STUDY OF THE TAR FRACTION OF OIL TAKEN FROM WATER

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Received: 01 october 2023 Accepted: 26 november 2023 Published: 16 february 2024

Among the numerous harmful substances of anthropogenicorigin that enter the environment, petroleum products belong to one of the first places. In this paper, changes in the physical and chemical properties of the oil of the Surakhany field of Azerbaijan from the well and from the surface of the water, under the influence of environmental factors, are investigated.

The composition and properties of oils after production and prolonged exposure to the surface of the water are compared. Oil samples are isolated according to GOST 11858-66 into three components: oils, resin and asphaltenes. The results of mass spectrometric, chromatographic and IR spectrometric examination of samples of crude and degraded oils are presented.

The results of the research showed that under the influence of natural factors on the surface of water bodies in the composition of degraded oil, the content of hydrocarbons decreases, and the content of resins and asphaltenes increases. The content of identified polycyclic aromatic hydrocarbons in both oil and resin fractions increases.

The change in the most toxic polycyclic aromatic hydrocarbons (PAHs) in the processes of oil degradation was studied, an increase in toxic effects in PAHs was established.

The content of various groups of hydrocarbons in the composition of the oil and resin fractions of freshly extracted and degraded oils on the surface of water is given. It was found that in the resinous fractions of both oils, the presence of the studied groups of PAHs exceeds their values in comparison with the oil fractions.

The results of IR spectroscopy of degraded oil samples showed the formation of more condensed aromatic rings in the structure.

The results of the studies indicate significant changes in the composition of oil degraded on the water surface. Analysis of the transformation of oil pollution when oil enters the environment is necessary to optimize the choice of remediation technologies.

Keywords: oil, degradation, resin, asphaltene, environment

INTRODUCTION

Oil and petroleum products are among the dangerous pollutants of water. Their sources are all stages of production, transportation and refining of oil, as well as consumption of petroleum products [1,2]. A lot of oil gets into the water due to leaks of oil pipelines, on railways, on the territory of oil storage facilities. Entering water bodies, wastewater contaminated with oil and oil products creates various forms of pollution: an oil film floating on the water; dissolved and emulsified petroleum products in water; heavy fractions that have settled to the bottom [3,4]. Oil in the aquatic environment is subject to degradation under the influence of environmental factors, and the effectiveness of the processes of purification of water resources from oil pollution depends on the degree of oil degradation [5].

Earlier [6-8] we published the results of a study of changes in the physical and chemical characteristics of the oils of the Absheron Peninsula degraded under the influence of various environmental factors.

Exposure to light and ionizing rays, pH of the environment, minerality of the aquatic environment, etc. affect their transformation in the environment. For Azerbaijani oils, degradation processes have been studied on the example of Balakhani oils [9-11]. However, issues related to the transformation of polycyclic aromatic hydrocarbons during oil degradation have been partially considered, and detailed studies have not been conducted.

This paper studies the influence of environmental factors on the molecular structure of oil in the process of degradation in the aquatic environment and the patterns of distribution of various groups of petroleum hydrocarbons, including alkanes, polycyclic aromatic hydrocarbons in the oily and resinous fractions of freshly extracted and degraded oil oinonen environment.

EXPERIMENTAL

The degradation of oil of the Surakhany field of the Absheron Peninsula in the aquatic environment has been studied. The physicochemical characteristics of the studied initial oil are given in [12].

To detect structural changes in oil, the IR spectrometer "Varian 640-IR"was used. The analysis of products in the liquid phase was carried out by the chromatography-mass spectrometric method. The chromatograph "Agilent GC 7890 A"and the GC/MS Trace DSQ-ThermoElectron mass spectrometer (Finngan USA, 2005) were used.

The samples studied were isolated from the surface of the water and directly from a nearby well by extraction using benzene as an extractant. The contents of the main components - hydrocarbons, resins and asphaltenes were determined in isolated oil samples in accordance with GOST 11858-66.

RESULTS AND DISCUSSION

Since oil is a very complex mixture consisting of aliphatic and naphthenic hydrocarbons, aromatic compounds, asphalt-resinous substances, the changes of which under the influence of various environmental factors can be different, to understand the mechanism of the ongoing processes, oil samples were divided into 3 fractions - oil, resinous and asphaltene. Table 1 shows the content of the main components of oil taken from the well and from the surface of the water - hydrocarbons, resins and asphaltenes.

These data show that after a long stay of oil on the surface of the water under the influence of natural factors, the material composition of oil changes- thecontent of hydrocarbons decreases, and the content of resins and asphaltenes increases. This is due to the influence of solar radiation, atmospheric oxygen and radiation of various origins on the destructive transformations of heavy components of oil [13].

Table 1. Fractional composition of oil samples taken from the well and from the surface of thewater (masses, %)

Sample	Hydrocarbons	Resin	Asphaltenes
From the surface of	82,8	16,8	0,4

the water			
From the well	92,5	7,45	0,05

5 groups of hydrocarbons are considered: TSN - the total content of separable petroleum hydrocarbons, UCM - the inseparable part of petroleum hydrocarbons, PAH-soderusting 2-6 benzene rings, NPD (Naphthalene, Phenanthrene- Dibenzo (ah) anthracen) and 16 EPa (16 pollutants of polycyclic aromatic hydrocarbons proposed by the Environmental Protection Agency in the USA - US Environmental Protection Agency - EPA) (Table 2).

Among the components of oil, polycyclic aromatic hydrocarbons (PAHs) are the most resistant to microorganisms and other environmental factors due to toxicity and insolubility in water [14]. On the one hand, insolubility in water reduces the likelihood or prevents PAHs from entering living organisms, on the other hand, it leads to their accumulation in the environment, for example, in the bottom sediments of water bodies.

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Oil fractions			Total PAHs		Total
	THC (C ₁₀ -	UCM (C ₁₀ -	with 2-6		16EPA
	C ₄₀)	C ₄₀)	benzene	INFD	
			Rings		
Fresh oil	620108	334974	14016	13652	962
Degraded oil	581873	402424	15759	15481	962
Fresh oil resin	523718	422817	20375	18912	1286
Degraded					
petroleum resin	453883	495555	28084	27310	1908

Table 2.The content of various groups of hydrocarbons in the composition of the oil and resin fractions of freshly extracted and degraded on the surface of water oils (mg / kg)

It should be noted that in the resinous fractions of both fresh and degraded oil on the surface of the water, the presence of all three groups of PAHs exceeds their values in comparison with the oil fractions (Table 2). Thus, in the resin fraction of freshly produced oil, the content of 2-6 PAHs is 45%, 16 EPAs - by 33.6%, and NPD - by 38.5% higher than in the oil fraction. In degraded oils, these values are: for 2-6 PAHs - by 78.2%, for 16EPA - by more than 2 times, and NPD - by 76.4%. In the process of degradation in oil and resinous fractions, the THC content decreases, and UCM is growing. In oils only for PAHs with 2-6 benzene rings, the concentration increases by 12.4%, for NPD - by 13.4%, and 16EPA does not change. In the resin fraction, these values increase by 37.8%, 44.4% and 48.3%, respectively. It should be noted that these changes are as measured in the composition of oil PAHs.

Thus, with the degradation of oil on the surface of the water, in addition to the fact that the content of the asphaltene fraction increases sharply, the content of identified PAHs in both oil and resin fractions also increases. There is also a tendency to increase the content of these groups of hydrocarbons with an increase in the molecular weight of PAHs and the number of benzene rings in their composition (Table 3). Only the content of naphthalene in the oil fraction is 47% higher than in the resin fraction. These patterns are most likely associated with specific processes of formation of various groups of compounds during the genesis and metamorphism of oil.

	Fresh	OII-	Fresh oil resin	Degraded		
Pau	oil	degraded		petroleum resin		
		Oil				
EPA 16	961.6	962	1 286	1 908		
Naphthalene	619	562	421	975		
Acenaphthylene	29	38	35	68		
Acenaphthene	36	25	52	43		
Fluorene	82	89	203	200		
Phenanthrene	162	202	404	511		
Anthracene	4,7	9,2	22,8	16,2		
Fluoranthene	1,6	3,1	8,2	9,2		
Pyrene	8,5	8,2	27,6	17,9		
Benzo(a)anthracene	4,0	4,0	17,5	11,7		
Chrysene	12,7	18,1	73,7	46,3		
Benzo(k)fluoranthene	0,3	1,4	11,2	5,9		
Benzo(b)fluoranthene	0,2	0,3	1,5	1,1		
Benzo(a)pyrene	0,5	0,2	1,7	0,4		
Indeno(123cd)pyrene	0,5	0,7	0,6	0,5		
Benzo(ghi)perylene	0,2	0,3	5,1	1,6		
Dibenzo(ah)anthracen						
е	0,4	0,5	0,7	0,1		

Table 3. Effect of oil degradation on PAH group 16 EPA (mg/kg)

Due to the fact that polycyclic compounds are the most toxic from an ecological point of view, it is interesting to study their changes during the processes of oil degradation in the environment [15]. The toxicity of individual PAHs, especially gasoline compounds, is thousands of times greater than that of others. Therefore, the mutual transformations of these PAHs are expedient from an ecological point of view, and the study of these processes under the influence of various factors is of great practical and scientific interest [16-17]. Toxic effects have been calculated for the group of PAHs 16 EPA present in oil as the most environmentally hazardous pollutants (Table 4).

As a result of the degradation of the oil fraction of oil, there is an increase of 12.2% in the toxic effects of group 16 OF PAHs.

Compounds contained in petroleum, initially in small quantities, such as polyaromatic hydrocarbons, can not only indicate the presence of petroleum pollution, but also under certain conditions act as identification criteria for judging the type of pollution and the conditions of its occurrence, as well as its distribution.

The nature of the change in the properties of oil taken from the surface of the water was traced by the IR spectra of oil fractions of oil, the change in the physical characteristics of the studied samples.

-	-		
Name	Toxicity coefficient	Oil fraction of oil	Oil fraction of
		from the well	degraded oil
EPA 16	0.001	4,3121	4,8403
Naphthalene	0.001	0,619	0,562
Acenaphthylene	0.001	0,029	0,038

Table 4. Changes in toxic effects in PAHs of group 16 EPA in the oil fraction of degraded oil

Acenaphthene	0.001	0,036	0,025
Fluorene	0.001	0,082	0,089
Phenanthrene	0.001	0,162	0,202
Anthracene	0.01	0,047	0,092
Fluoranthene	0.001	0,0016	0,0031
Pyrene	0.001	0,0085	0,0082
Benzo(a)anthracene	0.1	0,4	0,4
Chrysene	0.01	0,127	0,181
Benzo(k)fluoranthene	0.1	0,03	0,14
Benzo(b)fluoranthene	0.1	0,02	0,03
Benzo(a)pyrene	1	0,5	0,2
Indeno(123cd)pyrene	0.1	0,05	0,07
Benzo(ghi)perylene	1	0,2	0,3
Dibenzo(ah)anthracene	5	2	2,5

The structural-group composition of oils is determined by the intensity of characteristic absorption bands on the infrared spectra of samples [18, 19]. Below are the results obtained by IR spectroscopy of oil samples from the well and from the water surface. Figures 1-2 show the IR spectra of the initial samples of resinous fractions of oil from the well and from the surface of the water.

The results of IR spectroscopy of degraded oil samples indicate the formation of more condensed aromatic rings in the structure of the oil after a long stay in the water.



Figure 1. IR spectrum of resin fraction of oil from the well



Figure 2. IR spectrum of resin fraction of oil from the surface of water

The appearance of absorption bands at 1708 cm⁻¹ belonging to C = O groups indicates the process of oxidation of resins that occurs after a long stay of oil on the surface of water. This absorption band is an objective criterion for the accumulation of oxygen-containing products. At wavelengths of 3051 and 1603 cm⁻¹, intense absorption bands characteristic of valence oscillations C = C of the cyclic or benzene (aromatic) ring bond are observed, there are also stripes at 1030cm⁻¹corresponding to polynuclear aromatic structures. This indicates a strong accumulation (3-4 times) of condensed aromatic rings during oil degradation compared to samples from the well. There is also the appearance of absorption bands in the wavelength range of 600-1000cm⁻¹, corresponding to deformation oscillations - CH₂- and - CH₃ groups, and in the range of 1461cm⁻¹ and 1377cm⁻¹ - a strong increase in these groups. The data obtained indicate significant changes in the composition of oil due to the influence of environmental factors.

In Fig. 3-4 shows the IR spectra of samples of oil fraction of oil from the well and from the surface of the water.

The composition of oil fractions of oil is significantly different from the composition of resinous fractions. In the composition of oil fractions of oil, there is not a significant number of condensed aromatic rings, they mainly consist of paraffins of normal structure, and cycloparafins are mainly monocyclic [20].

Clear and intense absorption bands on the IR spectra of the oil fraction of oil taken from the well are as follows: 2919.2852 cm⁻¹ - characterize valence oscillations - CH₂- and CH₃ groups in alkanes, 2975.2992cm⁻¹- valence oscillations of C-H bonds in cyclic alkanes, 1461.1376cm⁻¹- deformation oscillations - CH₂- and CH₃ groups of branched paraffin chains, 760,820,880 cm⁻¹ – extraplane deformation oscillations of the benzene ring of mono- and polynuclear aromatic structures (Fig.3-4).

On the IR spectra of oil samples taken from the surface of the reservoir (Fig. 4), there is a decrease in absorption bands of 2919 and 2852 cm⁻¹, as well as 1461 and 1376 cm⁻¹, i.e. a decrease in CH₂- and -CH₃ groups, which is explained by condensation processes in the composition of oil as a result of oil compaction when on the surface of water. polyaromatic compounds of absorption bands at 760,820,880 cm⁻¹ as well as stripes at 2975,2992 cm⁻¹ - valence oscillations of C-H bonds in cyclic alkanes. This is due to the condensation of aromatic rings in the structure of oil fractions as a result of environmental factors.

According to ir spectra, it can be seen that according to the absorption bands of 1461 cm⁻¹, 1376 cm⁻¹·2860 cm⁻¹ and 2920 cm⁻¹, there is a redistribution of intensity - CH ₂- and - CH₃ groups, changes in the absorption bands corresponding to aromatic rings are not observed.



Figure 3. IR spectrum of oil fraction of oil taken from the well



Figure 4. IR spectrum of oil fraction of oil taken from the surface of water

Thus, from the IR spectra of the samples it can be seen that with a long stay of oil on the surface of the water, its structural-group composition changes. Changes are mainly undergone by the resinous fraction of oil.

With the help of gas chromatography, the distribution of oil hydrocarbons in the studied oil samples has also been established. The dynamics of changes in the composition of oil after being on the water surface is observed from the given chromatograms (Fig. 5-6). From the chromatograms it can be seen that in comparison with the samples from the well, in the samples from the surface of the reservoir there are significant changes in the peaks of n-alkanes, which is associated with the destruction processes that occur during the degradation of oil.





The decrease in the height of the peaks of n-alkanes, the shift of their maximum towards heavier hydrocarbons is one of the results of the destructive processes occurring during the degradation of oil.

CONCLUSION

Thus, when oil is found in the aquatic environment as a result of degradation, polycondensation processes occur, which leads to a decrease in the amount of hydrocarbons in the composition of oil by 10% and an increase in resins and asphaltenes by 2 and 9 times, respectively. The content of environmentally important 2-6 ring polycyclic aromatic hydrocarbons in degraded oil increases - in the oil fraction by 12%, in resinous ones by 37.8%, which is associated with the ongoing polycondensation processes.

The study of changes in oil degraded on water bodies under the influence of natural factors, knowledge of the composition of oil pollution is one of the conditions for extracting additional oil resources from oil-containing wastewater and for choosing methods for purifying water from oil degraded in the environment.

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