

## HYDROTHERMAL TRANSFORMATION OF ORGANIC MATTER IN THE PRESENCE OF ROCK-FORMING MINERALS

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### ABSTRACT

In the conditions of the deterioration of the structure of reserves of conditioned oil, development of non-traditional sources of hydrocarbon raw materials is becoming one of the promising directions of increasing the resource base of hydrocarbons. The work is devoted to the identification of changes in the chemical structure and composition of super-viscous oil as a result of steam-heat treatment in the presence of mineral compounds of carbonate reservoir rocks at temperatures of 250-300°C and pressures up to 1.6 MPa. As a result of the thermal effect, the hydrocarbon composition changed: the content of light hydrocarbons increased by 10%, the sulfur content decreased from by 7% due to the destruction of resinous compounds by 9%. The results of the conducted research contribute to the development of theoretical ideas on the transformation of biodegradable organic matter in hydrothermal processes in the presence of rock-forming compounds, and contribute to the development of scientific foundations for the creation of new technologies for extracting heavy hydrocarbon raw materials from rocks and upgrading their composition for their integrated development.

**Keywords:** hydrothermal transformation, organic matter, heavy oil, steam-thermal effect

### INTRODUCTION

To date, the development of old hydrocarbon deposits around the world is carried out in the conditions of residual reserves [1], and the production of wells has a high water content, the newly commissioned fields contain difficult-to-recover reserves due to geological and physical conditions, the presence of hydrocarbons in unconventional reservoirs and the presence of high-viscosity oils. World resources of heavy oils and natural bitumen significantly exceed the light oil reserves and are estimated at more than 810 billion tons [2]. Canada and Venezuela have the largest reserves, and Mexico, the United States, Russia, Kuwait and China also have significant reserves.

According to various estimates, 30 to 75 billion tons of heavy oil and natural bitumen are concentrated on the territory of the Russian Federation [2], [3], which indicates a high share of oil and gas reserves in low-permeability terrigenous reservoirs, carbonate



reservoirs, and high-water zones. Development of deposits of hydrocarbons are confined to non-traditional collectors begins, development of high-viscosity oil deposits that were not previously exploited is entered. The deterioration in the structure of reserves leads to a decrease in average well rates and a deterioration in the technological and economic performance of oil and gas fields. Fixed or inactive hydrocarbons in the geological and physical conditions of individual fields, for the production of which technologies with increased efficiency are required, new technologies and additional technical means that would ensure the extraction of these hard-to-recover reserves with a sufficient level of profitability, are now of great interest to scientists and practitioners [4], [5], [6], [7].

To develop effective methods for processing and further use of heavy oil conversion products or natural bitumen, knowledge is needed about the effect of the temperature and nature of the catalysts on various functional groups in the structure of resin and asphaltene molecules. These data are important for a deeper understanding of the changes that occur in resins and asphaltenes in the processes of thermal and catalytic cracking and the selection of optimal schemes for the modernization of plants and the determination of modes for the processing of heavy hydrocarbon feedstocks by refineries [8], [9], [10], [11], [12].

#### OBJECT OF STUDY

For our study, high-viscosity oil of the Ashalcha deposit from the Permian deposits of the Republic of Tatarstan, located in the western part of the South Tatar arch, was chosen. Natural bitumen of the Ashalchafield are typical representatives of super-viscous oil, a high proportion of which is occupied by aromatic compounds (13.7%) and tar-asphaltene substances (45%) [13].

Work on the thermos-catalytic conversion was carried out in a laboratory batch unit under isothermal conditions at high temperatures of 250-300°C and pressures of 13-20 atm. The experiment lasted 2.5 hours.

As rock-forming additives, carbonate (marble) was selected as separate compounds of calcite and dolomite; MnO<sub>2</sub> is a compound exhibiting catalytic functions and allowing oxidation-reduction processes to proceed even at low temperatures, and kaolin clay.

To study the component composition of liquid products, asphaltene were preliminarily deposited with 40-fold petroleum ether (boiling point 40-70°C), then a saturated hydrocarbon part and resins were isolated by liquid-adsorption chromatography. Benzene was used to separate the benzene resins, a mixture of benzene and isopropyl alcohol was used in the ratio 50:50 to isolate the alcohol-benzene resinous compounds.

Experimental studies of thermal analysis were carried out on a derivative of the 1064 (Hungary) production tool Q-1500D at a temperature range from 20 to 1000°C with a furnace heating rate of 10°C/min. The atmosphere in the furnace is stationary.

Chromatographic studies were performed on a Kristall 2000M (Chromatek) instrument by capillary gas-liquid chromatography in the temperature programming mode from 100°C to 300°C.



## RESULTS AND DISCUSSION

The composition of the initial reaction mixture consisted of heavy oil, distilled water and mineral additives (Table 1). The thermal catalytic conversion proceeded in the temperature range of 250-300°C and a pressure of 12-20 MPa. Pressure control was not directly performed, but its change is due to temperature regulation. The difference in the pressures in experiments is due to various gasses in the processes. This indicates that various additives caused the occurrence of various chemical reactions. The greatest pressure was achieved in experiment number 1, in which dolomite was used as an additive.

Resinous-asphaltene substances pass into lighter components during the destruction process, which is confirmed by an increase in the proportion of paraffin-naphthenic hydrocarbons. The content of paraffin-naphthenic hydrocarbons in the products of the control experiment was 57.93%. In the products of experiments with rock-forming minerals, the proportion of paraffin-naphthenic hydrocarbons increased from 2 to 9%, depending on the experiment. In the first experiment, the proportion of resins and asphaltenes practically did not decrease, and accordingly the proportion of paraffin-naphthenic hydrocarbons did not increase significantly. The most positive dynamics is observed in experiment 3 with the use of manganese oxide, where the total tar content decreased by 9% in comparison with the initial oil. It should be noted that in all experiments the content of asphaltenes practically did not decrease. In experiments using minerals, the course of desulphurization processes under conditions of hydrothermal action is observed. The greatest decrease in sulfur content from 2.8% to 0.8% was achieved in the first experiment using trace elements of calcite and dolomite at 300°C and 20 atm.

Table 1. Results of structural-group and elemental analysis

Composition of the initial reaction mixture	Group composition, % wt.			Asphalt. (A)	R+A/Oil
	HC (oil)	Resins (R)			
		B	SB		
<i>Source oil</i>					
Crude oil	57.93	19.76	11.22	11.09	0.72
<i>The product of test 1 (300 ° C, 20 MPa, oil: water (4: 1), calcite, dolomite 44.4%)</i>					
1. Crude oil, water, calcite, dolomite	60	20.83	8.4	10.76	0.66
<i>The product of test 2 (250 ° C, 16 MPa, oil: water (4: 1), calcite, dolomite 44.4%)</i>					
2. Crude oil, water, calcite, dolomite	63.43	15.98	9.55	11.04	0.57
<i>The product of the experiment 3 (300 ° C, 12 MPa, oil: water (4: 1), calcite, dolomite 43.5%, MnO<sub>2</sub> 2.1%)</i>					
3. crude oil, water, calcite, dolomite, MnO <sub>2</sub>	66.84	15.63	6.55	10.98	0.49

The results of fractional distillation at atmospheric pressure of the experimental products showed that the hydrothermal oil conversion in the presence of microelements of the carbonate rock leads to the formation of light fractions boiling up to 200°C, for the control experiment the boiling point temperature drops to 78°C, against 91°C - boiling of the original oil (Table 2).



**Table 2.** Fractional composition

Composition of the reaction mixture	Initial boiling point I.B.P °C	The yield of fractions, wt %		
		I.B.P.-200°C	I.B.P.-350°C	> 350°C
Crude oil	91	9.8	28.5	71.5
Crude oil, water, control	78	10.9	30.1	69.9

In the low-temperature degradation region (up to 420°C), more than 50% of the sample mass ( $\Delta m_1$ ) is lost, and for the experimental products, this value exceeds 50% for all samples. This indicates an increase in the content of light hydrocarbons, the presence of methyl-methylene and carboxyl groups. The fractional composition is described by the exponent  $F = * m_1 / (* m_2 + * m_3)$ , which also characterizes the transformation of oil in the reservoir as a result of hyper-energetic / geothermal transformations (Table 3).

**Table 3.** Thermal analysis data

№	$\Delta m_1$ %	$\Delta m_2$ %	$\Delta m_3$ %	F	P	$t_{10\%}$ °C	$t_{15\%}$ °C	$t_{20\%}$ °C	$t_{30\%}$ °C	$t_{50\%}$ °C
Control	50.5	28.0	21.5	1.0	1.3	201	238	265	319	405
1	54.9	26.3	18.8	1.2	1.4	137	169	208	273	380
2	54.2	27.6	18.2	1.2	1.5	127	163	203	270	378
3	57.7	23.5	18.8	1.4	1.3	115	144	184	256	365

The increase in F indicates an increase in the content of light fractions of relatively heavy and medium, as well as a greater degree of oil conversion. The mass fraction of peripheral substituents in condensed aromatic structures is characterized by the exponent  $P = * m_2 / * m_3$ , the value of which for experimental products either remains the same ( $P = 1.3$  for samples 3) or increases from 1.3 to 1.4 and 1.5 for samples 1 and 2. This indicates the transformation of the structure of the middle molecule of heavy oil: the formation of side alkyl substituents for the samples/products of Experiments 1 and 2. Peripheral substituents can be represented by oxidized structures and alkyl chains. However, according to the elemental analysis of oxygen, more oxygen is produced for all the samples, which indicates a preferential growth of peripheral alkyl substituents; enrichment with oxygen-containing structures is not so intense.

Based on the result of geochemical indicators presented in Figure 3, it can be concluded that the Ashalcha oil has biomarker signs of the participation of marine organic matter in the formation of oil deposits, since the ratio of P:F is 0.6. In addition, bituminous biodegraded oil is enriched with high molecular weight alkanes of various structures. In the opinion of a number of researchers, marine OM genesis in the composition contains a high amount of hydrocarbons of composition  $C_{27-31}$  and higher, as well as  $n-C_{15}-n-C_{17}$  n-alkanes, indicating predominantly the marine algal type of organic matter (Figure).

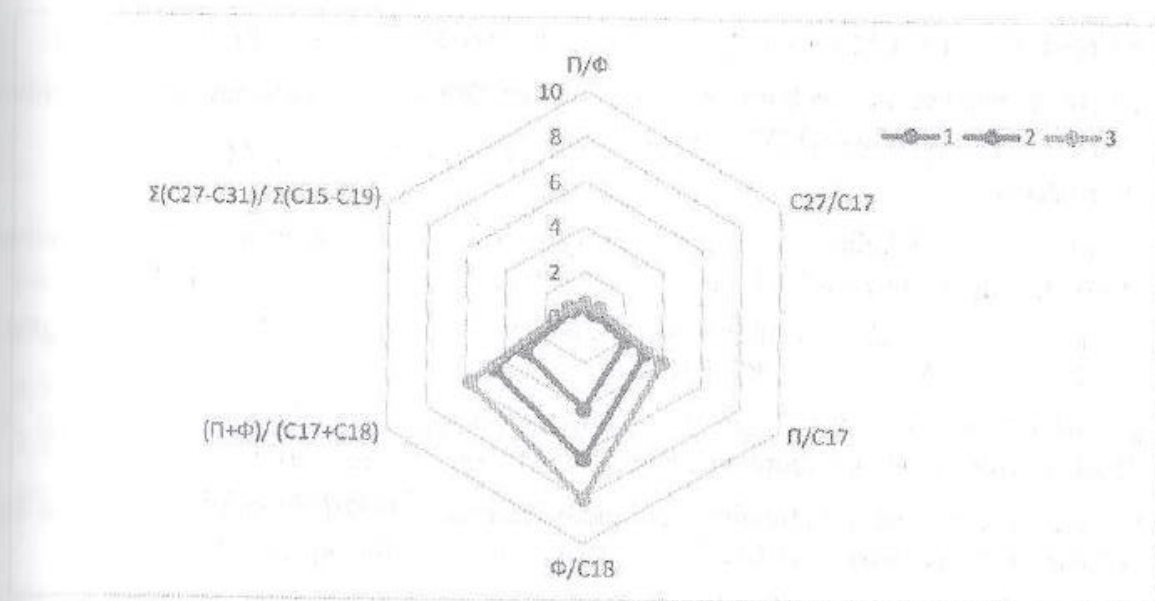


Figure. Coefficients of oil group composition from gas chromatography data

The individual composition of naphthenic hydrocarbons, especially steranes and terpanes, as well as isoprenoid alkanes - pristane and phytane, which are the most important chemofossils biomarkers, was studied by a chromatographic method. The highest peak in all samples is phytane (2,6,10,14-tetramethyl-hexadecane,  $C_{20}H_{42}$ ), slightly inferior to pristane (2,6,10,14-tetramethyl-pentadecane,  $C_{19}H_{40}$ ). These substances are present in each oil and do not change over the years of field operation. According to the theory of the organic origin of oil, they are amino acid residues, very stable, therefore they are present in large quantities in oils and remain even after thermal exposure. Chromatograms have a similar appearance, no new compounds are formed, the components are redistributed. In all experiments, the so-called paraffin-naphthenic background increases (Figure).

## CONCLUSION

As a result of the hydrothermal effect, an increase in the aromatization of oil (the ratio of H/C), the proportion of oxygen-containing compounds, the content of light fractions of relatively heavy and medium (by F in the thermal analysis), an increase in the size of trace elements occurred in all the experiments, which indicates the chemisorption on the surface of the additives. At the same time, no changes in the crystal structure of microelements occurred, which indicates that these additives produce a catalytic effect. The content of asphaltenes in all experiments remains practically unchanged, and the sulfur content is significantly reduced. The best oil conversion occurs in 3 experiments using manganese oxide, calcite, and dolomite at 300°C, 12 MPa. Here, the content of oils is increased by 7% due to the destruction of tarry compounds (by 9%). The improvement in oil is also confirmed by the thermal analysis of F and  $\Delta m_1$ . According to the results of gas chromatography, as well as calculated coefficients of group composition, all oils have a single genotype. The oil of the Ashalcha deposit belongs to the marine algal type of organic matter.



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