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Comparative Study of the Composition and Structure of Naphthenic Acids of Crude Oil from the Naftalan and Anastasievsko-Troitskoe Fields

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Abstract—A comparative analysis has been made of the physicochemical properties and structural-group composition of acids isolated from crude oils of the Anastasievsko-Troitskoe (Krasnodar krai, Russia) and Naftalan (Azerbaijan) oil fields. For each crude, the following three fractions of acids have been obtained by vacuum fractionation and analyzed: 240–350, 350–390, and >390; their elemental composition has been determined; and formulas for average acid molecules in each of the fractions have been derived. It has been shown that the acids of the 240–350°C fraction are monocyclic monocarboxylic acids with the five-membered naphthene ring. The fractions with the higher boiling points contain bicyclic naphthenic acids and, possibly, hydroxy acids. The acid fractions obtained from the Anastasievsko-Troitskoe oil are distinguished by the presence of aromatic structures and a significant amount of unsaponifiable components, especially in the 240–350°C fraction, which is of the greatest practical interest.

Keywords: naphthenic acids, composition and structure of naphthenic acids, elemental composition, comparative study

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Petroleum naphthenic acids (PNAs) are a complex mixture of alkylated cycloalkanecarboxylic acids of the general chemical formula $C_nH_{2n+z}O_2$, where n is the number of carbon atoms and z is the hydrogen deficiency due to ring formation or the degree of cyclization and is a negative integer from 0 to 12 [1]. Naphthenic acids are structures containing one or more five- or six-membered cycloalkane rings, an aliphatic chain, and the carboxyl group, which is believed to be linked to the naphthenic ring through several methylene groups. The value of n can be as high as 33, and the molecular mass varies from 100 to 500 g/mol [2].

Interest in the study of naphthenic acids is observed in many countries of the world, as can be seen in the increasing number of scientific publications devoted to this subject, especially in foreign media. However, the emphasis in the areas of naphthenic acid research is somewhat different in Russia and abroad.

The beginning of the development of Athabasca tar sands deposit in the province of Alberta (Canada) led to a sharp increase in the number of publications devoted to environmental problems caused by the ingress of naphthenic acids into water bodies [3]. Features of the production of Athabasca oil sands containing highly biodegradable oil, which is a viscous, tarry material (bitumen), using the extraction process with a hot aqueous alkali solution lead to the formation of significant quantities of oily water contaminated with naphthenic acids among other pollutants. This situation prompted the active development of semiquantitative methods for monitoring the concentration of naphthenic acids in industrial wastewater [4], including their determination in water to an ultratrace level using liquid chromatography coupled with quadrupole time-of-flight mass spectrometry [5]. Various analytical methods have also been developed that are used to assess the biodegradation of naphthenic acids in the environment [6] and study the toxic effect of PNAs on the biota of natural water bodies [7]. The use of modern highly informative analytical methods has revealed the need for model compounds that can be used to identify natural naphthenic acids. Rowland et al. [8], synthesized methyl and trimethylsilyl esters of monoaromatic and monocyclic ethanoic acids and characterized them using gas chromatography coupled with mass spectrometry and comprehensive two-dimensional gas chromatography–mass spectrometry. Model monocyclic naphthenic acids with branched and unbranched side chains were obtained. It has been shown that naphthenic acids with an *n*-alkane chain exhibit greater toxicity; however, they undergo faster biodegradation (97% within 30 days) [9].

The contents of publications devoted to naphthenic acids in Russian scientific journals are somewhat different and related, for the most part, to practical aspects of searching for natural sources of naphthenic acids, their determination in crude oils and oil fractions [10, 11], and consideration of possible ways of using naphthenic acids and their derivatives [12]. Scientific papers published in Russian journals are more focused on improving the PNA isolation methods [13, 14], the synthesis and study of the functional properties of naphthenic acid derivatives [15], the study of the biological activity of PNAs [16], and the use for preparing energized fertilizers in agriculture [17, 18].

In the view of a wide range of applications of naphthenic acids and their derivatives as surfactants, varnish and paint components, demulsifiers of oil-water emulsions, antiseptics, motor fuel and oil additives, catalysts for various petrochemical processes, etc. [19, 20] on one hand and the depletion of oil fields in Azerbaijan, which served for many years as a supplier of naphthenic acids for the entire post-Soviet space, on the other hand, studies on searching for new sources of naphthenic acids in Russia and their synthesizing are of great importance [20–22].

The objective of this study is to compare the physicochemical properties and structural-group composition of acids of the Naftalan field (Azerbaijan) and naphthenic acids obtained from oil of the Anastasievsko-Troitskoe field (Krasnodar krai, Russia) as an alternative to Azerbaijani naphthenic acids.

EXPERIMENTAL

Mixtures of naphthenic acids isolated from crude oils of the Anastasievsko-Troitskoe and Naftalan fields were fractionated under vacuum to obtain three fractions boiling at 240–350, 350–390, and >390°C. For each fraction, the elemental composition was determined: the C, H, N, S, O contents using a vario MICRO cube elemental analyzer (5 mg sample, sample decomposition in an oxygen stream at a furnace temperature of 1200°C, thermal conductivity detector); the concentration of individual structural groups was determined from IR spectra recorded on an Agilent Technologies Cary 600 Series Fourier-transform IR spectrometer in the wavelength range of 4000–650 cm^{-1} and ^1H NMR spectra obtained on a Jeol JNM-ECA 600 high-resolution NMR spectrometer. The molecular mass was determined cryoscopically.

Table 1. Material balance of fractionation of naphthenic acids isolated from (1) Anastasievsko-Troitskoe and (2) Naftalan oils

Taken:	1	2
	wt %	wt %
PNA mixture	100.00	100.00
Obtained:		
Fr. 240–350°C	59.23	65.96
Fr. 350–390°C	30.41	30.57
Fr. >390°C	2.97	0.98
Loss	4.67	2.47
Total	100.00	100.00

RESULTS AND DISCUSSION

The material balances of the fractionation of naphthenic acids isolated from Anastasievsko-Troitskoe and Naftalan oils are presented in Table 1.

As can be seen from the data given in Table 1, the fraction containing acids of industrial interest (fr. 240–350°C) makes 59.23% of total acids of the Anastasievsko-Troitskoe oil and 65.96% of total acids from the Naftalan oil. Note that the fractional composition of acids from both fields is approximately the same.

Table 2 shows the physicochemical properties of the fractions of naphthenic acids obtained from the Anastasievsko-Troitskoe and Naftalan oils.

The data presented in Table 2 show some differences in the physicochemical characteristics between the acid fractions obtained. For the acids of the Naftalan field, the molecular mass increases and the acid number decreases with an increase in the boiling temperature of the fraction, a change that is common sense and consistent with the existing ideas about the molecular-mass distribution of components over fractions. The fractions obtained by distillation of naphthenic acids from Anastasievsko-Troitskoe oil are not subject to this logic. It can be assumed that the low acid number for the 240–350°C fraction is due to the presence of unsaponifiable components in this fraction.

The results of elemental analysis of the fractions of naphthenic acids isolated from the Anastasievsko-Troitskoe and Naftalan oils showed (Table 3) that the mass fraction of carbon in the average acid molecule

Table 2. Physicochemical properties of fractions of naphthenic acids isolated from (1) Anastasievsko-Troitskoe and (2) Naftalan oils

Fraction	1			2		
	acid number	molecular mass	color	acid number	molecular mass	color
Fr. 240–350°C	100	249	yellow	324	208	yellow
Fr. 350–390°C	207	257	light brown	293	304	light brown
Fr. >390°C	221	408	black	211	389	black

remains practically unchanged with an increase in the boiling point of the acids; however, there are a noticeable decrease in the mass fraction of hydrogen and an increase in oxygen content for acids from the Anastasievsko-Troitskoe oil with an increase in the fraction boiling point.

Based on the obtained data, we calculated the number of carbon, hydrogen, and oxygen atoms in average molecule of naphthenic acids in each of the studied fractions and derived their average formulas (Table 4).

Considering the average formulas of acid molecules in the 240–350°C fraction, it can be concluded that these acid fractions in both the Naftalan and Anastasievsko-Troitskoe oils contain neutral hydrocarbons (the number of oxygen atoms of 0.95 or 1.4 is less than that for a monocarboxylic acid); moreover, in the acid fraction of the Anastasievsko-Troitskoe oil, only every second molecule is an acid. This explains the low acid number for this fraction. If we recalculate the average formulas, preserving the C : H : O ratio and taking the number of oxygen atoms to be 2 in the average molecule, the formulas for the 240–350°C fraction of the Anastasievsko-Troitskoe and Naftalan oils will be $C_{35.0}H_{68.3}O_2$ and $C_{14.3}H_{26.7}O_2$, respectively. The ratio of C : H : O atoms for the converted average molecules in these fractions corresponds to the general formula $C_nH_{2n-z}O_2$, where $z = -2$. Thus, it can be concluded that in accordance with published data [23] (Fig. 1), the acid fraction of 240–350°C of both oils contain monocyclic cycloaliphatic monocarboxylic acids with a total number of carbon atoms on average of 17 (for the Anastasievsko-Troitskoe field) or 13 (for the Naftalan field); consequently, the side alkyl chains include 11 to 12 and 7 to 8 carbon atoms, respectively. Since naphthenic acids were formed as a result of oxidation of natural compounds, primarily terpenes, which are widespread in nature, it can be assumed that one or two short alkyl groups ($R = -CH_3$, $-C_2H_5$, $-C_3H_7$) are present in the acid molecule; then the value of m, indicating the number of methylene groups separating the carboxyl group from the naphthenic ring, will be in the range of 8–9 and 4–5, respectively, for each of the oils under consideration [24]. The average molecular mass is slightly higher for the acids of the Anastasievsko-Troitskoe crude oil.

A similar recalculation of the composition of average molecule in the 350–390°C acid fractions for both oils made it possible to determine the z value as −4 for these fractions, which corresponds to bicyclic monocarboxylic naphthenic acids. For the >390°C acid fraction of the Naftalan oil, recalculation of the average formulas also led to a value of $z = -4$ as in the previous fraction, thereby indicating bicyclic structures with longer alkyl substituents. At the same time, a slight excess of oxygen atoms in the average molecule (more than two) as compared with the formula of monocarboxylic acid may indicate the presence of hydroxy acids.

The average acid formula in the >390°C fraction of the Anastasievsko-Troitskoe oil outstands from the general logic of reasoning, as it has $z = -22$, which indicates a high unsaturation of the molecule and most likely corresponds to condensed aromatic structures (for example, $z = -22$ corresponds to tetracyclic condensed aromatic structure $C_{16}H_{10}$). Another distinctive feature of the structure of acids in this fraction is the increased number of oxygen atoms in the molecule compared to monocarboxylic acids, which in turn

Table 3. Elemental composition of fractions of naphthenic acids isolated from (1) Anastasievsko-Troitskoe and (2) Naftalan oils

Element content, %	1			2		
	fr. 240–350°C	fr. 350–390°C	fr. >390°C	fr. 240–350°C	fr. 350–390°C	fr. >390°C
C	80.50	78.16	81.92	74.54	74.78	77.37
H	13.04	11.99	4.96	11.60	11.09	11.77
S	0.15	0.12	0.13	0.05	0.04	0.30
N	0.19	0.19	0.10	0.19	0.10	0.12
O	6.08	8.83	12.89	13.62	13.99	10.44
Σ	99.97	99.28	100.00	100.00	100.00	99.99

can be associated with the presence of phenolic moiety or hydroxy acids.

Naphthenic acid fractions isolated from the studied oils were analyzed by IR and ^{1}H NMR spectrometry. Although IR spectroscopy is known to be a qualitative analysis method, a procedure for semiquantitative determination using normalized optical densities has been proposed in the literature [25, 26], in which the ratio of optical densities of different absorption bands to relative optical density of the at 1460-cm^{-1} band due to C–H bond vibrations in aliphatic structures is calculated: $\Delta = D_\nu/D_{1460}$.

Figures 2 and 3 shown the IR spectra and Table 5 present optical densities and normalized optical densities of the absorption bands for the 240–350°C acid fraction of the Anastasievsko-Troitskoe and Naftalan oils, which are of the greatest interest from the practical point of view.

The results of calculating the normalized optical densities of the 240–350°C fractions of naphthenic acids obtained from the Anastasievsko-Troitskoe and Naftalan oils are consistent with the previously obtained data: the proportion of carboxyl groups in the mixture of acids of the Anastasievsko-Troitskoe oil is much lower, which is seen from the fact that the normalized absorbance at 1700 cm^{-1} for this object is more than four times lower than that for Naftalan oil acids. The relative amount of naphthenic structures (Δ_{940}) in the mixture of acids of the Anastasievsko-Troitskoe oil is also lower than in the acids obtained from oil of the Naftalan field, probably, because of the presence of aromatic structures (Δ_{1600}) (they are absent

Table 4. Calculation of average molecular formula of naphthenic acids contained in the fractions of acids extracted from crude oil of the (1) Anastasievsko-Troitskoe and (2) Naftalan fields

Number of atoms in average molecule	1			2		
	fr. 240–350°C	fr. 350–390°C	fr. >390°C	fr. 240–350°C	fr. 350–390°C	fr. >390°C
C	16.70	16.89	27.85	12.92	18.94	25.08
H	32.47	30.80	20.22	24.13	33.70	45.77
O	0.95	1.42	3.29	1.77	2.66	2.54
M	$C_{16.7}H_{32.5}O_{0.95}$	$C_{16.9}H_{30.8}O_{1.4}$	$C_{27.9}H_{20.2}O_{3.3}$	$C_{12.9}H_{24.1}O_{1.8}$	$C_{18.9}H_{33.7}O_{2.7}$	$C_{25.1}H_{45.8}O_{2.5}$

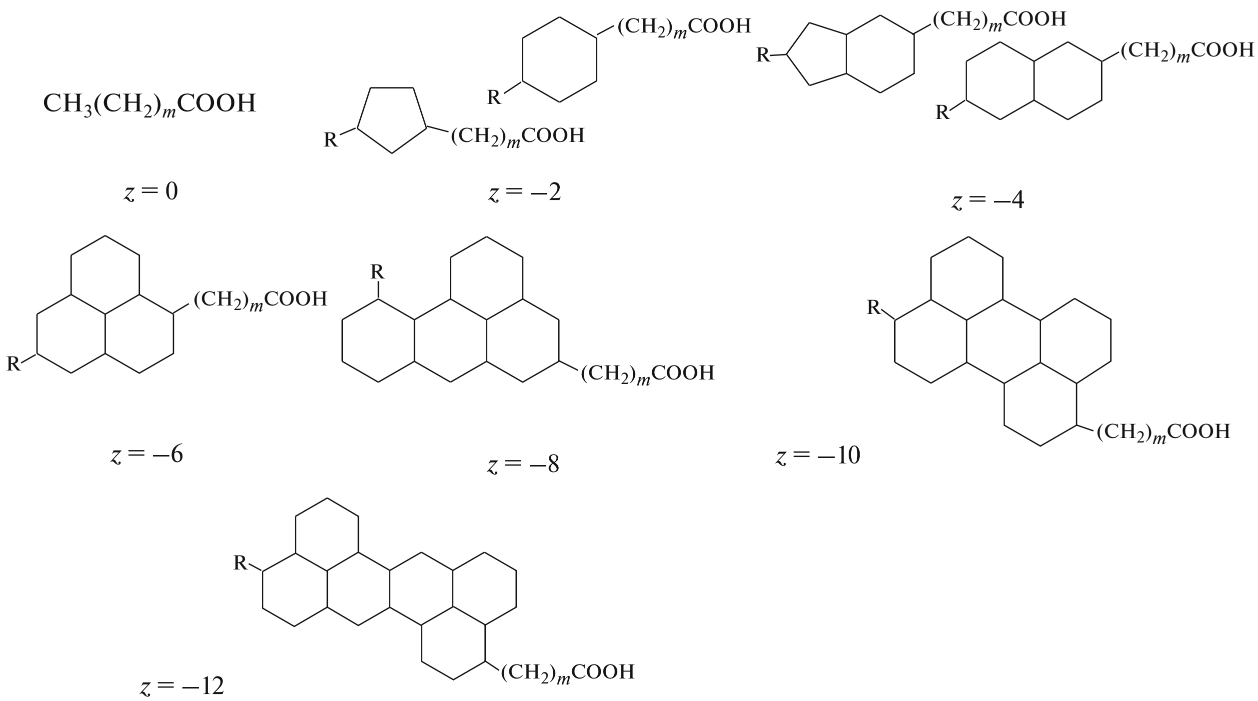

Fig. 1. Examples of possible structures of naphthenic acids depending on *z* characterizing hydrogen deficiency due to the presence of ring (degree of cyclization) [23].

Table 5. Optical density (D_x) and normalized optical density (Δ) of absorption bands for the 240–350°C fraction of naphthenic acids isolated from crude oil of the (1) Anastasievsko-Troitskoe and (2) Naftalan fields

1			2		
ν, cm^{-1}	D_x	Δ	ν, cm^{-1}	D_x	Δ
698	0.01	0.027	680	0.034	0.107
745	0.011	0.029	723	–	–
938	**0.345**	**0.920**	**936**	**1.339**	**4.224**
1228	0.059	0.157	1226	0.092	0.290
1290	0.182	0.485	1289	0.574	1.811
1377	0.124	0.331	1377	0.084	0.265
1412	–	–	1412	0.241	0.760
1456	0.375	1.000	1454	0.317	1.000
1604	**0.012**	**0.032**	**1600**	**–**	**–**
1704	**1.378**	**3.675**	**1702**	**5.089**	**16.054**
2856	0.452	1.205	2867	0.53	1.672
2921	0.76	2.027	2923	0.657	2.073
2951	0.237	0.632	2950	0.281	0.886

from the acids of the Naftalan oil) and short branched aliphatic moieties (Δ_{1380}).

Previous studies have shown that cyclopentane derivatives are characterized by an absorption band at 977 cm^{-1} and cyclohexane derivatives have characteristic absorption at wave numbers of 952–1005 and 1000–1055 cm^{-1} [27]. The absence of absorption bands in the region of 1030 cm^{-1} indicates the absence of six-membered naphthenic structures, suggesting that PNAs in the 240–350°C fraction mainly contain five-membered naphthenic rings. To characterize the side chains, one can use the "degree of branching" indicator, which is calculated from the ratio of absorbances at 720 and 1380 cm^{-1} ($C_b = D_{720}/D_{1380}$). The degree of branching of alkyl chains in acid molecules of the Anastasievsko-Troitskoe oil was found to be 0.032 and that in acid molecules of the Naftalan oil was 0.012.

The IR data obtained were confirmed by ^{1}H NMR spectrometry: the spectra of the 240–350°C fractions of naphthenic acids exhibits well-resolved groups of signals due to carboxylic protons at 12.0–12.5 ppm, with the proportion of this moiety in the acid fraction of the Naftalan oil being almost twice that in the fraction of acids of the Anastasievsko-Troitskoe oil. Comparison of the signals at 6.4–8.3 ppm indicates the predominance of aromatic structures in the fraction of

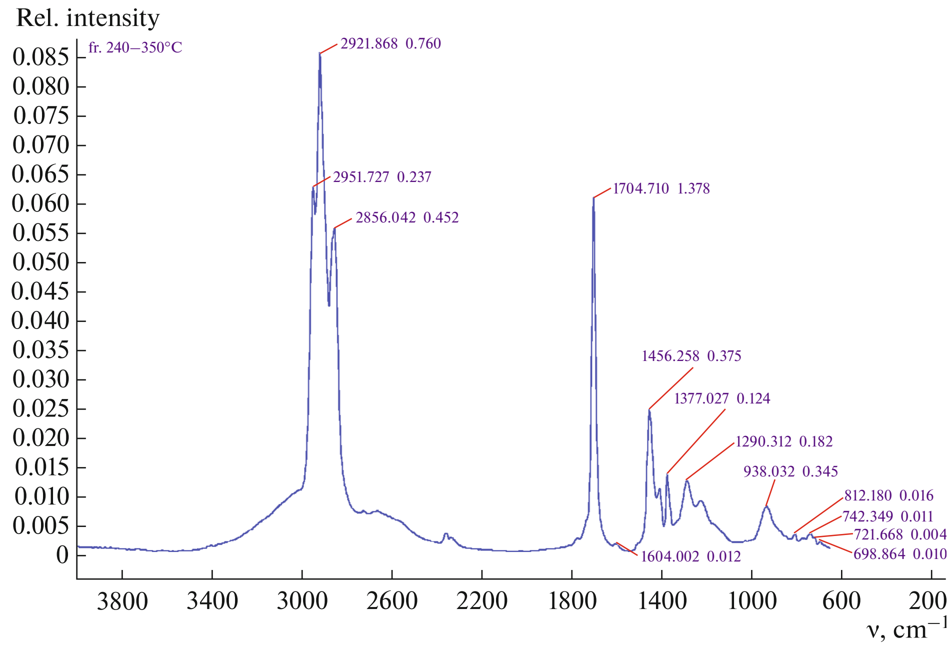

Fig. 2. IR spectrum of the 240–350°C fraction of naphthenic acids of crude oil of the Anastasievsko-Troitskoe field.

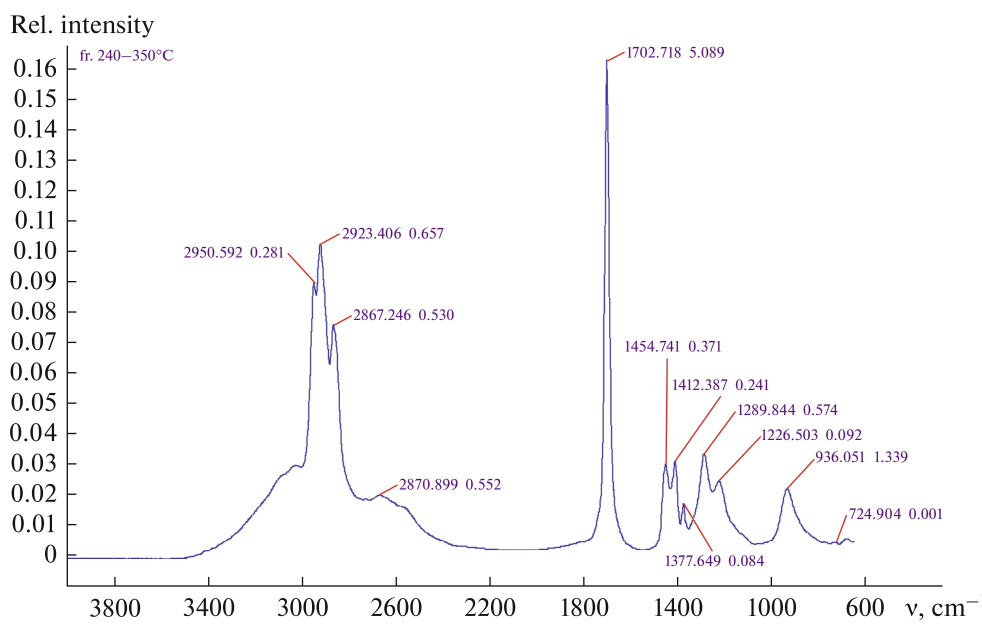

Fig. 3. IR spectrum of the 240–350°C fraction of naphthenic acids of crude oil of the Naftalan field.

acids of the Anastasievo-Troitskoe oil relative to the same fraction of Naftalan oil acids.

CONCLUSIONS

The comparative analysis of naphthenic acids isolated from two naphthenic oils of the Anastasievsko-Troitskoe and Naftalan fields has shown that they are fairly close in fractional composition but differ markedly in qualitative composition.

The molecular formula for average molecule of naphthenic acids in the Naftalan oil is close to the general formula $C_nH_{2n-z}O_2$, where $z = -2$ or -4, which corresponds to monocarboxylic acids containing monocyclic and bicyclic condensed cycloalkane structures. Regarding the acids of the Anastasievsko-Troitskoe oil, these trends are not observed for the >390°C fraction and indicate the presence of polycyclic condensed aromatic structures.

It has been shown that in the 240–350°C fraction of acids, which is of practical interest, both monocyclic monocarboxylic naphthenic acids containing mainly five-membered naphthenic rings are present in both studied oils. Short side alkyl chains and a higher degree of branching of the alkyl chains in the acids of the Anastasievsko-Troitskoe oil indicate a larger number of methyl groups in average molecule. The number of methylene groups separating the carboxyl group from the naphthenic ring can be about 8–9 in the acids of the Anastasievsko-Troitskoe oil and up to 4–5 in the acids of the Naftalan oil.

It has been established that the concentration of naphthenic acids in the 240–350°C fraction obtained by distillation of the acids isolated from the Anastasievsko-Troitskoe oil is lower than that in the similar fraction of the Naftalan oil. The molecular formula of average molecule for this fraction confirms the presence of saturated hydrocarbons of the C_nH_{2n} composition, which corresponds to naphthenic structures, and only every second molecule has a carboxyl group. The IR and ^{1}H NMR instrumental methods revealed that this fraction in addition contains aromatic structures.

In summary, it should be noted that the 240–350°C acid fraction, which is of practical interest, obtained from crude oil of the Anastasievsko-Troitskoe field is somewhat inferior in quality to the similar fraction obtained from oil of the Naftalan field, since it contains a smaller amount of naphthenic acids and a significant proportion of unsaponifiable components consisting of hydrocarbons, including cycloalkane and aromatic structures.

In view of the practical importance of naphthenic acids for manufacturing various petrochemicals, it should be considered expedient to develop synthetic methods for producing naphthenic acids along with searches for their natural sources.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest requiring disclosure in this article.

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