

Regularities of changes in fluid composition and properties in Vankor field pools: from light to heavy oil

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Abstract. Oil in layers Nkh 3-4, Nkh 1, Sd 9, Yak 3-7 and vYak 2-4 of the Vankor field occurs at the depth of -2,767 to -1,357 meters at strongly different temperatures: from 62 to 26 °C. Such temperature conditions contribute to oil biodegradation processes in the pool. Therefore, oils in different pools significantly differ from each other in terms of composition and properties depending on the intensity of biodegradation. At the same time, pools might embrace both oils that have practically been not exposed to biodegradation processes and significantly biodegraded oils. The most seriously altered oils are found in vYak 2-4 layer pools. They are the heaviest and the most viscous oils among the samples under study. Many typical oil components (alkanes, alkylbenzenes, naphthalenes, phenanthrenes, dibenzothiophenes) are absent in their composition. Besides, the initial distribution of hopanes in the composition of biomarkers is altered. Apart from the molecular composition of degassed oil samples, the work also studies the effect of biodegradation on the properties and the component and isotopic composition of oils, gases and formation fluid samples.

1. Introduction

The Vankor oil and gas field is located in the northeast of Western Siberia (Russia). The field is multilayer and major. Oil and gas are accumulated predominantly in its Lower Cretaceous deposits. At the same time, the main pools are located in sand layers Nkh 3-4, Nkh 1 of the Nizhnekhetskaya formation (age – $K_1 b_1-v_1$), layer Sd 9 of the Sukhodudinskaya formation (age – $K_1 v_1-g_1$) and Yak 1-2, Yak 3-7 and vYak2-4 of the Yakovlevskaya formation (age – $K_1 a_2-a_2$) at depths with not high formation temperatures (25-65°C). Such temperature conditions are rather favorable for the occurrence and development of a formation microflora that consumes and generates hydrocarbon components of crude oil with its life-sustaining activity. It results in significant changes in the composition and properties of the formation fluid depending on the degree of biodegradation. Biodegradation can be the reason for forming heavy and viscous oil pools that are much harder to develop vs. usual oils. This fact has already been discussed with regard to the Vankor field. [1][2][3][4][5][6][7].

Currently, a significant amount of experimental material on the Vankor field has been accumulated, including not only standard studies of the physical and chemical properties of wellhead and downhole fluid samples, but also detailed geochemical studies (Rock-Eval pyrolysis of oil-saturated sandstones, GC/MS and IRMS studies of oils, gases and extracts from oil-saturated rocks). All this allows comprehensively characterizing the pools of the Vankor field and track changes in the fluid composition and properties at different levels. The field section demonstrates that all its pools contain



the same oil generated by the Yanovstanskaya formation [2]. Therefore, this case is an excellent example of the influence of secondary oil transformation processes in a pool that are evident at the level of physical and chemical properties of oil, as well as its molecular and isotopic composition.

2. Signs of oil biodegradation in the Vankor field

The influence of the biodegradation process in reservoir conditions on the composition and properties of oil is well-known and has been described in the examples of numerous fields. Besides, biodegradation has been studied within the framework of numerous laboratory experiments. It is a well-known fact that one of the first signs of biodegradation is the reduced content and disappearance of light n-alkanes. Usually, they are C₃-C₁₅ n-alkanes. Specific groups of biomarkers, such as diasteranes, triaromatic steroids and porphyrins, are considered most resistant to biodegradation among the oil components that can be identified [8][9].

Performed microbiological studies have proved the presence of hydrocarbon-oxidizing microorganisms in the microflora of waters from layers Nkh 4, Sd 9 and Yak 3-7 (table 1). Apart from hydrocarbon-oxidizing microorganisms, methane-producing bacteria have also been found in the composition of the formation microflora. By consuming the metabolism products of hydrocarbon-oxidizing microorganisms (acetates and carbon dioxide), methanogens generate methane [10][11] and are one of the main reasons for forming gas caps in pools with biodegraded oils [12][13][14], including those in the Vankor field.

Table 1. Microbiological characteristic of formation water samples from the Vankor field (the sampling is near the OWC)

Layer	Eh, mB	pH	Number of microorganisms, cells/ml			
			Heterotrophs	Denitrifiers	Methanogens	Hydrocarbon-oxidizing microorganisms
Yak 3-7	-100	7.3	2.3×10 ⁶	45×10 ³	7.5×10 ³	800×10 ³
Sd 9	-65	8.4	1.8×10 ⁶	150×10 ³	1.5×10 ³	620×10 ³
Nkh 3-4	-60	7.7	1.1×10 ⁶	1.4×10 ³	1.2×10 ³	370×10 ³

It is widely accepted that microorganisms in a formation live in water environment and the biodegradation process itself occurs at the OWC. However, formation microflora can also be found above the OWC level, therefore, there are assumptions about possible biodegradation along the whole depth of an oil pool [9]. It is expected that the residual water adsorbed by a mineral rock matrix is quite sufficient for the live-sustaining activity of microorganisms. Nonetheless, it should be taken into account that the population and activity of microorganisms in these conditions are inconsistent with their activity at the OWC level and is expected to significantly drop in a direction away from the OWC.

The easiness of n-alkane utilization by microorganisms vs. other oil components is often applied to assess the level of biodegradation and is the basis for specific molecular parameters, such as $Ki = (Pr+Ph)/(nC_{17}+nC_{18})$ – isoprenoid coefficient [15][16], Pr/nC_{17} , Ph/nC_{18} [8][9]. However, the efficacy of such an approach is restricted with the complete utilization of n-alkanes by microorganisms at high-level biodegradation, which often does not allow assessing the degree of microbial changes accurately. Taking into account that formation oil is a complex mixture being predominantly composed of hydrocarbons, it can be stated that changes in its composition and properties under the influence of biodegradation are to a certain extent step-by-step and consistent and depend on the biodegradation-resistance of separate component groups. Therefore, the resistance of different classes of compounds

and their generalized sequence of utilization by microorganisms [9] has become the basis of the 10-point scale of biodegradation level assessment [8] that allows ranking not only oils with not high microbial activity level, but also severely biodegraded oils. The degree of oil biodegradation in the Vankor field determined in such a way changes within a relatively wide range and corresponds to 0-7 levels.

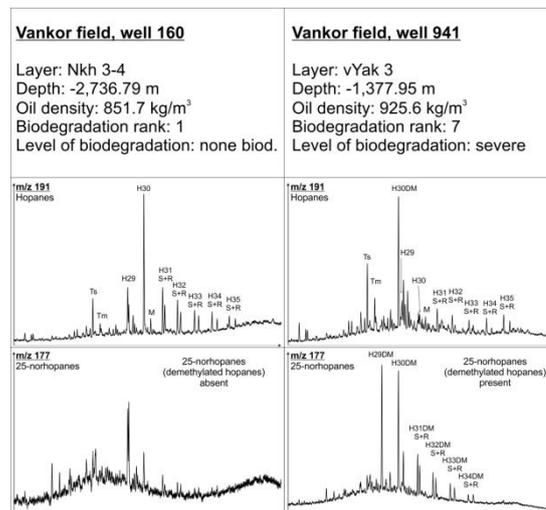
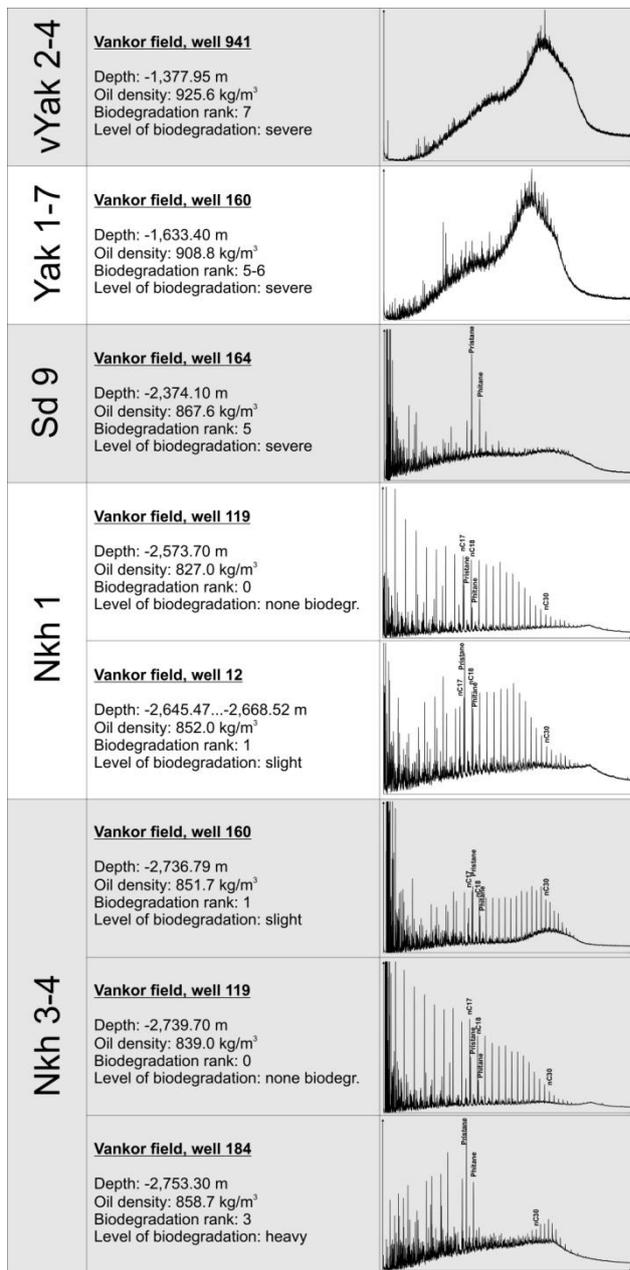


Figure 2. Comparison of the composition and distribution of hopanes and demethylated hopanes (25-norhopanes) in oils with slight and severe biodegradation.

Figure 1. Typical chromatograms of crude oils from different layers of the Vankor field (the level of biodegradation is determined with a scale [8], the level of biodegradation is assessed in compliance with [9]).

Oils from Nkh 3-4, Nkh 1, Sd 9, Yak 1-2, Yak 3-7 and vYak2-4 are significantly different in terms of the biodegradation degree. Figure1 shows typical chromatograms for oils from the pools of different formations and some characteristics of degased oil samples. At the same time, the deepest layers, Nkh 3-4 and Nkh 1, comprise both oils with heavy biodegradation (level 3) and oils that have been practically not been affected by biodegradation processes. This becomes evident from the drastically different chromatograms (figure 1) and the presence or absence of a range of n-alkanes. However, the

chromatograms for samples from less deep-lying layers of the Yakovlevskaya formation (Yak and vYak) are characterized by the complete absence of normal- and isomeric-structure alkanes. In comparison with oils from other formations, the chromatograms show the prevalence of a hump or unresolved complex mixture (UCM). Nonetheless, the oils of the Yakovlevskaya formation itself reveal significant differences. The oils from its upper part (vYak) practically do not have the peaks of individual components at all, whereas, the hump itself becomes “balder” vs. other oils from the Yak layers.

As for all oils from the Vankor field under study, special attention should be paid to oils from the vYak layers that demonstrate the highest level of biodegradation. These samples lack not only the easiest to utilize components, such as n- and iso-alkanes, but also components being more biodegradation-resistant, i.e. alkyl-cyclohexanes, alkylbenzenes, naphthalene and alkyl-naphthalenes, phenanthrene and alkyl-phenanthrenes, dibenzothiophene and methyl-dibenzothiophenes. Besides, this severe biodegradation leads to the distorted distribution of hopanes (figure 2). Earlier, biodegradation of hopanes in Russia’s oils from the Timan-Pechora and Volga-Ural regions, the Pre-Caucasian region and Sakhalin, as well as in Cenomanian oil pools in Western Siberia has already been mentioned in a range of publications [1][17][18] [19].

Hopanes are rather resistant to the impact of microorganisms, whereas their disappearance from the composition of oils depending on the mechanism usually complies with biodegradation of the 7th or 9th rank [8]. Biodegradation in Vankor field oils follows the demethylation route with the generation of 25-norhopanes, therefore they are revealed in the composition of vYak oils on the basis of the m/z 177 characteristic ion (figure 2), and the level of biodegradation is considered equal to 7. Besides, no significant changes have been found in the composition of steranes, which testifies the fact that the degree of biodegradation is not higher than 7.

3. Consequence of biodegradation effect on the composition and properties of Vankor field fluids

Indubitably, all changes in the composition of oils resulting from biodegradation lead to changes in their physical and chemical properties. As it can be seen from figure 3, the lightest oils with the lowest viscosity, low sulfur content, the highest production of light ends, high content of parafins and lower content of resins are found in layers Nkh 1 and Nkh 3-4. As the depth of the pools drops and the level of biodegradation resulting from utilization of the lightest ends in the oil composition grows, the composition and properties change to heavier. The least deep pools of the vYak layers where formation temperatures are about 25 °C contain oil that is characterized by the complete absence of fractions boiling off under 200 °C. The density of oil from the vYak layers, on average, makes 925.6 kg/m³, whereas, its viscosity reaches the values of 415 cP. These oils have the highest contents of resins (up to 15 %), but they do not stand out from other samples under study in terms of the amount of asphaltenes.

As for the oils from the Yakovlevskaya formation under consideration, there is one sample from well 164 (layer Yak 3-7, sampling depth -1,594.5 m) that stands out in terms of a range of physical and chemical characteristics. In comparison with other oils from the Yakovlevskaya formation, this oil is characterized by significantly lower density and viscosity, lower sulfur content and higher content of parafins, as well as a lower biodegradation level (figure 3). Its presence cannot be explained with a crossflow or inappropriate formation tests. The presence of so strongly different oil in Yak 3-7 can be explained by the occurrence of zones having a worsened hydrodynamic connection with the main part of the pool and the OWC area in Yak 3-7.

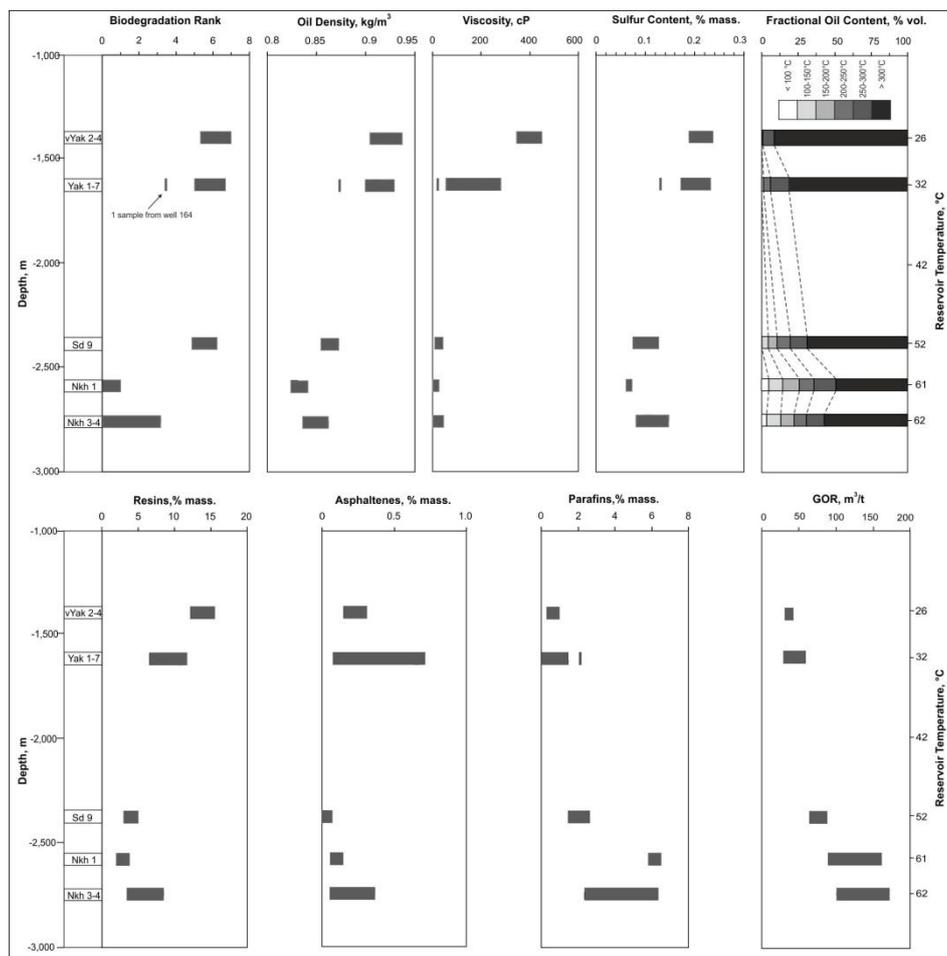


Figure 3. Physical and chemical properties of degassed oils and GOR of formation oils from different layers of the Vankor field (the biodegradation rank is determined with [8]).

In addition to the studies of physical and chemical properties and molecular composition, the following were also analyzed- the isotopic composition of oil carbon, extracts from oil-saturated rocks and fractions of saturated, aromatic hydrocarbons, resins and asphaltenes derived from them (figure 4). The figure shows that as the degree of biodegradation grows from layer Nkh 3-4 to the Yak and vYak layers, the strongest weighting of the isotopic composition of carbon occurs in saturated hydrocarbon fractions. It is quite logical and expectable, as saturated hydrocarbons are most prone to biodegradation. Taking into account the sufficiently high level of biodegradation in Yakovlevskaya formation oils vs. oils from the Nkh layers where many aromatic hydrocarbons (naphthalenes, phenanthrenes, etc.) and some heteroatomic compounds (dibenzothiophenes, etc.) are impacted, it is also possible to state that the heavier isotopic composition of the carbon in the fractions of aromatic hydrocarbons and resins is quite explainable. The differences in the isotopic composition of carbon in asphaltenes derived from the oils and extracts of various layers are insignificant. However, it is not clear enough whether this slight difference is the consequence of a biodegradation effect or it is initially implied in the composition of original fluids. It can result from both the step-by-step formation of the pools (portions of oil belonging to different generation stages) and an insignificant distortion in the process of secondary migration (influence of the oil travel path length).

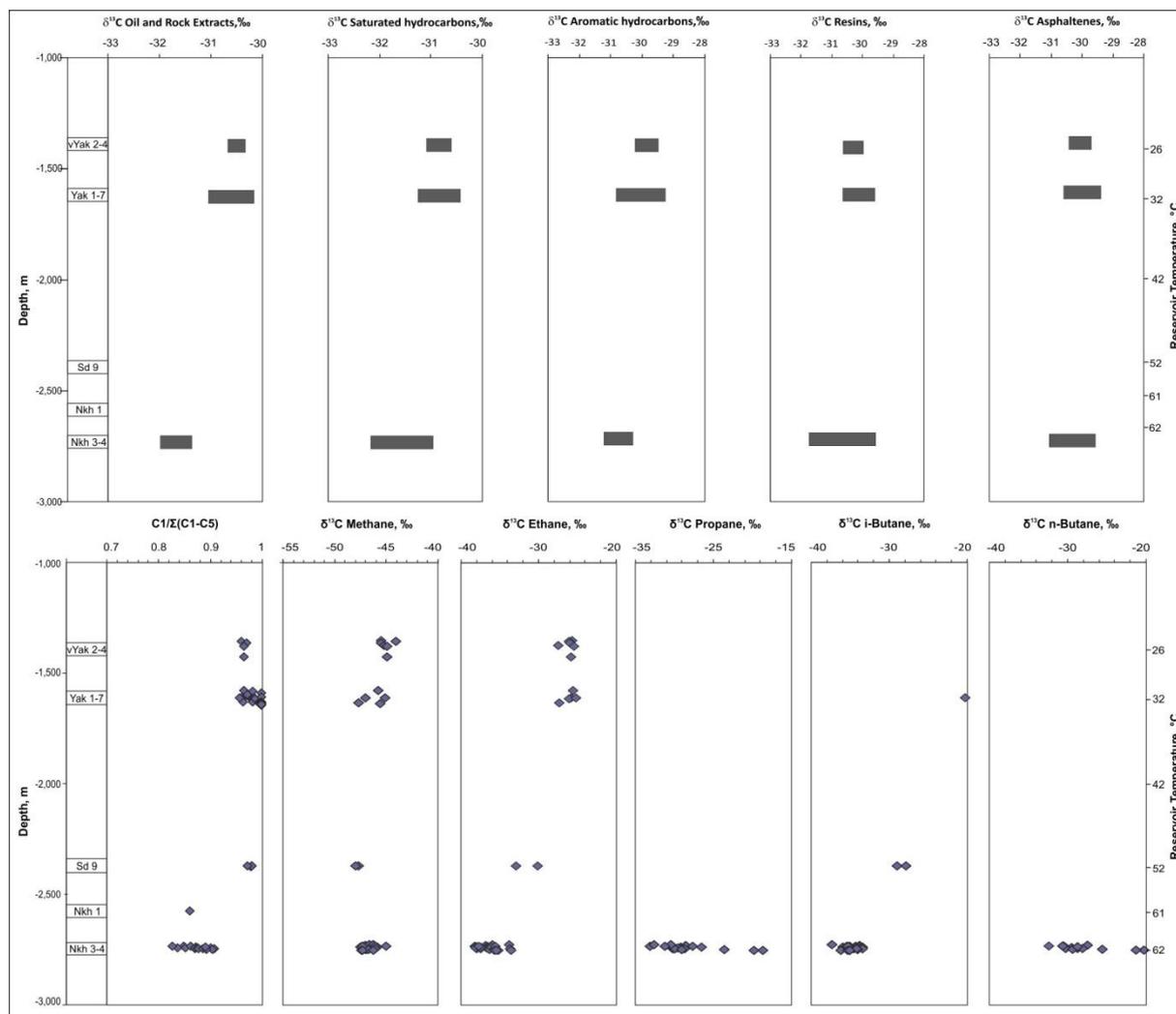


Figure 4. Isotopic composition of carbon in oils, extracts from oil-saturated rocks and their fractions, and changes in the component and isotopic composition of gases dissolved in oils from different layers of the Vankor field.

The composition of solution gas experiences significant changes too, and these changes are evident not only at the level of the component composition, but can also be detected in the isotopic composition of carbon (figure 4). The gas from the upper beds with the most significantly biodegraded oil (Sd 9, Yak 1-7, vYak 2-4) is methane-containing. Its share vs. other homologous compounds is 0.96-0.99. Unfortunately, it is impossible to determine the influence of biodegradation and methanogenesis on $\delta^{13}\text{C}$ methane values at this stage, as the Vankor field does not comprise pools that are not influenced by secondary transformations, the $\delta^{13}\text{C}$ methane values of which could be used as the reference characteristic of the initial fluid filling in the traps. Even the methane from the least biodegraded pool in Nkh 3-4 practically does not differ from the upper pools with a higher biodegradation rank in terms of its isotopic composition. Besides, there are no significant changes in the isotopic composition of methane carbon from layer to layer. The values of $\delta^{13}\text{C}$ methane – both dissolved in the oil rim and methane from the gas caps of the pools – vary within -48...-44 ‰. Such values are quite typical for both thermogenic methane and secondary microbial methane [13]. On the other hand, it is necessary to take into account the experience of geochemical studies [20] for the oil fields of the southeastern part of Western Siberia (Tomsk Oblast). Several fields were formed there due

to generation of the Bazhenov formation, being the age and facies analog to the Yanovstanskaya formation, a source rock generating oil at the Vankor field [2]. The methane carbon in the non-biodegraded oil pools from these fields is isotopically lighter (-52...-57 ‰). It is quite possible that the methane of the initial fluid filling in traps in the Vankor field could have a similar isotopic carbon composition before being distorted by biodegradation and methanogenesis.

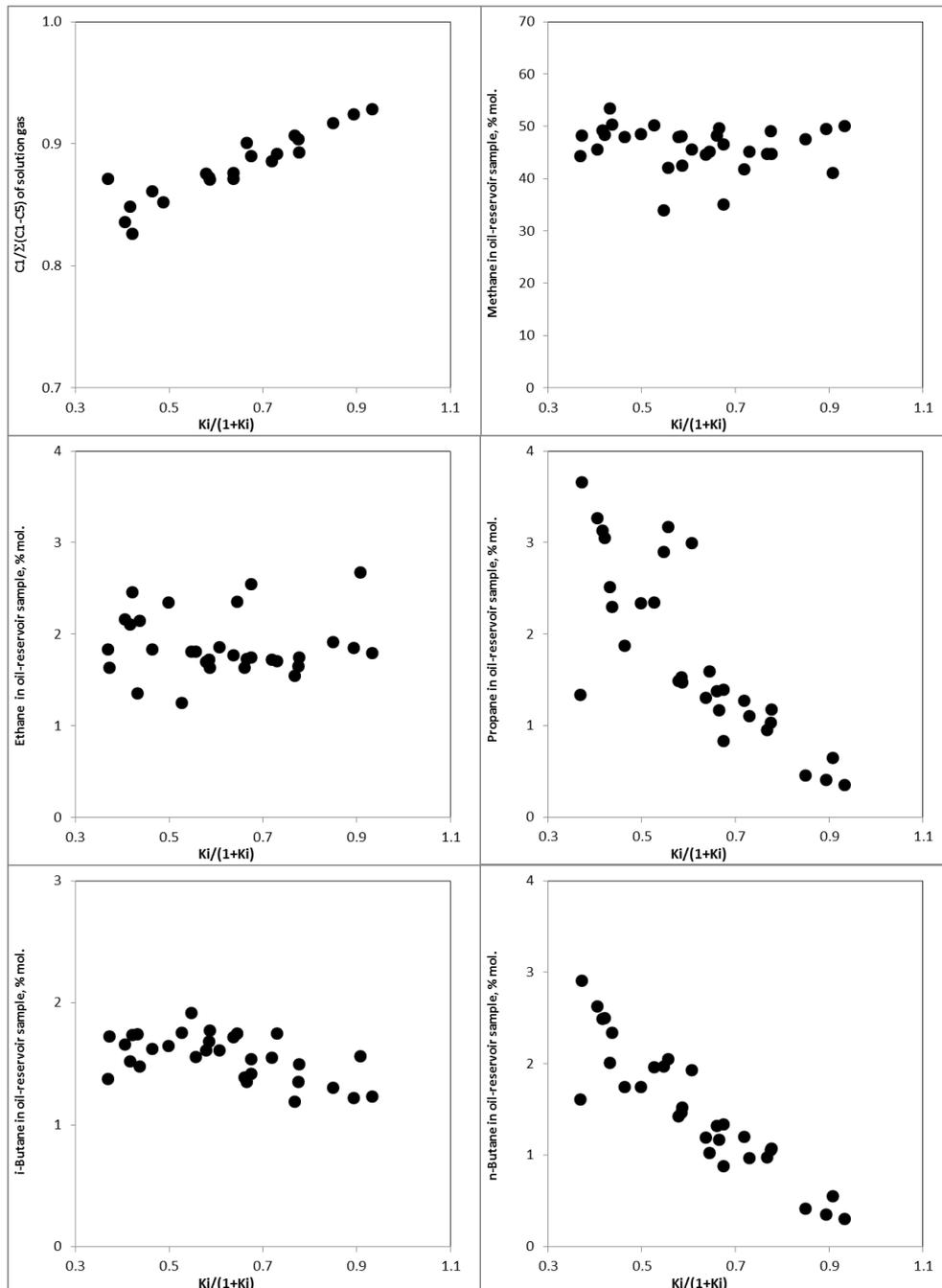


Figure 5. Relationship between separator gas composition and content of gaseous components in Nkh 3-4 downhole oil samples and isoprenoid coefficient $K_i/(1+K_i)$.

The isotopic composition of ethane carbon consistently becomes heavier from the bottom to the top of the section: from -38 ‰ in Nkh 3-4 to -25 ‰ in the Yakovlevskaya formation layers. A more

significant weighting is relevant to iso-butane: from -37 ‰ in Nkh 3-4 to -20 ‰ in Yak 3-7 (due to the low iso-butane content, this evaluation is performed only for one gas sample from the Yakovlevskaya formation). Because of the low content of propane and n-butane in the gases of heavily biodegraded fluids, isotopic assessments for these components are mainly performed only for gases from a deeper-lying layer, Nkh 3-4.

The wide dispersion of the methane content, 0.84-0.92, in gas from Nkh 3-4 and the significant range of changes in the isotopic composition of propane (-35...-18 ‰) and iso-butane carbon (-36...-20 ‰) testify the fact of active biodegradation processes in dissolved gaseous components.

Really, if the isoprenoid coefficient is used as a biodegradation criterion for oil from Nkh 3-4 and compare it with the share of solution hydrocarbon gases in formation oil (based on the results of downhole sample studies), it can be seen that there is a good correlation between the decreasing propane and n-butane content and the growing share of pristane and phytane vs. alkanes (growing isoprenoid coefficient) (figure 5). Consequently, the solution gas itself becomes leaner, which is evident from the growing $C1/\Sigma(C1+C5)$ values. In addition, there is a slight trend towards the decrease in the iso-butane content with biodegradation, which probably testifies to its insignificant biodegradation. It is noteworthy that there is a clear connection between the decreasing content of propane and n-butane in formation oil and the isotopic composition of carbon in these components (figure 6). Some researchers [9][21] have demonstrated the selective utilization of propane vs. other homologous compounds, which results in changes to the isotopic composition of carbon only in propane without affecting other components. Layer Nkh 3-4 is characterized by the synchronous consumption of both propane and n-butane by microorganisms, which is testified by the relationship of their isotopic compositions (figure 6). Besides, the relationship between the parameters of oil and gas dissolved in it (figure 7) reflecting the proportion between the content of branched and normal alkanes testifies the synchronous utilization of low-molecular and heavier compounds by microorganisms, which is somewhat out of keeping with the generally accepted viewpoint about the easier biodegradation of lighter compounds.

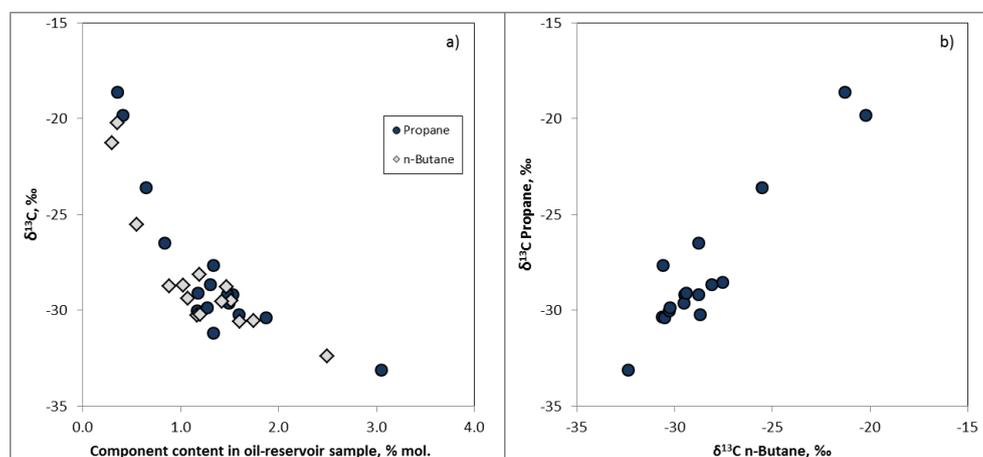


Figure 6. Relationship between isotopic composition of carbon in propane and n-butane and the share of these components in reservoir oil samples from Nkh 3-4 (a) and relationship of the isotopic composition of carbon in propane and n-butane (b).

The reason for the weighting of the isotopic composition of carbon in gaseous components with biodegradation is rather obvious. As the bonding strength of $^{12}\text{C}-^{12}\text{C}$ is lower vs. $^{12}\text{C}-^{13}\text{C}$, the metabolism products of bacteria utilizing hydrocarbons are expected to be enriched with a lighter carbon isotope. Consequently, methanogens, ethanogens and propanogens using these products will generate isotopically light methane, ethane and propane. In other words, biogenic (newly formed) gases cannot be isotopically heavier than initial oil. On the other hand, microbiological degradation is

relevant not only to liquid oil compounds, but also gases dissolved in it. In this case, molecules with ^{12}C - ^{12}C bonds will also be primarily utilized in them, whereas the remaining gas will be enriched with heavy carbon. It has been found that the isotopically heaviest propane in Nkh 3-4 in a sample is from the near-OWC area (well .184). In this sample, it was detected that $\delta^{13}\text{C}$ propane is equal to -18.6 ‰, and the authors [22] have obtained the value of -2.6 ‰. Apparently, the deeper degradation of $\delta^{13}\text{C}$ propane can have a positive influence (over zero). Obviously, the speed of biochemical gas utilization drops in the following order: propane, n-butane, iso-butane, ethane. Consequently, the residual accumulation of isotopically heavy molecules in gases will grow in a reverse order: from ethane to propane.

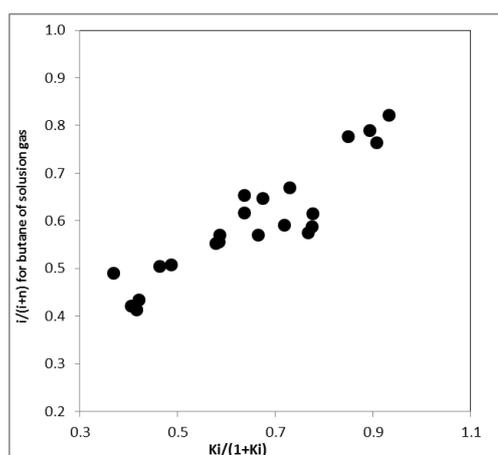


Figure 7. Relationship between $i/(i+n)$ for butane of solution gas in Nkh 3-4 oil and isoprenoid coefficient $K_i/(1+K_i)$.

4. Conclusion

Oil fluids from Nkh 3-4, Nkh 1, Sd 9, Yak 3-7 and vYak significantly differ from each other in terms of their physical and chemical properties, gas saturation level, molecular and isotopic composition. As oils from different layers have the same origins (generated by the organic matter of the Yanovstanskaya formation at close catagenesis stages), the differences revealed are the consequences of secondary transformations in a pool, and namely – biodegradation.

The value of oil biodegradation in the pools of different layers varies from 0 to 7 on a 10-point scale. The deepest layers, Nkh 3-4 and Nkh 1, where reservoir conditions do not contribute to high microflora activity, comprises zones where non-biodegraded and slightly biodegraded oils (the value of biodegradation making 0-3) are spread. The most biodegraded oil samples under study are those from the vYak layers (the biodegradation rank being 6-7). These samples lack not only the easiest to utilize components, such as n- and iso-alkanes, but also components being more biodegradation-resistant, i.e. alkyl-cyclohexanes, alkylbenzenes, naphthalene and alkyl-naphthalenes, phenanthrene and alkyl-phenanthrenes, dibenzothiophene and methyl-dibenzothiophenes. Besides, such severe biodegradation leads to the distorted initial distribution of hopanes.

The influence of biodegradation processes is reflected in changes to the component and isotopic composition, as well as properties of reservoir oils due to the step-by-step utilization of primarily light components from propane to nC_{18} . Thus, the evaluation of the biodegradation level based on the study of degassed oil samples and extracts from oil-saturated core allows predicting the composition and properties of reservoir oil.

Another equally important process of secondary transformation occurring in the pools is methanogenesis that resulted in the formation of gas caps in the Vankor field pools.

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