

Physical evidence of abiogenous synthesis of oil hydrocarbons

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On the basis of the study a fetch from 21 sample of oil is established that the molecular- mass distribution of n-alkanes in oil well described by the Anderson-Schulz-Flory formula that used in the theory of polycondensation synthesis of hydrocarbons. It is shown that the distribution of n-alkanes in the oils is identical to their distribution in the products of the Fischer-Tropsch on catalysts of Fe₂O₃. It is concluded that a significant portion of petroleum hydrocarbons are generated in the upper floors of the Earth's crust in processes of the polycondensation.

Key words: Oil, hydrocarbons, n-alkanes, formula Anderson-Schulz-Flory, polycondensation synthesis, molecular mass distribution

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It is known that oil and gas hydrocarbons may be formed as a result of destruction of bioorganic molecules, and as a result of processes of abiogenous synthesis. On this basis, it is suggested that oil and natural gas on the Earth origin from dead organic matter contained in the rocks – the organic hypothesis [Kontorovich, 1998], or they occurred in polycondensation synthesis reactions of hydrocarbons from carbon oxides and hydrogen, are part of the underground fluids and gas occurring in the terrestrial depths – the mineral hypothesis [Journal, 1986]. Also there is the views [Dmitrievsky, 2008] that oil and gas born with the participation of both biogenous and abiogenous mechanisms of hydrocarbons formation.

In accordance with the results of [Barenbaum, 2004], the hydrocarbons of oil and gas are formed mainly in two ways: 1) in the reactions of polycondensation synthesis of hydrocarbons on the catalysts included in rock formation, and 2) by means of the extraction of hydrocarbons formed in the processes of diagenesis and catagenesis organic substance of sedimentary rocks by underground fluids and waters.

The first process determines presence into oil the normal alkanes, alkanols, and other relatively simple structured hydrocarbon. The second is responsible for presence into the oil a much more complex carbon-containing compounds, including the biomarkers are structurally relating with organic matter from which they originated, as well as hydrocarbons, which have experienced changes during biodegradation processes [Petrov et al., 1994].

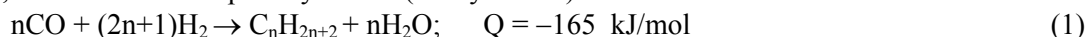
Biomarkers serve irrefutable proof of participation destruction processes of dead organisms of sediment rocks in formation of the oil. By means of biomarkers can be judged about geological conditions of formation and the conversion degree of the original organic substance, on the conditions of formation of oil and gas, as well as solve other tasks [Bazhenova et al., 2000].

The share of biomarkers in untransformed oils, however, is insignificant; it usually does not exceed a few percent. The bulk of oil hydrocarbons (primarily aliphatic) have not a pronounced structural connection with the organic substance of sedimentary rocks. The formation of these hydrocarbons can in principle be explained due to biogenous and abiogenous mechanisms of their genesis. The choice between these alternatives has long served as a point of contention of supporters of organic and mineral hypotheses origin of oil and gas.

The well-defined evidences syntheses of oil hydrocarbons, however, are absent. Attracted to this argument, such as atypical agents to isotope ratio C¹³/C¹² in some oil and gas, the absence in many cases the "mother bed of oil", accumulations are confined to a "channels of degassing" or placing their deposits in the crystalline basement, etc. were indirect. These facts cannot be reliable evidence of abiogenous synthesis hydrocarbons of oil.

In the present work we are proving the involvement of abiogenous synthesis oil hydrocarbons on base of study the molecular weight distribution of normal alkanes in the raw oils. This group is usually dominant in the raw oil type of A1 on the classification Petrov [Petrov *et al.*, 1994], which did not undergo biodegradation. The content n-alkanes in such oil, in contrast to biomarkers, can reach tens of percent.

Normal alkanes are the core group of hydrocarbons synthesized from the oxides of carbon and hydrogen in many polycondensation reactions [Rudenko, 1969] and, in particular, in the simplest of them, in the Fischer-Tropsch synthesis (FT-synthesis):



where: $\text{C}_n\text{H}_{2n+2}$ – notations of n-alkanes, Q – enthalpy, "minus" indicates the exothermic reaction nature.

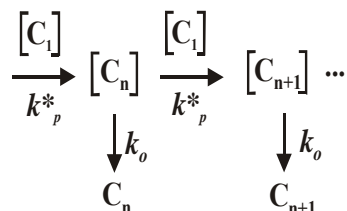
In contrast to other polycondensation reactions, today Fischer-Tropsch synthesis found application in the industrial production of hydrocarbons. Therefore now it has been well studied theoretically and experimentally. Analysis of the distributions of hydrocarbons in products FT-synthesis consisting primarily of alkanes, alkenes, alkanols and alkanaley with number carbon atoms in the chain of 1 to 100 and above, shows that in many cases these distributions obey the classical equation of the Anderson-Schulz-Flory [Glebov, Kliger, 1994]:

$$\lg(g_n/n) = \lg(\ln^2\alpha) + n \cdot \lg\alpha \quad (2)$$

where: g_n – the mass fraction of hydrocarbons with n carbon atoms in molecules, α – constant factor ($0 < \alpha \leq 1$).

The equation (2) has been obtained by G. Schultz (Schulz, 1935) for the molecular mass distribution of polymers in processes radical polymerization. For such polymers obtained by linear polycondensation P. Flory (Flory, 1936) proposed the close equation. American chemists G. Henritsi-Olive and S. Olive [Henritsi-Olive, Olive, 1987] used this formula for the products of Fischer-Tropsch and they found that for values $\alpha > 0.5$, formula (2) also well describes the distribution of individual monokomponent FT-synthesis which been installed by R. Anderson (Anderson *et al.*, 1951).

Thus, it became clear that equation (2) reflects a universal physical-chemical process of grow chain hydrocarbons that bears a probabilistic nature. Equation (2) is theoretically explained [Glebov, Kliger, 1994] by means a number of assumptions based on the pattern formation of polymers:



where: $[\text{C}_1]$, $[\text{C}_n]$, $[\text{C}_{n+1}]$ – the concentration of intermediates with number of carbon atoms on catalyst surface 1, n and n+1; k_p and k_o – the rate of growth and breakage of the carbon chain, respectively.

These conditions as applied to the synthesis of n-alkanes are: 1) the increment of hydrocarbon chain occurs in result of accidental accession $[\text{C}_1]$ -intermediate (molecule CH_2), 2) the chain undergoes by a random breakage, and 3) k_p and k_o are constants which do not depend on chain length.

In this case formula (2) describes a molecular-mass distribution of polycondensation products, where the parameter α has a physical meaning:

$$\alpha = k_p / (k_p + k_o) \quad (3)$$

Equation (2) and its modifications are now turned into an effective tool for studying mechanisms formation of hydrocarbons in the FT-synthesis [Glebov, Kliger, 1994].

The applicability of the formula (2) for n- alkanes of oil for the first time has been demonstrated Glebov [Glebov, 2002]. Barenbaum [Barenbaum, 2007] indicated the possibility of its application in other cases as well as suggested the advisability of its use at analyzing the composition of hydrocarbon in aquamarine gas-hydrates. These studies, however, were only preliminary.

The present work aims to extending the Anderson-Schulz-Flory model, to include the rationale for the possibility of polycondensation of the simplest hydrocarbon of oil.

To this end we studied and systematized the distribution of n-alkanes into 21 samples of "crude" oil type A₁. Investigations were carried out on chromatograph Trace Ultra Thermo Finnigan, on a column of a Sol-Gel 1-MS with a neutral phase, column length 60 m and diameter 0.25 mm, layer of 0.25 nm, temperature of the detector 320°C and the evaporator 300°C, temperature mode is 3°C/min. Verification and identification of hydrocarbons with high-resolution was on performed spectrometer

Thermo Finnigan MAT 900 (with chromatograph Trace GC) with the same column and at the same temperature regime.

We investigated oils of various deposits in the Early Paleozoic sediments, which mainly were at depths exceeding 2 km. The average weight of oil was 0.85 g/cm^3 . Content of the polar fractions in the group composition of oil did not exceed 10%. The methane hydrocarbons of normal structure (80%) and the aromatic hydrocarbons are dominated. Also were investigated very light oil consisting mainly of hydrocarbons of the normal range.

The distributions n-alkanes in the oils were analyzed in a semilogarithmic coordinate system equation (2), starting the number of carbon atoms in the molecule $n = 10$ (Fig. 1a). The normalized results of the measurements were processed by least squares method which allowing to assess in what degree the distribution n-alkanes in oil fit with the theoretical dependence (2) as well as allowing to determine the coefficient α .

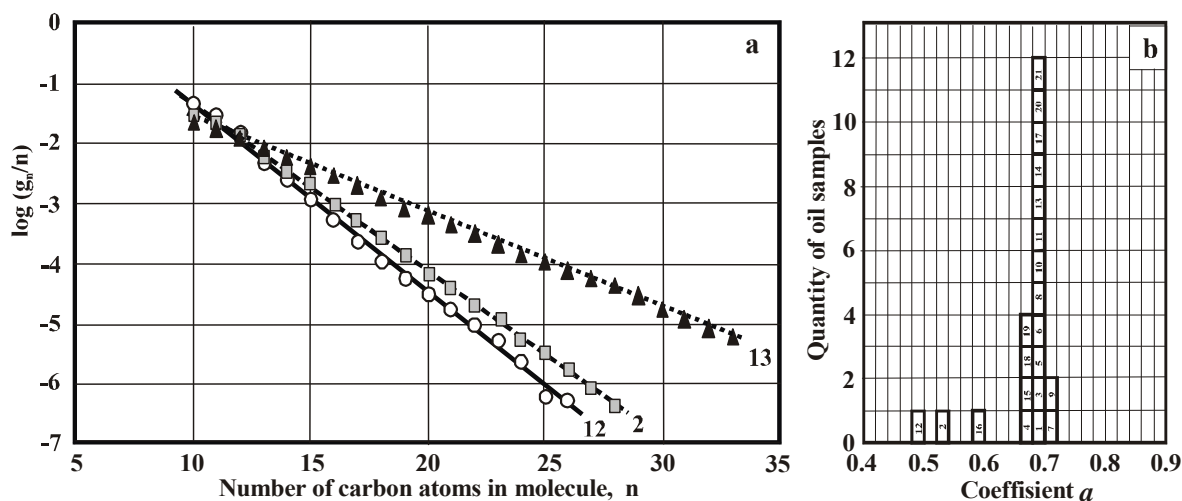


Fig. 1. a) Molecular-mass distribution of normal alkanes three samples of oil in the coordinate system of the Anderson-Schulz-Flory equation and b) distribution of coefficient α for oils. Numerals are numbers of oil samples in Table 1.

Based on formula (2) the value of parameter a can be found in two independent ways: 1) from the tangent of angle slope of the line in Fig. 1a to the x-axis and 2) using the length of line segment that she intercepted on the ordinate. In the cases when chromatograms contain information on all n-alkanes of oil, including gas and gasoline fractions, values of parameter α , calculated by both methods agree well with each other [Glebov, 2002].

In our case we calculated the value of the parameter a from the slope of the line to the abscissa. The processing results are shown in Table 1.

Analysis of the data in Table 1 leads to the following conclusions.

1. Molecular-mass distribution of n-alkanes in the oils with high precision (coefficient of determination over 0.99) is described by the Anderson-Schulz-Flory formula characterizing the hydrocarbons of polycondensation synthesis.

2. The value of the parameter a lie ranges from 0.488 to 0.714, forming a sharp maximum at $\alpha = 0.69$ (Fig. 1b). The samples 2, 12 and 16 differing from the general pattern. They are characterized by a greater slope distributions of hydrocarbons. According to its physical properties we have classified all three samples as condensate rather than as oil.

3. Comparison of the distributions of n-alkanes in crude oils and products FT-synthesis shows that for ours oils the average value parameter $\alpha = 0.69$ is almost identical to the experimentally obtained in the FT-synthesis on catalysts from Fe_2O_3 , at temperatures of $150\text{--}300^\circ\text{C}$ [Glebov, Kliger, 1994]. In experiments the temperature and pressure as well as the composition of synthesis gas (the ratio of H_2 to CO) at comparable amounts of CO and H_2 affected on the value parameter α weakly. The value of this parameter α decreased, when hydrogen is sharp prevail.

A similar increase in the steepness of molecular-mass distribution of n-alkanes observed in crude oils and condensates at depths of more than 3–4 km [Sokolov, Abliia, 1999].

Thus, according to the present materials and the results of [Barenbaum, 2004, 2007] suggest that: 1) significant portion of oil hydrocarbons can be generated in the processes of polycondensation synthesis and 2) hydrocarbons of oils forming in the upper floors of the earth's crust rather than in the depth of the mantle, where sustainable the existence of hydrocarbons is problematic [Melenevsky, Kontorovich, 2007].

Table 1. The results of processing of chromatograms of crude oils

№ of sample	Tangent of angle inclination line on Fig. 1a	Length of line on the ordinate	Coefficient of determinacy	Value of coefficient α
1	- 0.1576	- 0.0280	0.9963	0.696
2	- 0.2783	+ 1.4311	0.9995	0.527
3	- 0.1629	+ 0.0625	0.9982	0.687
4	- 0.1694	+ 0.1106	0.9990	0.677
5	- 0.1656	+ 0.0893	0.9979	0.683
6	- 0.1675	+ 0.0117	0.9931	0.680
7	- 0.1515	- 0.1259	0.9990	0.705
8	- 0.1634	+ 0.0207	0.9977	0.686
9	- 0.1465	- 0.2715	0.9715	0.714
10	- 0.1669	+ 0.0244	0.9960	0.681
11	- 0.1595	+ 0.0487	0.9949	0.693
12	- 0.3115	+ 1.7538	0.9966	0.488
13	- 0.1575	- 0.0260	0.9989	0.696
14	- 0.1644	+ 0.0585	0.9990	0.685
15	- 0.1691	+ 0.1142	0.9986	0.677
16	- 0.2264	+ 0.6971	0.9952	0.593
17	- 0.1559	- 0.0361	0.9985	0.698
18	- 0.1732	+ 0.1789	0.9979	0.671
19	- 0.1698	+ 0.1381	0.9989	0.676
20	- 0.1670	+ 0.1080	0.9984	0.681
21	- 0.1603	+ 0.0082	0.9990	0.691

References

- Barenbaum, A. A (2004). The mechanism of formation of oil and gas fields, *Doklady Akademii Nauk*, V.399, №6, pp. 802–805.
- Barenbaum, A. A. (2007). On possible relationship between gas-hydrates and submarine groundwater, *Water Resources*, V.34, №5, pp.587–592.
- Bazhenova, O. K., Yu. K. Burlin, B. A. Sokolov, V. E. Khain (2000). *Geochemistry and geology of oil and gas*, Moscow State University Press, 384 p (in Russian).
- Dmitrievsky, A. N. (2008). Polygenesis of oil and gas, *Doklady Akademii Nauk*, V.419, №3, pp. 373–377.
- Glebov, L. S. (2002). Molecular weight distribution of n-paraffins Tengiz oil, *Neftekhimiya*, V.42, №2, pp. 92–94.
- Glebov, L. S., G. A. Kliger (1994). Molecular weight distribution of the products of the Fischer-Tropsch, *Uspekhi khimii*, V.63, №2, pp. 192–202.
- Journal of the All-Union Chemical Society named DI Mendeleev* (1986). V.31, №5 (in Russian).
- Henrizi-Olive, G., S. Olive (1987). *Chemistry of Catalytic Hydrogenation of CO*, Moscow: Mir, 248 p (in Russian).
- Kontorovich, A. E. (1998). The sedimentary-migration theory oil-genezis. The status at the turn of XX and XXI centuries, the ways of further development, *Gyeologiya nefti i gaza*, №10, pp. 8–16.
- Melenevsky, V., A. Kontorovich, (2007). Deep-seated (mantle) synthesis of oil: Myth or Reality?, *Tekhnologii TEK*, №1, pp.18–21.
- Petrov, Al. A., N. N. Abryutina, O. A. Arefev, et al (1994). Biomarkers and geochemical typing of crude oils. In book: *Problems of the origin of oil and gas*, Moscow, Nauka, pp. 54–87 (in Russian).

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Rudenko, A. P. (1969). *Theory of self-development of open catalytic systems*, Moscow State University Press, 272 p (in Russian).

Sokolov, B. A., E. A. Abliya, (1999). *Fluids-dynamic model of oil-gas formation*, Moscow, GEOS, 79 p (in Russian).