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EFFECT OF THE METHOD OF EXTRACTION ON THE STRUCTURAL-GROUP COMPOSITION OF NAPHTHENIC CONCENTRATES FROM NAFTALAN CRUDE OIL

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Naftalan crude oil is the only crude in the world with high therapeutic efficacy. Its therapeutic properties are due to the chemical composition and basic biologically active components, fossil hydrocarbons – naphthenes with isoprenoid chains, steranes, hopanes, etc. [1 – 8]. The necessity of scientifically substantiated refining and rational use of this crude oil makes the study of its chemical composition and the products made from it for medicine urgent.

The 300 – 450°C lube cut obtained in distillation of Naftalan crude oil in an ARN-2 was used as the feedstock for studying the effect of the method of separation of naphthene concentrate (white oil) on its structural-group composition. The group hydrocarbon composition of this cut, determined by chromatographic separation on silica gel according to GOST 11244–76, is reported in Table 1. Methods of physicochemical analysis were used to determine its structural-group composition: elemental, PMR spectroscopy, etc. The structural-group parameters of average molecules extracted from the hydrocarbon cut investigated were calculated with the data obtained.

The elemental composition of the products was determined with a Perkin–Elmer-240 analyzer and the molecular weights of the hydrocarbons were determined by cryoscopy in naphthalene with a 0.5 wt. % concentration of analyzed substance. The PMR spectra were recorded on a Tesla BS-487 C with a magnetic field frequency of 80 MHz. Hexamethyldisiloxane (HMDS) was used as the internal standard. The structural parameters of the hydrocarbons were calculated with the method described in [9]. Their designations are identical to the ones in this study.

As Table 1 shows, the average molecular weights of the extracted hydrocarbons and resins were comparatively low: 258 – 302. The average naphthenes and paraffins contained 22 carbon atoms, 37 hydrogen atoms, less than one sulfur and oxygen atom, and no nitrogen atoms. The average molecule of the aromatic hydrocarbons contained 19 – 21 carbon atoms, 29 – 35 hydrogen atoms, less than one sulfur and oxygen atom, and no nitrogen atoms.

The quantitative distribution of hydrogen and carbon atoms in the molecules of these hydrocarbons was determined with the data from the PMR spectra. The molecules of the naphthenes and paraffins did not contain unsubstituted H_a protons bound with aromatic carbon atoms. The molecules of the aromatic hydrocarbons contained more of these protons or protons contained in groups in the $\alpha, \beta,$ and γ positions to the aromatic rings $(H_\alpha, H_\beta,$ and $H_\gamma)$ and less hydrogen atoms in the saturated fragments of the molecules, which confirms the higher aromaticity of the hydrocarbons. The naphthene and paraffin molecules contained 4 – 5 rings. In the molecules of the aromatic hydrocarbons, K_0 = 1.5 – 3.3, including K_n = 0.95 – 2.68.

In addition to polycyclic naphthenes, the lube cut contained mixed naphthenic-aromatic structures with 2 – 3 aromatic rings. The number of C_β atoms was higher in the paraffinic fragments. The degree of

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TABLE 1

Indexes	Products of extraction of the lube cut					
	naphthenes and paraffins	aromatic hydrocarbons from group				resins
		I	II	III	IV	
Yield, wt. %	51.5	18.6	5.2	6.4	14.6	3.7
Refractive index n_D^{20}	1.4848	1.5070	1.5442	1.5730	1.6136	–
Density at 20°C, kg/m^3	892.5	929.5	947.0	987.0	1035.0	1044.0
Molecular weight	302	291	286	274	259	258
Elemental composition, wt. %						
C	87.42	87.90	87.70	87.60	88.26	88.17
H	12.31	12.10	12.30	11.57	11.46	11.52
N			None			
S	0.15	0.08	0.082	0.29	0.28	0.22
O	0.12	None	0.078	0.54	None	0.09
H:C (atomic)	1.7	1.64	1.67	1.57	1.55	1.56
Empirical formula $C_nH_{2n-z}N_pS_qO_r$	$C_{22}H_{36.8}S_{0.11}O_{0.02}$	$C_{21.3}H_{34.9}S_{0.01}$	$C_{20.9}H_{34.8}S_{0.01}$	$C_{20}H_{31.4}S_{0.03}$	$C_{19}H_{29.4}S_{0.02}$	$C_{18.9}H_{29.4}S_{0.02}$
z	7.2	7.7	7.0	8.6	8.6	8.4
Proportion of protons of different types, %						
H_a	–	4.2	8.8	14.1	24.5	3.6
H_{sat}	100	95.8	91.2	85.9	75.5	96.4
H_α	–	12.8	24.6	29.8	33.9	17.7
H_β	69.8	56.0	46.8	38.3	28.7	54.1
H_γ	30.2	27.0	19.8	17.8	12.9	24.6
Number of protons in average molecule						
H_a	–	1.5	3.1	4.4	7.2	1.1
H_{sat}	36.8	33.4	31.7	27.0	22.2	28.3
ΣH	36.8	34.9	34.8	31.4	29.4	29.4
H_α	–	4.5	8.6	9.4	10.0	5.2
H_β	25.7	19.5	16.2	12.0	8.4	15.9
H_γ	11.1	9.4	6.9	5.6	3.8	7.2
Number of carbon atoms						
C	22.0	21.3	20.9	20.0	19.0	18.9
C_a	–	3.8	5.7	7.0	7.6	3.8
C_n	18.3	10.0	3.8	3.8	4.1	11.6
C_p	3.7	7.5	11.4	9.2	7.3	3.5
Number of rings in molecule						
K_o	4.6	2.95	1.65	1.80	1.5	3.3
K_a	–	0.63	0.70	0.85	0.48	0.62
K_n	4.6	2.32	0.95	0.95	1.02	2.68
Proportion of carbon atoms, %						
C_a	–	17.8	27.3	35.0	40.0	20.1
C_n	83.2	47.0	18.2	19.0	21.6	61.4
C_p	16.8	35.2	54.5	46.0	38.4	18.5
Number of carbon atoms in fragments of the molecule						
C_α	–	2.4	4.1	4.5	5.1	2.8
C_β	18.3	11.9	8.8	6.6	5.0	9.9
C_γ	6.7	3.2	2.3	1.9	1.3	2.4
$C_{\beta a}$	–	4.3	9.1	7.3	6.0	1.1
σ_a	–	0.62	0.57	0.51	0.41	0.72
χ_β	1.40	1.64	1.85	1.82	1.68	1.61

Note. Absolute errors of measurement: $\Delta H_a = \pm 0.2$; $\Delta H_\alpha = \pm 0.3$; $\Delta H_\gamma = \pm 0.5$; $\Delta H_{sat} = \pm \Delta H_a$; $\Delta H_\beta = \pm(\Delta H_a + \Delta H_\alpha + \Delta H_\gamma)$.

TABLE 2

Indexes	Lube cut	Sample of concentrate of naphthenes and paraffins			
		1	2	3	4
Density at 20°C, kg/m^3	934.0	892.3	892.4	899.7	891.7
Viscosity at 50°C, mm^2/sec	35.6	24.0	26.5	18.94	12.58
Refraction index, n_D^{20}	1.5150	1.4850	1.4852	1.4903	1.4868
Flash point, °C	182	182	182	175	150
Solid point, °C	–38	–38	–40	–46	–50
Aromatic hydrocarbon content (data from UV spectra), wt. %	40.47	0.31	0.30	1.11	0.77
benzene	17.7	0.25	0.24	1.05	0.57
naphthalene	12.36	0.05	0.04	0.056	0.20
phenanthrene	10.41	0.03	0.02	–	–
Yield, wt. % in feedstock	–	35.7	35.2	41.2	52.2

aromaticity (C_a) varied from 17.8 to 40%. The resins consisted of mixed naphthenic-aromatic structures whose presence could only be determined by PMR spectroscopy – the advantage of this method over others.

The naphthene and paraffin concentrates from the investigated cut were extracted by several methods: the first two samples were extracted by oleum treatment of the lube cut and its raffinate from furfural treatment, and the last two were extracted by step hydrogenation of the lube cut and its raffinate.

Sample 1 was prepared using oleum with a 19 – 20% content of free SO_3. Treatment was conducted in 12 stages with feed of 5% oleum into each stage at a temperature of 40°C. After each portion of oleum, the lube oil was allowed to settle from the acid vacuum resid, neutralized with an alcohol–water solution, and then underwent final contact purification with aluminosilicate adsorbent at a temperature of 120°C.

Sample 2 was obtained after preliminary treatment of the lube cut with a selective solvent furfural (300%), i.e., with an additional process – selective treatment – included in the technology for production of white oil. The lube cut raffinate was subsequently treated by stages with oleum, neutralized with alcohol– water solution, and then finally treated with powdered adsorbent at 120°C. Oleum consumption was cut from 60 to 25% by preliminary treatment with furfural, and production wastes consequently also decreased.

Sample 3 was prepared with environmentally clean, zero-waste technology – treatment by stage hydrogenation of the lube cut on different catalysts, changing the temperature in each stage with a hydrogen flow rate of 1000 liters per liter of feedstock, feed stock space velocity of 0.5 h^{-1}, and hydrogen pressure of 6 MPa.

Sample 4 was prepared by two-stage hydrogenation of raffinate. The first stage of hydrogenation was conducted on Al–Co–Mo catalyst at a temperature of 300°C and pressure of 6.5 MPa, and the second stage was conducted on Ni–Cr catalyst at 280 – 290°C and pressure of 9 MPa.

The physicochemical properties of these samples are reported in Table 2. In all samples except for sample 3, the aromatic hydrocarbon content (based on data from the UV spectra) was under 1%.

The structural-group composition of the samples was determined to determine the degree of preservation of the components of the saturated part of the lube cut in the naphthenes and paraffins (Table 3). The average molecules in all samples contained 18-23 carbon atoms and 34-41 hydrogen atoms. The value of the hydrogen deficit index indicates predominance of polycondensed naphthenic structures in the molecules. The molecules of the concentrates contained no unsubstituted H_a protons bound with aromatic carbon atoms.

The average structural parameters of the sample 1 molecule consisted of naphthenic structures with 4 – 5 rings containing methyl groups alone as substituents ($C_p >> C_\gamma$). A decrease in *z* and the molecular weight and an increase in the proportion of paraffinic structures were observed in the molecules of the other samples (2 – 4), and the number of terminal methyl groups almost did not change. The number of naphthenic

TABLE 3

Indexes	Saturated part of lube cut	Sample of naphthene–paraffin concentrate			
		I	II	III	IV
Molecular weight	302	320	320	303	257
Elemental composition, wt. %					
C	87.42	86.56	86.49	85.56	84.62
H	12.31	12.40	12.80	12.85	13.34
N			None		
S	0.15	0.26	0.04	0.10	0.20
O	0.12	.078	0.67	1.49	1.84
H:C (atomic)	1.70	1.71	1.76	1.79	1.88
Empirical formula $C_nH_{2n-z}N_pS_qO_r$	$C_{22}H_{36.8}S_{0.01}$	$C_{21.3}H_{34.9}S_{0.01}$	$C_{20.9}H_{34.8}S_{0.01}$	$C_{20}H_{31.4}S_{0.03}$	$C_{19}H_{29.4}S_{0.02}$
z	7.2	6.9	5.6	4.7	2.3
Fraction of protons of different types, %					
H_a			None		
H_{sat}	100	100	100	100	100
H_α			None		
H_β	69.8	70.9	70.7	71.4	70.5
H_γ	30.2	29.1	29.3	28.6	29.5
Number of protons in average molecule					
H_a			None		
H_{sat}	36.8	39.3	40.6	38.5	33.9
ΣH	36.8	39.3	40.6	38.5	33.9
H_α			None		
H_β	25.7	27.9	28.7	27.5	23.9
H_γ	11.1	11.4	11.9	11.0	10.0
Number of carbon atoms					
C	22.0	23.1	23.1	21.6	18.1
C_a			None		
C_n	18.3	19.1	16.6	14.9	10.3
C_p	3.7	4.0	6.5	6.7	7.8
Number of rings in molecule					
K_o	4.6	4.45	3.80	3.35	2.15
K_a			None		
K_n	4.6	4.45	3.80	3.35	2.15
Proportion of carbon atoms, %					
C_a			None		
C_n	83.2	82.7	71.9	69.0	56.0
C_p	16.8	17.3	28.1	31.0	43.1
Number of carbon atoms in fragments of the molecule					
C_α			None		
C_β	18.3	19.3	19.1	17.9	14.8
C_γ	3.7	3.8	4.0	3.7	3.3
$C_{\beta\pi}$	None	0.2	2.5	3.0	4.5
χ_β	1.40	1.45	1.50	1.54	1.62

rings in the average molecule decreased in the order samples 1–2–3–4, and the number of C_p increased so that the proportion of C_p correspondingly increased.

It should be noted that signals of protons from aromatic structures did not appear in the PMR spectra of

these samples [10]. The data obtained indicate that the concentrates from oleum treatment (samples 1 and 2) basically consist of polycyclic naphthenes with short alkyl chains – $C_1 - C_4$.

Concentrates of naphthenes and paraffins separated by oleum treatment (K_n = 4.45 instead of 4.6) are thus closest in composition to the saturated part of the lube cut. Preliminary furfural treatment of the lube cut and subsequent oleum treatment of the raffinate decreased the number of naphthene rings from 4.6 to 3.8 in the average molecule. After stage hydrogenation, the number of naphthene rings in the average molecule decreased from 4.6 to 3.35, and the proportion of C_p almost doubled.

Sample 4 had the worst composition. Preliminary furfural treatment of the lube cut and subsequent two-stage hydrogenation caused an even greater decrease in the polycyclic naphthene content (K_n = 2.15), which is undesirable.

As a consequence, the feedstock used in production of white oil of the medicinal Vaseline type from naphthenic base crude oils, including Naftalan crude, should be treated by a method that allows maximum preservation of the components of the saturated part of the feedstock, especially polycyclic naphthenic hydrocarbons, the carriers of the therapeutic properties [3, 6].

White oils for use in other areas of the national economy can be produced from any crude oil using any of the indicated treatment technologies, as demonstrated previously in [11].

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