. The main change in composition of oil is observed in Ekaterina heavy oil, which is differed by high density (1.0174 g/cm$^3$) and high resin content and asphaltene. The least conversion is seen in Ashalcha oil with a density of 0.97 g/cm$^3$.

**Figure 2.** GC chromatograms saturated fractions of heavy oils from the Olimpiada deposit.

In Olympiad oil with a density of 0.9598 g/cm$^3$, as well as Ashalcha oil, alcohol-benzene resin content decreases. The light hydrocarbons are increased slightly. In the products of experiments new formed n-alkanes are observed which resemble C$_{10}$-C$_{16}$, among which homologue of even Carbon atoms prevail.

Apart oils, in the same experimental conditions the composition of Spiridonovsky bitumen-asphaltite is less stable to thermo-catalytic processes (Tab.1). It is explained by the change in natural conditions of secondary low-temperature biochemical processes. That results to accumulation of thermally unstable resin-asphaltene components in its composition [4]. As a result of decreasing alcohol-benzene resins, the light hydrocarbon content increases 4 times in asphaltite composition under hydrothermal-catalytic influence. The asphaltene content decreases as well. The benzene resin content slightly increases.

Spiridonovsky asphaltite corresponds to B$^1$ chemical type and they contain almost no alkanes (Fig. 3). Among isoprenoid alkanes which are in slight concentrations, one can identify Prystane (C$_{19}$) and Phytane (C$_{20}$). The coefficient ($K_i=Pr+Ph/n-C_{17}+n-C_{18}$) representing character and degree of naturally conversed oil for initial crude oil is 0.64. Generally in Spiridonovsky asphaltite composition the pentacyclic hydrocarbon – hopane components C$_{27}$-C$_{29}$ prevail (Fig. 3a). Probably in initial composition of bitumen a bacterial material was prevailing. This is supported by low sterane content, rather than pentacyclic triterpanes [12]. The composition of Spiridonovsky bitumen was generated under surface condition effects: in the intensive contact with formation and surface waters, where a good
environment exists for oxidation and the sustainability of bacteria. In the product of samples (Fig. 3b) the significant increase in n-alkane C\textsubscript{10}-C\textsubscript{39} is observed. The prevailing component belongs to homologue of carbon atoms with even numbers in molecules. The maximum concentration has n-alkanes with even carbon atom in C\textsubscript{14} and C\textsubscript{16} compositions.

![GC chromatograms hydrocarbon fractions of Spiridonovsky asphaltite: a - before experiment, b - after thermal treatment.](image)

The K\textsubscript{i} parameter after experiments declines till 0.2, which is related with n-alkane formations with prevailing even numbered Carbon atom. This is supported by significant decrease in Ph/n-C\textsubscript{18} value. However, the value Ph/n-C\textsubscript{17} doesn’t change.

The mono-, di-, and tri methyl naphthalene are observed in products of samples by mass-spectrometer. Tetra methyl naphthalene can be observed. However, in initial native asphaltites they were not identified. There are phenanthrenes and new compounds, both in the low-molecular and high-molecular regions of the mass fragmentogram. According to IR spectroscopy the product of asphaltite conversions generally characterized by less aromaticity.
and low degree of sulfur content comparing with initial asphaltites. The increase in oxygen containing groups, corresponding to alcohol and ethers indicate oxidation reactions. It is also reflecting the group composition of conversion products of resin and asphaltenes.

4. Conclusion
The distinctive features of heavy hydrocarbon with different chemical types and natural solid asphaltite conversions under hydrothermal-catalytic processes at 250°C with using catalysts based on hematite mineral, containing iron oxides are revealed. Increasing light hydrocarbon and significant decrease of alcohol-benzene resin content in compositions of investigated sample products confirm destruction of high molecular components of oil. The different stability of investigated fluid components to conversion processes in hydrothermal-catalytic conditions is demonstrated. The destructive and hydrogenation processes in hydrothermal-catalytic systems play a clue role in changing the structure of asphaltite compositions. It is supported by significant increase of light hydrocarbon amount and tremendous decrease in resin and asphaltene contents. It is revealed that new formed n-alkanes in sample products have homologue of Carbon atom with even number. This can be used as an indicator feature for hydrothermal-catalytic conversion of heavy oil and natural bitumen, particularly solid asphaltites. Thus, results of experimental investigations revealed the composition conversion of not only heavy crude oil with significant high viscosity, but also solid bitumen – asphaltite types. In contrast in easy hydrothermal-catalytic condition the light hydrocarbon fractions are gained. Hereby, the given processes are perspective to apply for upgrading compositions of heavy hydrocarbon resources.

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