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HYDROCARBON COMPOSITION AND PROPERTIES OF OILS OF THE APSHERON PENINSULA AND THEIR CONNECTION WITH GEOLOGICAL MODE OF OCCURRENCE

M. F. Tagiyev*, S. R. Veliyeva, I. N. Asgarov, F. A. Mammadova, Kh. R. Akhundova

«OilGasScientificResearchProject» Institute, SOCAR, Baku, Azerbaijan

ABSTRACT

Hydrocarbon accumulations in the Lower Pliocene Productive Series of Apsheron Peninsula have formed owing to subvertical hydrocarbon migration from the underlying Maykop and Diatom source formations. This concept has been substantiated by the recent studies based on the molecular-isotopic characteristics of organic matter, oil and gas. The most notable feature of the Apsheron oils is the stable predominance of paraffin-naphthene HCs in all oil fractions, and this is true for all the fields considered. Meanwhile two geological features had major influence on formation of the composition and properties of Lower Pliocene oils in Apsheron Peninsula. In structures unaffected by tectonic erosion more mobile light components of oils happened accumulated in upper stratigraphically younger horizons due to natural fractionation of hydrocarbons on their upward migration routes. In anticlinal folds with washed out crestal part physical and biochemical degradation has caused the loss of light hydrocarbons, first of all of methane fraction, and in this way weighting up of oils. From top to bottom, towards the basal PS suites the distillate fractions show reduction in the light ends (gasoline and naphtha), which is predictably accompanied by an increase in the amount of bottoms. Compositional variation in oil hydrocarbons laterally and through the section of the peninsula is graphically demonstrated on the basis of gasoline, ligroin, kerosene and diesel cuts of oil. In terms of elemental composition, the deeper the stratigraphic occurrence of the reservoir, the more the whole oil is enriched in sulphur- and nitrogen-containing polar compounds.

Keywords: oil; hydrocarbon composition; Apsheron Peninsula; the Productive Series; Lower Pliocene.

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1. Introduction

The primary stratigraphic unit under industrial hydrocarbon development in the Apsheron Peninsula and adjacent areas is the Lower Pliocene Productive Series (PS) lying between the Upper Pliocene Akchaghylian and the Upper Miocene Pontian deposits. Exceptions are Binagadi and Shubany oil fields, where aside from the PS, the Diatom Formation (Middle-Upper Miocene) layers were also involved into oil production.

The present-day composition and properties of hydrocarbon fluids in ancient sediments are the result of long evolutionary process. Depending on the geological history of the region considered it can span hundreds of thousands to hundreds of millions of years.

In subsurface conditions formation of oil composition occurs under influence of a number of physical and chemical factors, the most important of which are temperature, pressure, filtration processes, adsorption, solubility of substances and biochemical changes in hydrocarbons (HC) in the geological environment.

Deposition of the Lower Pliocene sediments in Apsheron region is associated with large volumes of terrigenous material brought in by the Paleo-Volga fluvial system, which formed a thick series of alternating clayey and sandy layers.

The prevailing concept is that the PS reservoirs were filled with HC fluids stemming from underlying catagenetically more mature oil and gas generative sediments. Development and substantiation of the idea of upward migration is based on the recent data on molecular-isotopic characteristics of organic matter, oils and gases. The underlying Diatom and Maykop Formations are recognized to be main hydrocarbon generators with a certain contribution coming from the organic-rich argillaceous layers of the PS lower division [1, 2]. Migration of fluids from the underlying PS sediments along fractures, faults and through the channels of mud volcanoes made a large contribution to their mass transfer. At the same time, the importance of lateral flows in movement of fluids in sedimentary layers should be underlined [3].

During a relatively short geological time period of Pliocene-Quaternary ascending HC flows from these deposits entered the PS section, in a sense, special conditions for migration and accumulation of HCs. At the same time within the depositional sequence of 2-4 km and more in thickness

*E-mail: tagiyevm@hotmail.com

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oils underwent physical changes and compositional transformations.

Within the Apsheron Peninsula more than thirty structures related to the Pliocene-Quaternary stage have been identified. Commercial oil and gas reserves have been discovered and put into development in 24 fields.

Geological and geochemical studies in the Apsheron region have a solid history. While noting achievements, it should nevertheless be emphasized that a number of questions about oil-producing strata, hydrocarbon migration and formation of deposits remains to be answered.

2. History of studying physical and chemical properties of the oils

The Apsheron oil and gas bearing region (OGBR) is one of the oldest oil and gas producing regions in the world. Here you can find both low-resin light and high-resin heavy oils with varying contents of asphaltenes and paraffins. Two major groups of oil have been differentiated: methane-based and naphthene-based [4].

Ali-zade A. A. et al. (1981) proposed a subdivision of Azerbaijan oils into seven genetic types. Specifically, types I-V are referred as methane base, type VI - methane-naphthenic base, and finally type VII - purely naphthenic base crude oils. Geographically, occurrence of the naphthenic type is associated with the Western Apsheron and Apsheron Archipelago.

As oil fields were discovered and new data on oils became available, geologists, chemists and researchers of the Apsheron Peninsula tried to find an answer to the question: what is the cause for the diversity of specific gravity of oil both in a horizontal and vertical sense.

It was found that two main types of oil differentiation are characteristic for the fields in the Apsheron Peninsula: I) increase in oil density and other physico-chemical properties with depth – the most common type inherent to the deposits confined to closed structures; II) decrease in oil density with depth. This type is less commonly occurring and observed in the deposits with surface exposure.

Composition and physico-chemical properties of the PS oils of Azerbaijan have long been subjects for study. Most extensively the petrochemical properties and features of the HC composition of Apsheron oils were covered in the fundamental works of Gutryra et al. (1945), Ashumov [5] and Samedova [6].

The earliest study of specific gravity and changes in petrochemical properties in geological context goes as far back as the beginning of the 20th century. Benkendorf A. M. (1915) presented a geological explanation for specific gravity variation of oils within the Khyrdalan-Surakhany anticline and depicted a theoretical curve of this parameter across the depth. The author interpreted the density distribution of oils from shallow reservoirs of the indicated anticlinal line by the ability of rocks to retain unsaturated HCs and pass saturated ones. In other words, on their upward migration asphalt substances of oils tend to be predominantly retained in layers, while movement of paraffins and naphthenes are less interfered with.

By analyzing the geological settings of Balakhany, Surakhany and Gala anticlines and studying composition of the corresponding oils, Benkendorf A. M. concluded that so-called filtering rocks and preservation degree of

caprocks are the key factors influencing composition of the reservoir oils.

Abramovich M. V. (1939) took oil specific gravity as a main indicator of oil composition, most clearly reflecting the relationship between this composition and the mode of reservoir occurrence. The disruptions observed in the folded structures of Apsheron belong mainly to two types – longitudinal (relative to the axial lines of the folds) and transverse. The former are distinguished by large amplitudes, extent and often have the character of thrusts. Transverse faults are characterized mainly by low amplitudes and are confined only to the most elevated parts of folded structures. Longitudinal disruptions can dramatically affect distribution of oil in the layers they dissect and the composition of crude. Transverse faults, on the contrary, are linked with minor fluctuations in the composition of oil and do not significantly affect its distribution in oil-producing formations. Abramovich M. V. noted that disruptions in the form of fracturing of beds have a significant impact on oil distribution, and therefore further study of their influence on the processes of formation of deposits is necessary.

Yeremenko N. A. (1941) based on comparison of the oil specific gravity curves for Bibiheybat and Surakhany oilfields, established common regularities in their change with stratigraphic depth. It was shown that in these locations the specific gravity of oil in the PS upper division is characterized by higher gradients. As one approaches the Balakhany Suite's uppermost layers the gradients flatten out. At Surakhany oilfield in the PS lower division the curve of the parameter in question is characterized by significantly smaller gradients.

According to Gorin (1953) sedimentary interval of Supra Kirmaki Sandy and Supra Kirmaki Shaly Suites is an important historical milestone in formation of oil deposits in the Lower Pliocene. Accumulation of this section had a considerable impact on oil migration processes in the overlying Upper division of the PS. Particularly, two phases or two periods are distinguished in charging the PS reservoirs in Apsheron Peninsula. Saturation of the Lower division with oil is related to the first phase of oil migration, while the second phase is linked to charging the Upper division.

Ashumov G. G. concluded that the diversity of oils in Apsheron Peninsula is closely related to geological conditions of the region's development. In particular, the mode of oil occurrence in the PS section suggests the influence of tectonics, sedimentation conditions and oil migration. The distinction between HC compositions of gasoline cut (chiefly on aromatic to paraffin ratio) in oils from the Lower and Upper divisions of Apsheron Peninsula is explained by the difference in natural geological conditions of their occurrence. Ashumov G. G. believed that the observed spectrum of oils has formed under the complex influence of aluminosilicate rocks on primary oil under conditions of high pressure, relatively low temperatures, and other factors. According to his estimates formation of oils in Apsheron Peninsula took place in temperature range of 100-206 °C, with the PS lower suites requiring higher thermal conditions. Regarding the temperatures of oil generation, offshore fields such as Pirallahy (206 °C) and Neft Dashlary (203 °C) were attributed with the highest values. Research conducted by Ashumov G. G. allowed him to identify twenty grades of oils from the PS strata of Azerbaijan [5].

Physico-chemical properties of oils depend to a certain extent on the mode of occurrence of the hosting reservoir. Gadzhi-Kasumov A.S. (1971) noted that in most Apsheron deposits, distribution of oil properties within the horizon obeys the principle of gravitational differentiation, as a result lower part of reservoir contains oil of higher density than the upper part does. At the same time gravitational lamination of oils can also reflect on their other physico-chemical properties. The greater part of the dissolved resins and solid hydrocarbons, following the law of gravity, accumulate in lower parts of the deposit, and most of the dissolved gas in its upper parts.

Numerous scientific research works and publications have been devoted to hydrocarbon fluids of the Pliocene-Quaternary sedimentary complex of the region. Nonetheless, there is a need for a more in-depth analysis of the composition and properties of oils, as well as their areal and stratigraphic distribution regularities.

3. Changes in composition and properties of the oils with stratigraphic depth

The above publications noted the diversity of composition and properties of oils from the PS of Apsheron Peninsula, depending on stratigraphic age and location of the deposits. The purpose of this work is to present a picture of changes in composition and properties of the Apsheron oils with a wider coverage of the PS stratigraphic section. This paper presents the results of a study of oils within Apsheron Peninsula, in doing so stratigraphic range from the basal Gala formation of the PS to the overlying Apsheronian Stage of Quaternary is covered.

Oils of the known fields of Apsheron which are geographically not far from each other (fig. 1) became the subject of analysis. Based on examination results of individual oil samples (about 60) similar and distinctive compositional features of oils from individual PS suites were investigated. The data were gathered from a series of published [5-11] and non-published sources.

Density, HC composition and sulfur content are important characteristics of petroleum. According to physicochemical indicators, most of the Apsheron Peninsula oils can be classified as light, with a low content of sulfur and resins.

Density of the Apsheron Peninsula oils varies within a wide range from 0.78 to 0.92 gr/cm³. The greatest density gradients with depth are observed in oils of the PS lower horizons (fig. 2).

Molecular weight of many Lower Pliocene oils is in the range of 220-280. In particular, the least hypergenically transformed oils have a relatively low molecular weight, an example of which is the oils of Gala and Surakhany fields (see fig. 2). High molecular weight oils, as a rule, contain a significant amount of silica gel resins, specifically in Balakhany and Buzovna field oils their content is above 15%.

In this regard offshore fields situated to the south of Apsheron Peninsula are of a certain interest. Neft-Dashlary and Guneshli oilfields are producing oil and gas from the Lower Pliocene Productive Series conventional clastic reservoirs of fluvial delta origin. Physico-chemical studies of oils encompassed a wide stratigraphic range from the basal Kala Suite to the VII horizon of Balakhany Suite [7]. Oils were obtained from multiple wells spanning a collection depth range of 1300-4400m.

A linear gradient around 1 kg/m³ per 100 m has been deduced from the dataset of dispersed in 835-918 kg/m³ range oil analyses with a sufficiently noticeable trend of oil gravity to decrease with depth. Mode of the distribution was found to be at 855 kg/m³, pointing out a clear bias towards lower densities.

An essential characteristic of oil is its fractional composition, determined by temperature limits of boiling of narrow fractions withdrawn at appropriate intervals. Potential content of target fractions in the original oil is calculated based on the fractional composition. With the use of fractional composition oils from different fields, various tectonic blocks and horizons can be compared [6].

The amount of gasoline, naphtha, kerosene fractions and diesel fuel, i.e., light products with a boiling point up to 350 °C, is an important source of information on the composition of oils. With depth the proportion of heavy fractions in Apsheron oils increases, and the amounts of gasoline and naphtha expectedly decrease. This trend is especially clear at the Bibiheybat, Surakhany, Balakhany-Sabunchi-Ramana and Gala fields, where the samples cover the widest stratigraphic range of the PS (fig. 3). The resins content in oils varies from tenths of a percent in methane-type oils to 50% in heavy, tarry oils.

Diversity of oils in Apsheron Peninsula is most clearly revealed when considering pie charts of the group HC composition of oils (fig. 4). The content of naphthenic HCs in the PS oils of Apsheron Peninsula increases as boiling temperature rises. In the composition of all four temperature fractions, there is a clear predominance of naphthenes over the other two groups (methane and aromatic HCs). This feature is preserved regardless of the geographic coordinates and stratigraphic affiliation of the samples. Some exception is the HC composition of gasoline fraction, in which with stratigraphic depth the paraffins portion slightly rise in expense of some decrease in naphthenes. This becomes especially noticeable beginning with the Supra Kirmaki Shaly Suite.

With stratigraphic depth the aromatics portion in kerosene and higher temperature fractions of Apsheron oils increases (see fig. 4). It is interesting to note that in these

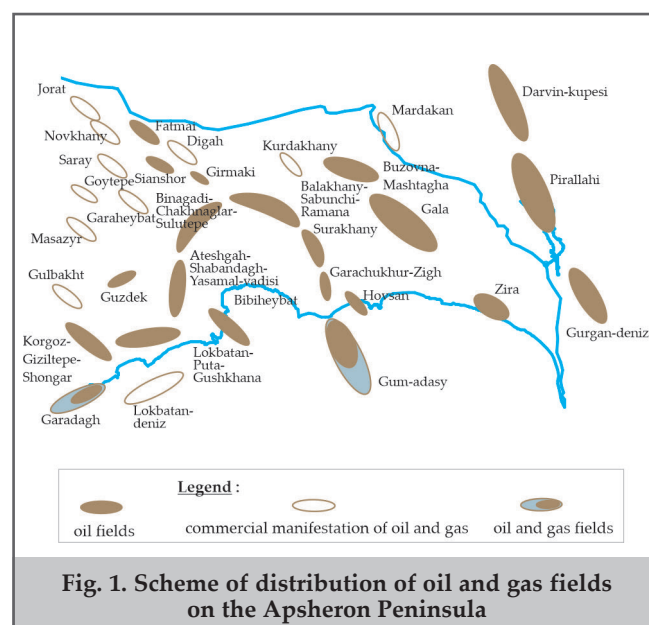


Fig. 1. Scheme of distribution of oil and gas fields on the Apsheron Peninsula

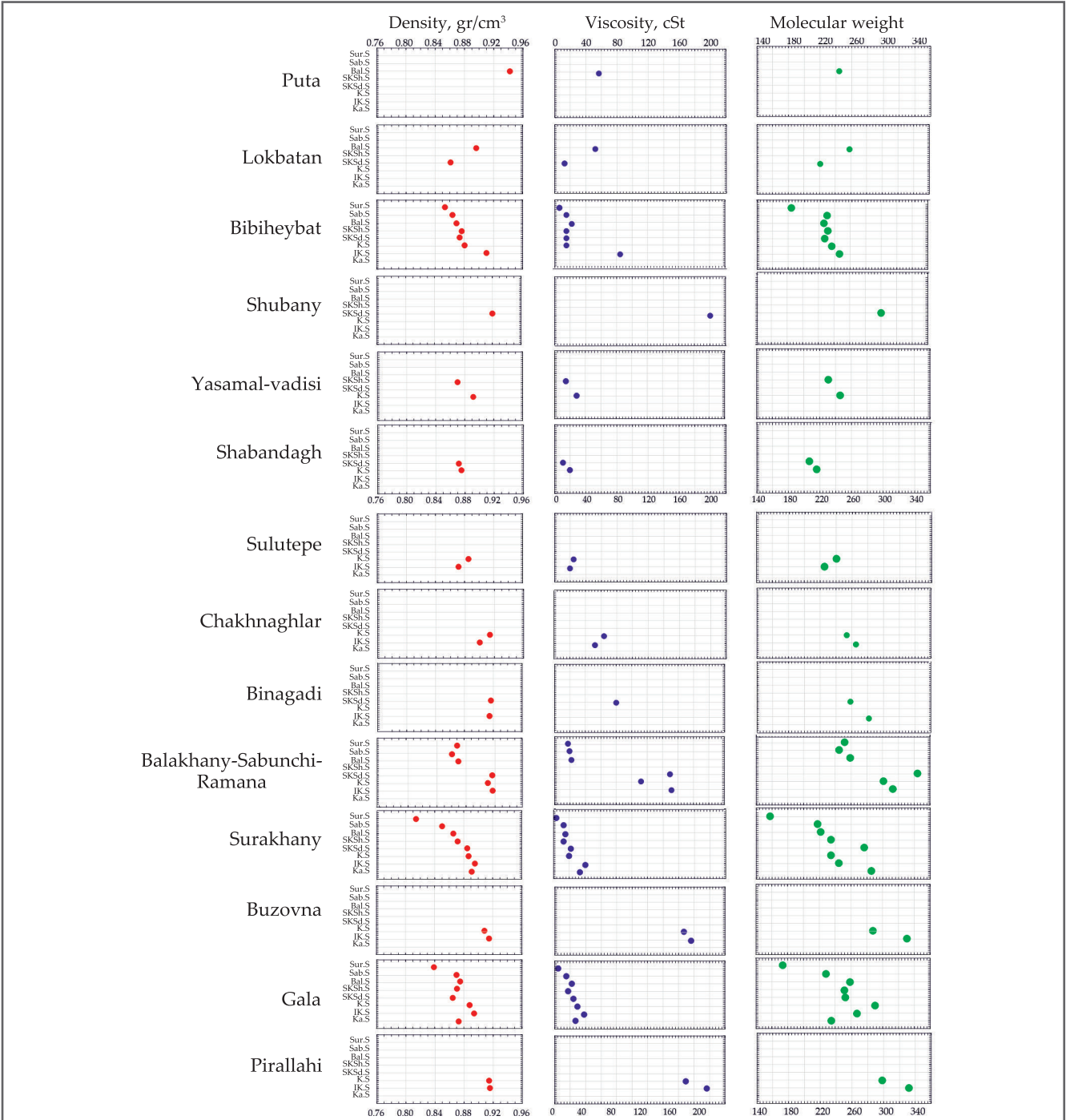


Fig. 2. Changes in density, viscosity, and molecular weight along the stratigraphic section for oils from the Apsheron Peninsula fields. The PS stratigraphy (from young to old): Sur.S – Surakhany Suite; Sab.S – Sabunchi Suite; Bal.S – Balakhany Suite; Fas.S – Fasila Suite; SKSh.S – Supra Kirmaki Shaly Suite; SKSd.S – Supra Kirmaki Sandy Suite; K.S – Kirmaki Suite; IK.S – Infra Kirmaki Suite; Ka.S – Kala Suite

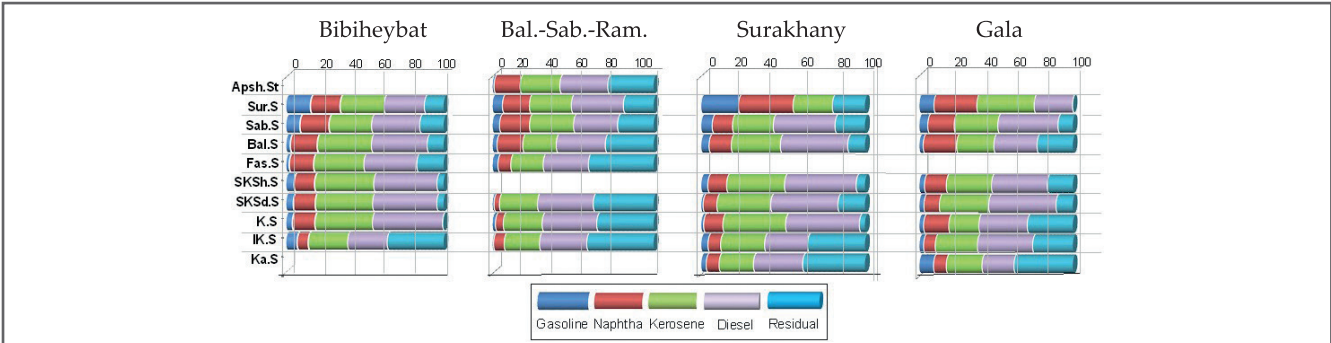


Fig. 3. Diagram illustrating changes in fractional composition of oils along the stratigraphic section of a number of oil fields on the Apsheron Peninsula

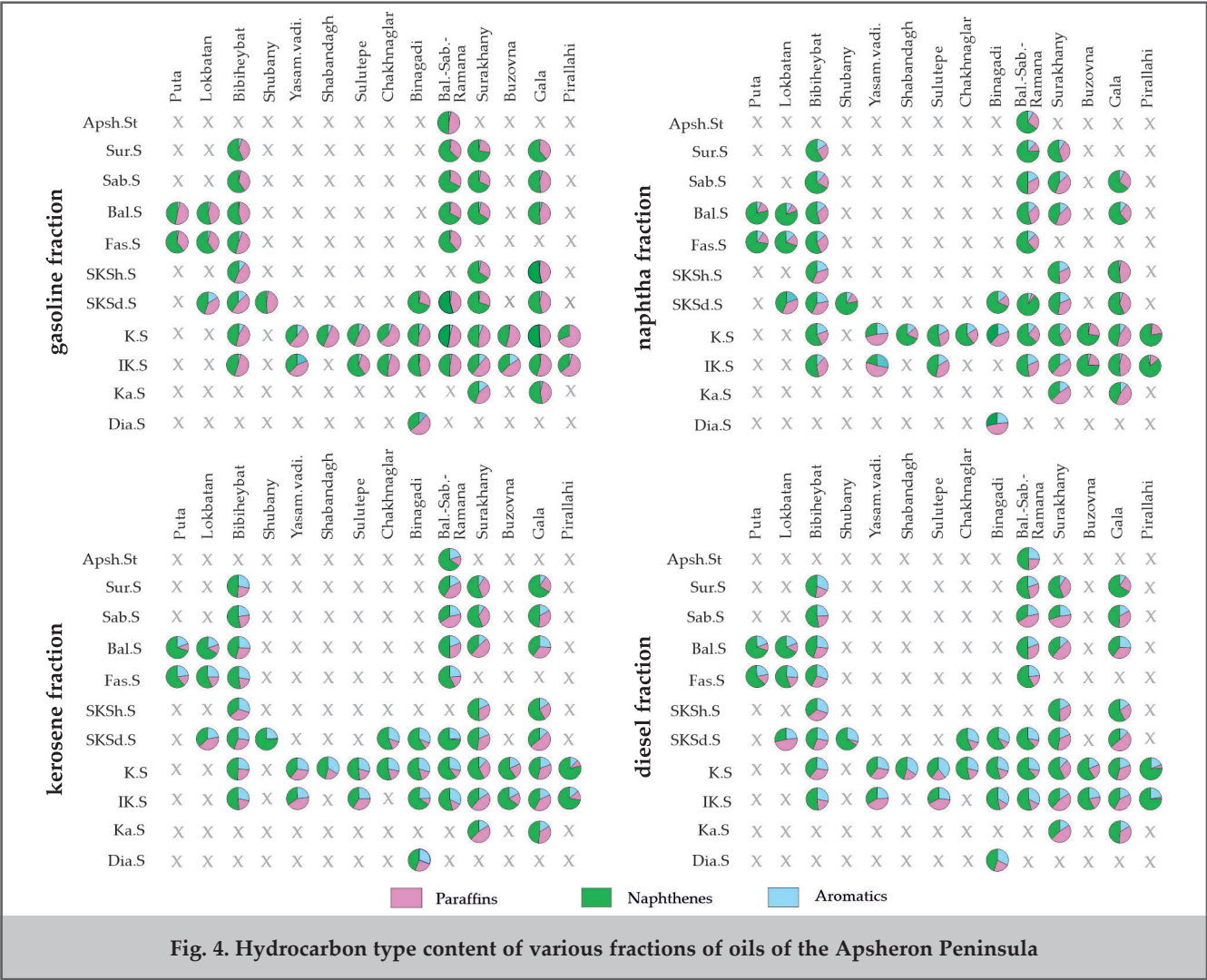


Fig. 4. Hydrocarbon type content of various fractions of oils of the Apsheron Peninsula

fractions the ratio of paraffins to naphthenes is extremely variable and therewith there is no stable, much less a common trend for all oilfields under consideration.

In comparison with the oils from other regions those of Apsheron region contain significantly high (within 0.1-2.0 %) amounts of naphthenic acids. This indicator is highest (up to 2%) in oils from the Balakhany-Sabunchi-Ramana, Binagadi, Chakhnaglar, Shabandagh fields.

According to Samedova F. I. [6] oil species from Apsheron OGBR have density ranging between 830.0-925.7 kg/m³, contain 2-16 % of resins, to 13.8% of paraffins and asphaltenes

from traces to 1.2%. Recent liquid adsorption chromatography data on oils from Balakhany and Surakhany fields confirm prevalence of paraffin-naphthene compounds in the composition of liquid HCs [8-11]. Alongside with that, in heavy oils higher concentrations of aromatic compounds and resins are noted (table).

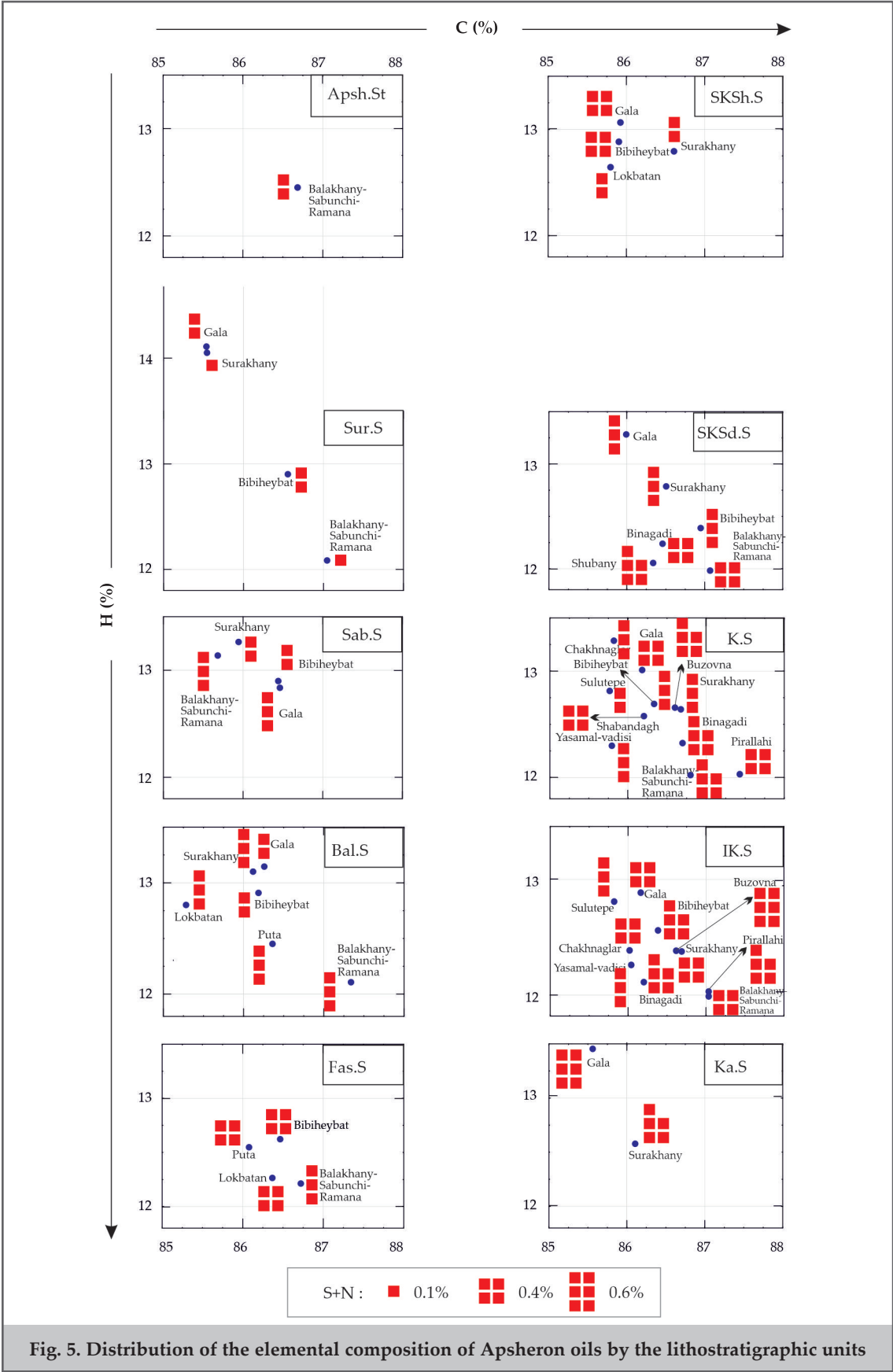
For comparison purposes an oil analysis was added to the table which was collected from producing reservoir at Zaghyly area [12]. The latter falls within Guba-Khazaryani region, another OGBR in Azerbaijan located north-westerly of the Apsheron Peninsula. The area is a part of Siazan oil-

Hydrocarbon composition of oils from Balakhany, Surakhany and Zaghyly fields									Table
No.	Crude oil [Reference]	Specific gravity (kg/m ³)	Molecular weight (g/mol)	Compositional analysis of crude oil, %					
				Paraffin-naphthene group	I aromatic group	II aromatic group	III aromatic group	IV aromatic group	Resins
1	Surakhany light oil [8]	798.90	157.40	74	3.9	5.0	1.3	0.0	0.95
2	Heavy Surakhany oil [9]	825-1003*	182-550*	75.42	5.87	3.68	6.23	4.7	4.1
3	Balakhany oil [10]	887.80	284.00	66.0	6.0	6.46	3.19	9.48	8.87
4	Heavy Balakhani oil [11]	911.50	254-630*	52.04	8.1	7.1	8.6	13.0	11.0
5	Zaghyly [12]	847.9	?	40.5	15.3	4.5	7.8	18.9	13.2
*refers to the range of oil constituents									

field, where production is carried out from steeply plunging monocline reservoir interval stratigraphically spanning Upper Cretaceous–Lower Miocene age. The compositional differences among compared fluids can readily be noticed: the pre-Pliocene oil of Zaghly area is characterized with the low content of paraffin-naphthene constituent (40.5%), the

contrastingly elevated sum of aromatic groups (46.5%) and the significant content of resins (13.2%).

Analysis of the balance of carbon and hydrogen atoms in oil, according to classical elemental analysis, is one of the main methods of oil characterization. Figure 5 displays «carbon : hydrogen» relationship for oils from various



fields, where data for the individual PS suites are reflected on separate graphs. For additional illustration, pictograms of percentage of the sum of elemental sulfur and nitrogen in overall oil specimen are superimposed on these charts. Let us remember that these elements are part of polar compounds, in other words are not chemically associated with HC compounds. These images show a relatively increased content of S and N elements in oils of the lower PS suites (Kirmaki, Infra Kirmaki and Kala Suites), which fits well

with the picture of natural migration fractionation of light HC compounds and the saturation of residual oil with molecularly heavy polar substances.

In conclusion, it should be noted that the picture of the distribution of density and composition of oils along the PS section presented in this article is in good agreement with the results of a number of previous publications, which emphasized the allochthonous nature of HCs in the Lower Pliocene reservoirs [1, 13].

Conclusion

In the section of the PS of Apsheron region, oil fractionation by specific gravity and composition is noted, which is most contrasting between the suites of the Lower and Upper divisions of this stratigraphic unit.

The most notable feature of the Apsheron oils is the stable predominance of paraffin-naphthene HCs in all oil fractions, and this is true for all the fields considered. With the stratigraphic depth of the PS deposits the relative amount of naphthenic HCs increases due, mainly, to a decrease in the content of methane HCs.

The tendency for the specific gravity of oil to increase with depth is characteristic of fields confined to folds, the upper layers of which are untouched by tectonic erosion processes.

In deposits confined to folds with eroded domes, the specific gravity of oil is characterized by a decreasing trend with increasing reservoir depth, which indicates greater preservation with distance from the day surface.

From top to bottom, towards the basal PS suites the distillate fractions show reduction in the light ends (gasoline and naphtha), which is predictably accompanied by an increase in the amount of bottoms. In terms of elemental composition, the deeper the stratigraphic occurrence of the reservoir, the more the whole oil is enriched in sulphur- and nitrogen-containing polar compounds.

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