Method for calculating the individual hydrocarbon composition from the accumulated fractional composition of oil and condensate samples

Metoda obliczania jednostkowego składu węglowodorów na podstawie skumulowanego składu frakcyjnego próbek ropy naftowej i kondensatu

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ABSTRACT: The composition of oils is the main source of information that enables the evaluation and modeling of their physical, thermal and chemical properties (including their critical properties) across a wide range of state parameters. The more comprehensively the composition of oils is analyzed, the more precise information is provided for calculations and problem-solving in the field of oilfield mechanics and related areas, such as the extraction, preparation, transportation, and processing of oils and their fractions. The principal constituents of oils are hydrocarbons. Oils contain hydrocarbons of three homologous series: paraffins, naphthenes and aromas. In oils, there may be hydrocarbons of a mixed composition containing both naphthenic and aromatic rings. In addition to hydrocarbons, oils also contain oxygen, sulfur, nitrogen and other constituents. These compounds are the primary elements of asphaltene-resinous substances (ARS) found in oil. They are characterized by high relative densities (often exceeding 1 g/cm^3), dark coloration, and relative chemical instability when exposed to elevated temperatures, oxygen, adsorbents, etc. The composition of asphaltene-resinous substances encompasses a wide range of substances. The validity of the proposed technique is justified by the observation that the data of molecular weight, Watson characteristic factor, and experimental density calculated from molar compositions should align on the same surface with a high degree of correlation. In addition, the experimental and calculated values, in terms of molecular composition, of molecular weights should lie on a straight line passing through the origin of coordinates with a slope coefficient equal to unity and exhibit high degree of correlation.

Key words: oil, composition, asphaltene-resinous substances, hydrocarbon gases, chemical properties, paraffins, mixtures of pure components, gas-condensate systems, individual hydrocarbon, Watson characteristic factor, high degree of correlation.

STRESZCZENIE: Skład ropy jest głównym źródłem informacji umożliwiającym ocenę i modelowanie jej właściwości fizycznych, termicznych i chemicznych (włącznie z właściwościami krytycznymi) w szerokim zakresie parametrów stanu. Im bardziej dokładnie analizowany jest jej skład, tym dokładniejsze informacje są dostarczane na potrzeby obliczeń i rozwiązywania problemów w dziedzinie mechaniki złóż ropy i powiązanych obszarach, takich jak wydobycie, przygotowanie, transport i przetwarzanie rop i ich frakcji. Głównymi składnikami ropy są węglowodory. Ropa zawiera węglowodory z trzech szeregów homologicznych: parafiny, nafteny i aromaty. W skład ropy mogą wchodzić węglowodory o mieszanym składzie, zawierające zarówno pierścienie naftenowe, jak i aromatyczne. Oprócz węglowodorów, ropa zawiera także tlen, siarkę, azot i inne składniki. Związki te są podstawowymi składnikami substancji asfaltenowo-żywicznych (ARS) występujących w ropie naftowej. Charakteryzują się one wysoką gęstością względną (często przekraczającą 1 g/cm^3), ciemnym zabarwieniem i względną niestabilnością chemiczną po ekspozycji na działanie podwyższonych temperatur, tlenu, adsorbentów itp. Skład substancji asfaltenowo-żywicznych obejmuje szeroki zakres substancji. Uzasadnieniem proponowanej techniki jest fakt, że dane dotyczące masy cząsteczkowej, współczynnika Watsona i gęstości eksperymentalnej obliczonej na podstawie składu molowego powinny znajdować się na tej samej powierzchni z wysokim stopniem korelacji. Ponadto, wartości eksperymentalne i obliczone w odniesieniu do składu molekularnego mas cząsteczkowych powinny znajdować się na linii prostej przechodzącej przez początek współrzędnych ze współczynnikiem nachylenia równym jedności i wykazywać wysoki stopień korelacji.

Słowa kluczowe: ropa, skład, substancje asfaltenowo-żywiczne, gazy węglowodorowe, właściwości chemiczne, parafiny, mieszaniny czystych składników, systemy gazowo-kondensatowe, pojedynczy węglowodór, współczynnik Watsona, wysoki stopień korelacji.

Introduction

The composition of oils is the main source of information that enables the evaluation and modeling of their physical, thermal and chemical properties (including their critical properties) in a wide range of state parameters.

Oils contain hydrocarbons of three homologous series: paraffins, naphthenes and aromas. Hydrocarbons of a mixed composition containing both naphthenic and aromatic rings also contain oxygen, sulfur, nitrogen and other constituents of oils.

These compounds constitute the primary components of asphaltene-resinous substances (ARS) in oil. They are characterized by high relative densities (often exceeding one), dark coloration, relative chemical instability when exposed to elevated temperatures and oxygen. Heavy oils do not disperse completely even when distilled under a vacuum, and a significant part of them remains as non-distillable residue. Light oils can be characterized by the content of individual hydrocarbons in them. By distilling the lightest fractions from the oil, the content of individual hydrocarbons up to C_9 is determined by chromatographic analysis (Falovsky et al., 2011).

Degassed oil without hydrocarbons with up to nine carbon atoms in the molecule is often considered as a single "component". However, as this "component" is actually made up of a large number of individual chemicals, it is called a conditional component. The symbol C_{10+} (or C_{n+}) adopted for this conditional component means that the component consists of substances containing ten atoms (or *n* atoms) of carbon plus higher-boiling substances.

However, when solving a number of problems on modeling the development and operation of gas-oil, gas-condensate and gas-condensate-oil fields, it becomes necessary to divide the conditional component into parts. Distillation or chromatographic analysis data are usually used for this purpose, with individual fractions being treated as conditional components in turn. This is also necessary for calculating the composition of the reservoir system. The amount of each component in the reservoir oil is obtained by summing the mass of this component found in the degassed oil and in the gas (Grigoryev et al., 2016).

At the same time, it should be taken into account that degassed oil cannot be equated with a conditional heavy component. In addition to the conditional heavy component, it may contain noticeable amounts of hydrocarbons up to C_9, which should be distilled off when heated and using data on the composition of the distilled product, added to the amount of the corresponding components contained in the gas.

It should be noted that even though the replacement of reservoir oil with mixtures of pure components is also a crude technique, mixtures of pure hydrocarbons possess many important properties, distinctive for reservoir oils or gases of gas-oil and gas condensate fields. The influence of nitrogen, naphthenic and aromatic hydrocarbons on the phase behavior of natural systems can be qualitatively assessed based on data from the study of phase equilibria in some systems consisting of pure hydrocarbons.

Binary and ternary mixtures of normal paraffinic hydrocarbons can only qualitatively reflect some important features of natural gas-oil and gas-condensate systems (Ramazanova et al., 2003). On the quantitative side, deviations can be significant, and these are determined by the specificity of the composition of natural systems, which, in addition to hydrocarbon gases, may contain non-hydrocarbon gases (nitrogen, carbon dioxide, hydrogen sulfide, etc.). In addition to liquid paraffinic hydrocarbons, natural systems also contain liquid naphthenic and aromatic hydrocarbons, as well as various derivatives of hydrocarbons.

Furthermore, some insights into the properties of oil and oil fractions can be obtained from their density and molecular weight. To calculate the molar concentrations of the components, knowledge of the molecular weights of oil and its fractions is necessary.

In the processes associated with oil production, it is also highly valuable to determine the amount of gas and liquid formed from reservoir oil at specific pressures. These data are important in studying the movement of gas-liquid mixtures in a reservoir, wells, and in field communications. Data on the volume of condensate released from gas-condensate mixtures during pressure reduction is similarly important in the production of gas condensate systems. The volume of gas and liquid phases formed from the initial mixture with decreasing pressure can be calculated using data on the compositions of the phases in equilibrium (Bursilovsky, 2002).

The most reliable information about phase equilibria in natural gas-oil and gas-condensate systems can be obtained through experimental studies. Studies of phase equilibria should include data on the composition of equilibrium coexisting phases at various pressures and temperatures. While determining the content of low molecular weight hydrocarbons is very simple, characterizing the composition of phases based on the content of components with molecular masses exceeding 80–90 units presents challenges and introduces some uncertainty into the results obtained.

A large amount of experimental material on the fractional composition of natural oils of the fields has been gathered, but its use is difficult due to the lack of an individual hydrocarbon composition (Thermodynamic studies of reservoir fluids in order to develop recommendations for increasing the hydrocarbon recovery coefficients of gas condensate-oil fields, 2003; Study of the physical and chemical properties of oils from the Apsheron and Kura depressions, 1971–1975).

Particular difficulties arise when attempting to utilize these data for calculating phase equilibria and modeling the processes of developing oil and gas condensate fields, collecting, processing and transporting crude oil.

Thus, a method for calculating the individual hydrocarbon composition by the fractional weight composition of oils, oil fractions and condensates has been developed.

The essence of the developed method for calculating the individual hydrocarbon composition based on the accumulated fractional weight composition of samples (the accumulated weights of fractions are usually fixed, starting from the beginning of boiling to the end of boiling of an oil sample) is as follows:

1. Based on the standard boiling points of normal hydrocarbons $(T_{boil.i})$, their accumulated weight fractions (G_i) are calculated by linear interpolation as follows:

$$G_i = G_{2j} - \frac{G_{2j} - G_{1j}}{T_{boil.2j} - T_{boil.1j}}(T_{boil.2j} - T_{boil.i}) \qquad (1)$$

where: $T_{boil.1j}$ and $T_{boil.2j}$ are, respectively, the temperatures at the beginning and end of the boiling of the j-th fraction in the initial fractional composition, a $T_{boil.i}$ is the boiling point of the i-th individual hydrocarbon; G_{1j} and G_{2j} are, respectively, the accumulated weight fractions at the temperatures of the beginning and end of boiling of the j-th fraction in the initial fractional composition, and   is the desired accumulated value of the weight fraction of the i-th individual hydrocarbon.

In this case, sequentially, the boiling points of individual hydrocarbons are compared with the boiling points of the fractions of this oil. If the boiling point of individual hydrocarbons is less than the initial boiling point (278.15 K in this case) of this oil, then the weight fraction of this component is equal to zero. In cases where the boiling points of individual hydrocarbons are greater than the final boiling points of this oil, then the calculation for these hydrocarbons is not performed.

2. The differences in the accumulated values of weight fractions for each individual hydrocarbon and the sum of the differences are calculated using the formulas:

$$G_i - G_{i-1} \quad \text{and} \quad \sum_1^n (G_i - G_{i-1}) \qquad (2)$$

3. The normalized weight individual hydrocarbon composition is calculated (in %) according to the formula:

$$g_i = \left(\frac{G_i - G_{i-1}}{\sum_1^n (G_i - G_{i-1})} \right) \cdot 100 \qquad (3)$$

where: g_i is the weight percentage of the i-th hydrocarbon component in the sample under consideration.

4. Mole fractions of hydrocarbon components and the sum of mole fractions are calculated according to the formulas:

$$X_i = \frac{g_i}{M_i} \quad \text{and} \quad \sum_1^n X_i \qquad (4)$$

where: X_i and M_i are, respectively, the molar fraction and the molecular weight of the i-th hydrocarbon component.

In this case, the molecular weight of the residue (C_{n+}) is calculated according to the following formula, derived from the material balance (6):

$$M_{Cn+} = \frac{\left(100 * M_n - \sum_i^{n-1} X_i * M_i\right)}{X_{Cn+}} \qquad (5)$$

where: M_n is the molecular weight of the sample; M_{Cn+} and X_{Cn+} are respectively, the molecular weight, and the molar fraction of the hydrocarbon residue.

5. In the absence of experimental data, the molecular weights of samples and their fractions are calculated from their known densities and average boiling points, based on empirical Watson plots. According to (Danko and Kuznetsov, 2012), to characterize oil and its fractions, a value known as Watson characteristic factor can be used. This value lacks theoretical justification and is chosen empirically. It is determined by the ratio of the cube root of the average boiling point $T_{boil.av.}$ (in °K) of the product to its density at 15.6°C, that is, according to the following formula:

$$k = 1.216 \frac{\sqrt[3]{T_{boil.av.}}}{\rho} \qquad (6)$$

The Watson characteristic factor decreases with the transition from paraffinic hydrocarbons to naphthenic and aromatic ones, providing insight into the content (fraction) of hydrocarbons of various series in oil.

The characteristic factor of the mixture can be calculated as the mass average value:

$$k = \sum g_i k_i \qquad (7)$$

where: g_i is the mass fraction and k_i is the characteristic factor of the i-th fraction.

6. The individual hydrocarbon molar composition is calculated (as %) according to the formula:

$$x_i = \left(\frac{X_i}{\sum_1^n X} \right) \cdot 100 \qquad (8)$$

The molecular weight of an oil sample is calculated based on the molar composition according to the additivity rule using the following formula:

$$M_n = \sum_1^n x_i \cdot M_i / 100 \qquad (9)$$

The proposed method was tested on reference data on the properties and fractional compositions of about 700 samples of oils, oil fractions and condensates from the fields of Azerbaijan and Russia (Zozulya et al., 2006).

As an example, below are the results of calculating the molar composition of an oil sample from well production (well No. 245 of the Neftchala field, Azerbaijan).

Data on the fractional composition and molecular weight of oil are given in Table 1. The molar composition of this oil was calculated using the method described above, and the calculation results are shown in Table 2. The calculation was carried out in the following sequence:

Table 1. Oil properties data (well No. 245 of the Neftchala field, Azerbaijan)

Tabela 1. Dane dotyczące właściwości ropy (odwiert nr 245, złoże Neftchala, Azerbejdżan)

Mo-lecular weight [g/mol]	Distillation of oil using the Gadaskin apparatus, in weight % of the initial sample mass					
	Boiling point, B					
	Start of boiling					End of boiling
	278.150	273.150	423.150	273.150	523.150	573.150
197.71	0	10	20	29	39.5	50

1. The calculation of the accumulated weight fractions of individual hydrocarbons was carried out according to the formula (1). In this case, hydrocarbons, ranging from methane to n-butane, inclusive, had lower boiling points than the starting point of boiling. As a result, the weight fractions of these components were set to zero. For hydrocarbons starting from C_{18} and above, the boiling point is greater than the end of the boiling point of this oil, therefore, they were taken as a C_{18+} residue, and for this residue the accumulated weight fraction was assumed to be 100%. The calculation results are listed in the 4th column of Table 2.

2. The differences in the accumulated weight fractions of individual hydrocarbons and the sum of these differences were calculated according to formulas (2) (5th column).
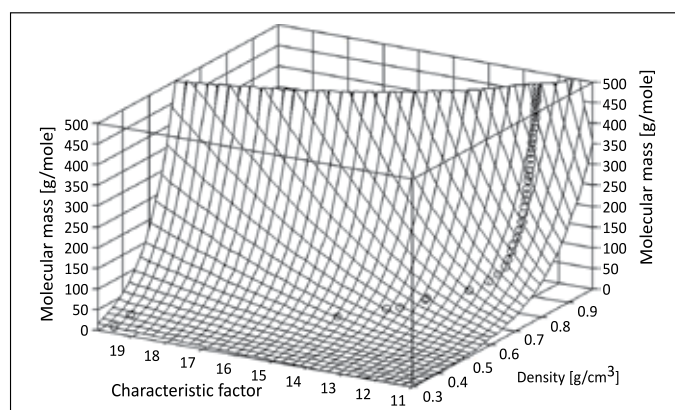
Figure 1. Correlation dependence of molecular mass, density and characteristic factor for individual hydrocarbons $lnz = a + be^{(-x)} + c/y^{(1.5)}$; $r^2 = 0.99990906$; $a = 18.326255$; $b = -17.668583$; $c = -217.23877$

Rysunek 1. Zależność korelacyjna masy cząsteczkowej, gęstości i współczynnika Watsona dla poszczególnych węglowodorów $lnz = a + be^{(-x)} + c/y^{(1,5)}$; $r^2 = 0,99990906$; $a = 18,326255$; $b = -17,668583$; $c = -217,23877$

Table 2. The results of the calculation of the molar composition of the oil sample (well No. 245 of the Neftchala field, Azerbaijan)

Table 2. Wyniki obliczeń składu molowego próbki ropy (odwiert nr 245, złoże Neftchala, Azerbejdżan)

| Components	Molecular weight	Boiling temperature	Accumula-ted weight	Differences accumulated	Weight com-pound	Molar factions	Molar compound	Molecular calculation
	[g/mol]	[K]	[%]	[weight %]	[weight %]		[mol %]	[weight]
1	2	3	4	5	6	7	8	9
C_1	16.043	111.600	0.000	0.000	0.000	0	0.000	0.00
C_2	30.070	184.600	0.000	0.000	0.000	0	0.000	0.00
C_3	44.097	231.100	0.000	0.000	0.000	0	0.000	0.00
$I-C_4$	58.124	261.400	0.000	0.000	0.000	0	0.000	0.00
$n-C_4$	58.124	272.700	0.000	0.000	0.000	0	0.000	0.00
$I-C_5$	72.151	301.000	2.405	2.405	2.405	0.03334	6.507	4.69
$n-C_5$	72.151	309.200	3.268	0.863	0.863	0.01196	2.335	1.68
C_6	84.000	337.200	6.216	2.947	2.947	0.03509	6.848	5.75
C_7	96.000	365.600	9.205	2.989	2.989	0.03114	6.078	5.83
C_8	107.000	390.000	13.370	4.165	4.165	0.03892	7.597	8.13
C_9	121.000	415.600	18.490	5.120	5.120	0.04231	8.259	9.99
C_{10}	134.000	439.400	22.925	4.435	4.435	0.03310	6.460	8.66
C_{11}	147.000	460.600	26.741	3.816	3.816	0.02596	5.067	7.45
C_{12}	161.000	481.700	30.796	4.055	4.055	0.02518	4.915	7.91

cont. Table 2/cd. Tabela 2

| Components	Molecular weight	Boiling temperature	Accumula-ted weight	Differences accumulated	Weight com-pound	Molar factions	Molar compound	Molecular calculation
	[g/mol]	[K]	[%]	[weight %]	[weight %]		[mol %]	[weight]
1	2	3	4	5	6	7	8	9
C_{13}	175.000	500.600	34.765	3.969	3.969	0.02268	4.427	7.75
C_{14}	190.000	520.000	38.839	4.074	4.074	0.02144	4.185	7.95
C_{15}	206.000	539.400	42.913	4.074	4.074	0.01978	3.860	7.95
C_{16}	222.000	556.700	46.546	3.633	3.633	0.01636	3.194	7.09
C_{17}	237.000	573.300	50.032	3.486	3.486	0.01471	2.871	6.80
C_{18+}	355.952	586.100	100.000	49.969	49.969	0.14038	27.399	97.53
			Sum	100.000	100.000	0.51236	100.000	195.18
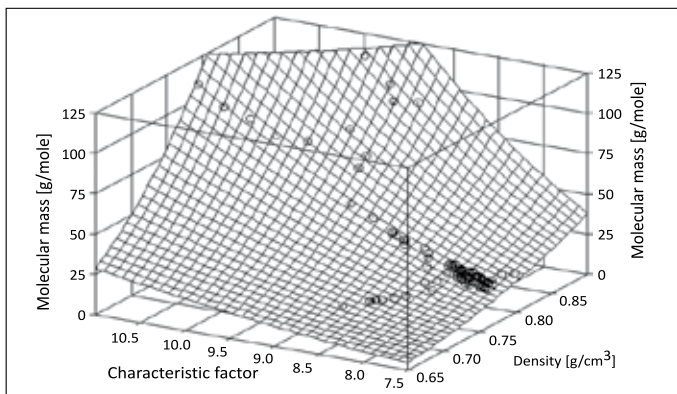
Figure 2. Correlation dependence of molecular mass, density and characteristic factor for condensate $lnz = a + b/x + c/y^{\wedge}(1.5)$; $r^{\wedge}2 = 0.99795971$; $a = 13.338326$; $b = -4.9483236$; $c = -86.238223$

Rysunek 2. Zależność korelacyjna masy cząsteczkowej, gęstości i współczynnika Watsona dla kondensatu $lnz = a + b/x + + c/y^{\wedge}(1,5)$; $r^{\wedge}2 = 0,99795971$; $a = 13,338326$; $b = -4,9483236$; $c = -86,238223$
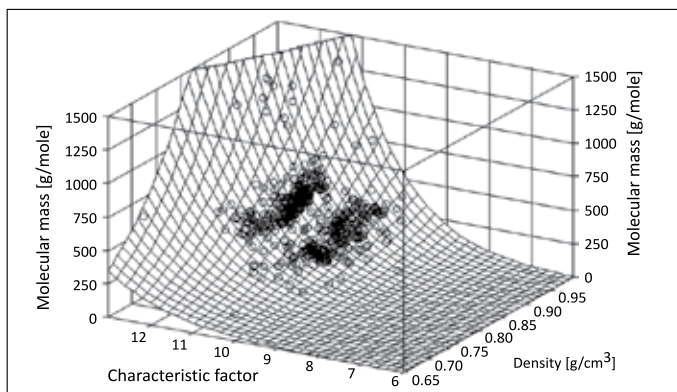
Figure 3. Correlation dependence of molecular mass, density and characteristic factor for oils, oil fractions and condensates $lnz = a + blnx + clny$; $r^{\wedge}2 = 1$; $a = -13.919242$; $b = 6.2887554$; $c = 8.7637513$

Rysunek 3. Zależność korelacyjna masy cząsteczkowej, gęstości i współczynnika Watsona dla ropy, frakcji ropy i kondensatów $lnz = a + blnx + clny$; $r^{\wedge}2 = 1$; $a = -13,919242$; $b = 6,2887554$; $c = 8,7637513$
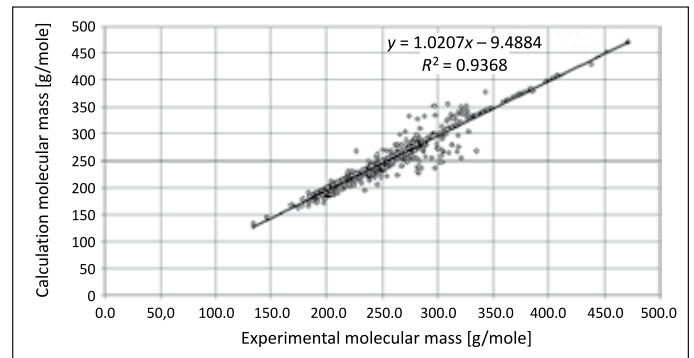
Figure 4. Correlation between experimental and calculated (based on composition) molecular masses (for 670 samples of oils and oil fractions from the fields of Azerbaijan and Russia)

Rysunek 4. Korelacja między eksperymentalnymi i obliczonymi (na podstawie składu) masami cząsteczkowymi (dla 670 próbek ropy i frakcji naftowych ze złóż Azerbejdżanu i Rosji)

3. The weighted hydrocarbon composition was calculated using formula (3) (6th column).
4. The molecular weight of the conditional component (in this case, C_{18+}), molar fractions of individual components and their sum were calculated using formulas (5) and (4). Data on mole fractions are listed in column 7 of Table 2, and the value of the molecular weight of the conditional component C_{18+} is shown in column 2 for the molecular weights of the components, labeled as C_{18+}.
5. The molar composition of this oil was calculated using formula (8) (column 8).
6. To check the reliability of the results, the molecular weight of the oil sample was calculated using formula (9). The calculation results are listed in the 9th column of the table. The calculated value of the molecular weight of this oil was 195.18 g/mol. The discrepancy between the calculated value of the molecular weight and the experimentally determined value given in Table 1 was 1.28%.

The validity of the proposed technique is supported by the fact that the data on molecular weight, Watson characteristic

factor, and experimental density, calculated from molar compositions, should lie on the same surface with a high degree of correlation. In addition, the experimental and calculated values, in terms of molecular composition, of molecular weights should lie on a straight line passing through the origin of coordinates with a slope coefficient equal to unity and with high degree of correlation.

Conclusion

For clarity, Figures 1–3 show the dependencies of molecular weight on the experimental density and the Watson characteristic factor for individual hydrocarbons and samples of oils, oil fractions and condensates from the fields in the above-mentioned oil regions. As it can be seen, there is a high correlation between the molecular weight, the Watson characteristic factor and the experimental density. Figure 4 shows the correlation between the calculated and experimental values of the molecular weights of oils, oil fractions and condensates (670 samples) from fields in Azerbaijan and Russia.

Thus, it can be confirmed that the developed method allows, with sufficient reliability for practical applications, the calculation of the molar composition of natural oils and condensates.

The results of this work can be used to enhance the informational quality of the study of the compositions of a vast number of oils from fields in a number of countries.

References

Brusilovsky A.I., 2002. Phase transformations in the development of oil and gas fields. *M: Grail, Moscow*, 1-575.

Danko M.Yu., Kuznetsov S.V., 2012, Calculation of phase equilibrium in the system "gas–oil–paraffin". *Oil, Gas, Innovations*, 8: 40–43.

Falovsky V.I., Khoroshev A.S., Shakhov V.G., 2011. Modern approach to modeling phase transformations of hydrocarbon systems using the Peng-Robinson equation of state. *Proceedings of the Samara Scientific Center of the Russian Academy of Sciences*, 13(3): 120–125.

Grigoryev B.A., Brusilovsky A.I., Zinchenko I.A., 2016. Methods for modeling phase behavior reservoir systems. *Scientific and technical collection, Vesti Gas Science*, 28(4).

Ramazanova E.E., Ibishov B.G., Ramazanova Z.E., Gurbanzade T.S., 2003. Study of multicomponent gas condensate systems by reducing them to ternary hydrocarbon systems. *Scientific works of Research Institute "GPOG and Chemistry"*, 4: 106–120.

Study of the physical and chemical properties of oils from the Apsheron and Kura depressions, 1971–1975. *Fund of the Azerbaijan State Oil Academy*.

Thermodynamic studies of reservoir fluids in order to develop recommendations for increasing the hydrocarbon recovery coefficient of gas condensate-oil fields, 2003. *Report of the problematic laboratory "Gas-thermodynamic studies of reservoir hydrocarbon systems" ASOA Fund*.

Zozulya G.P., Kuznetsov N.P., Yagafarov A.K., 2006. Physics of the oil and gas reservoir. *Tyumen State University*.
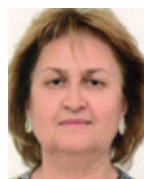
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