

Transformations of Various Hydrocarbon Groups in Oil Degradation on the Water Surface

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ABSTRACT

The contents of oil, resinous and asphaltene fractions in the freshly extracted and degraded oil of the Surakhani deposit of Absheron have been determined. The regularities of distribution of various groups of hydrocarbons in oil and resinous fractions of freshly extracted and degraded oil on the water surface of have been studied. Three groups of PAHs - 2-6 benzene rings, NPD (Naphthalene, Phenanthrene-Dibenzo(ah) anthracene) and 16 EPA were considered. It is shown that when changing from the oil fraction to the resinous one, the content of 2-6 PAH increases by 45%, 16 EPA by -33.6%, and NPD - by 38.5%. With the degradation of oil in water, in addition to the fact that the content of the asphaltene fraction increases sharply, the total content of the identified PAH-16ER in the oil fraction does not change, and in the resinous fraction increases by 1.5 times. The regularities of degradation of various groups of petroleum hydrocarbons are explained within the framework of the mechanism of the influence of environmental factors on their reactivity.

Keywords: oil, degradation, ecology, environmental chemistry

INTRODUCTION

Oil pollution of reservoirs is formed as a result of extraction, separation from formation water, transportation of the oil, catastrophes, industrial and urban discharges [1]. The extent of the spread and evolution of the behavior of oil pollution in the water basin depends on the composition of the oil, microbiological processes, water conditions, wind force, temperature, solar and ionizing radiation, etc.

Oil and its degradation products create serious environmental problems in the environment, adversely affects human health and the ecosystem as a whole. Among the oil components, polycyclic aromatic hydrocarbons (PAHs) due to toxicity and insolubility in water are the most resistant to the effects of microorganisms and other environmental factors. On the one hand, insolubility in water reduces the likelihood or prevents the entry of PAH into living organisms, on the other hand, leads to their accumulation in the environment, for example, in bottom sediments of the water bodies. The effect of light and ionizing rays, pH of the medium, the minerality of the aquatic environment, and so forth influence their transformation in the environment [2-4].

For the last 35-40 years, serious research has been carried out to clean up water resources from oil pollution. However, the problems of oil degradation in soil and water are not studied enough. At the same time, the degree of oil degradation significantly influences the efficiency of processes of oil purification from oil pollution.

For the Azerbaijan oils degradation processes have been studied as exemplified by Balakhani oils [5-6]. However, issues related to the transformation of polycyclic aromatic hydrocarbons in the degradation of the oil have been considered partially [7-8], no detailed studies have been carried out.

In this paper, the regularities of the distribution and conversion of various groups of hydrocarbons in oil and resinous group fractions in the freshly extracted and degraded oil of the Surakhani deposit of Absheron are studied.

METHODICAL PART

Samples of fresh oil were taken from products of thermo chemical separation of crude oil, and degraded oil was taken in the vicinity of the contaminated reservoir. The contents of the main components - hydrocarbons, resins and

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asphaltenes were determined in isolated oil samples in accordance with GOST 1158-66.

Absorption spectroscopy methods (IR-spectra) were used to determine the structure-group composition of these components on a VARIAN 640-IR spectrophotometer in the wavelength range 4000-600 cm⁻¹. Indication of the bands of the obtained spectra were performed in accordance with [9]. The kinematic viscosity was determined in accordance with GOST 33-82, density - according to GOST-3900-85. Liquid products were analyzed on the chromatograph «GCFID (GS-450, Varium-2010 USA)». Polycyclic aromatic hydrocarbons from the groups 16EPA, NPD and 2-6 aromatic rings were analyzed on a GC / MS Trace DSQ mass spectrometer (Thermo Electron, Finnigan USA, 2005).

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Oil is a complex mixture consisting of aliphatic and naphthenic hydrocarbons, aromatic compounds, asphalt-resinous substances, whose behavior in the aquatic environment is different. So, environmental factors differently act on different group fractions (oil, tar, asphaltenes) of natural oil. To understand the very complex mechanism of the ongoing processes in the

degradation of oil, we divided the samples of both crude and degraded oil into three fractions. Table 1 shows the contents of group fractions in samples of freshly extracted and degraded oil.

Table1. Fractional composition of oil samples (mass%) taken from the well and from the water surface

Sample	Hydrocarbons	Resins	Asphaltenes
From the well	92,5	7,45	0,05
From the water surface	82,8	16,8	0,4

The represented data show that after a long stay of oil on the surface of the water under the influence of natural factors the group composition of the oil changes - the content of hydrocarbons decreases, but the content of resins and asphaltenes increases. This is due to the influence of microorganisms, atmospheric oxygen and radiations of different origin on the destructive transformations of various oil components [10].

The regularities of the degradation processes were studied as exemplified by the oil and resinous fractions separated from fresh and degraded oils. As an example, chromatograms and IR-spectra of the oil fraction are given here.

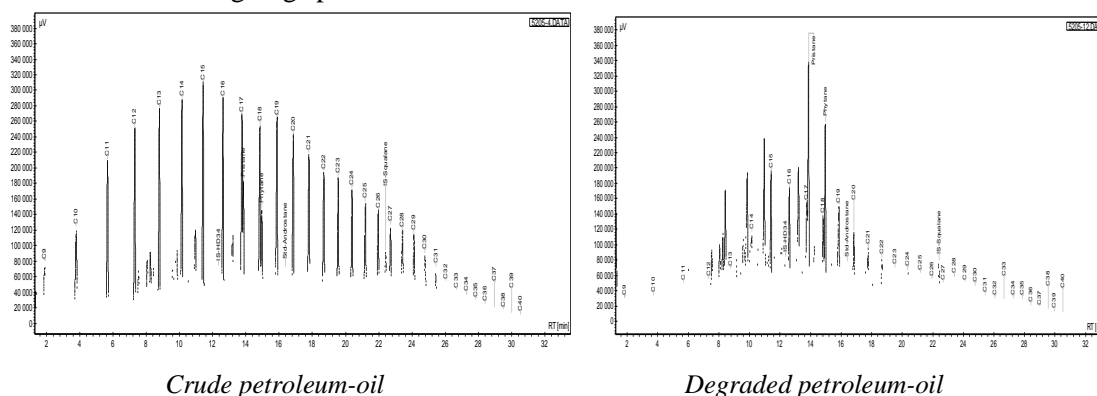


Figure1. Chromatograms of the oil fraction of fresh and degraded petroleum

The quantitative identification of petroleum hydrocarbons C10-C40 from the chromatograms shows that the total concentration of these hydrocarbons in the oil decreases from 581.8 g/kg to 453.8 g/kg during degradation. In the resinous fraction, on the contrary, the concentration of hydrocarbons increases from 523.7 g/kg to 620.1 g/kg. This, apparently is connected with the transformation of hydrocarbons in the environment and their transition from one fraction to another.

The change in the molecular-group composition of the oil and resinous fractions of oil during its degradation on the water surface was studied by

IR-spectroscopy. The IR-spectra of the oil fraction of the petroleum taken from the well have the following absorption bands:

2919.2852 cm⁻¹ - characterize the valence vibrations of -CH₂- and -CH₃ groups in alkanes

2975.2992 cm⁻¹ - valence vibrations of C-H bonds in cyclic alkanes

1461.1376 cm⁻¹ - deformation vibrations of -CH₂- and -CH₃ groups of paraffin chains

760.820.880 cm⁻¹ - out-of-plane deformation vibrations of the benzene ring of mono- and polynuclear aromatic structures.

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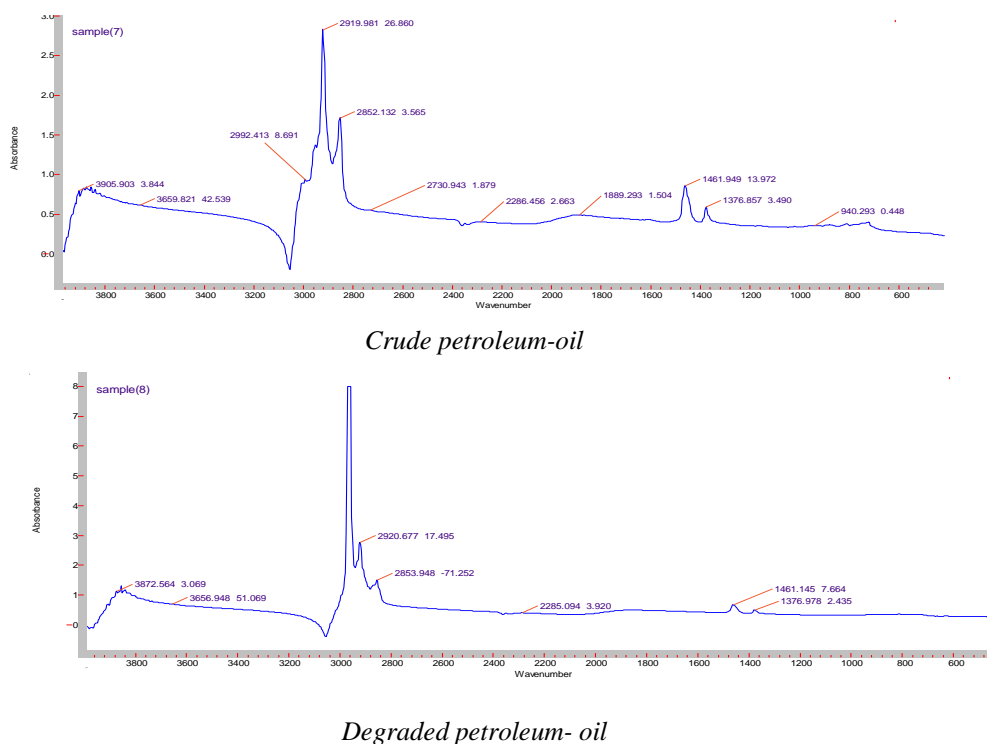


Figure 2. IR-spectra of the oil fraction of fresh and degraded petroleum

The IR-spectra of oil samples taken from the surface of the reservoir show a decrease in the absorption bands of 2919 and 2852 cm^{-1} , as well as of 1461 and 1376 cm^{-1} , reduction of -CH₂- and -CH₃ groups, which is explained by condensation processes in the composition of oil as a result of oil thickening when being on the water surface. The absorption bands 760.820.880 cm^{-1} , corresponding to the deformation vibrations of the benzene ring of mono- and polyaromatic compounds, as well as the bands 2975 cm^{-1} , 2992 cm^{-1} corresponding to valence vibrations of C-H bonds in cyclic alkanes, disappear. This is due to condensation of aromatic rings as a result of the effect of the environmental factors.

Thus, under the influence of the environment, the structure of oil after being on the water surface undergoes significant changes.

The regularities of distribution of polycyclic aromatic hydrocarbons (PAHs) in oil and resinous fractions of freshly extracted and water-degraded petroleum were studied in

Table 2. The effect of petroleum degradation in the aquatic environment on its hydrocarbon composition (mg / kg)

Fraction	THC (C ₁₀ -C ₄₀)	Total 2-6 ring PAH	NPD	Total EPA 16
Oil from fresh petroleum	620108	14016	13652	962
Oil from the degraded petroleum	453883	15759	15481	962
Resin from fresh petroleum	581873	20375	18912	1286
Resin from degraded petroleum	352718	28084	27310	1908

detail. Three PAH groups containing 2-6 benzene rings, NPD (Naphthalene, Phenanthrene-Dibenzo(ah)anthracene) and 16 EPA, as well as normal petroleum hydrocarbons were considered.

It should be noted that in the resinous fractions of both fresh and degraded petroleum on the water surface, the presence of all three PAH groups exceeds their values in comparison with oil fractions. As can be seen from Table 2, in the resin fraction of freshly extracted petroleum, the content of 2-6 PAH is 45%, 16 EPA - 33.6%, and NPD - 38.5% higher than in the oil fraction. In degraded oils these values are: for 2-6 PAH - by 78.2%, for 16EPA - more than 2 times, and for NPD - by 76.4%. In oils, PAH values with 2-6 benzene rings increase by only 12.4%, NPD - by 13.4%, 16EPA - does not change. In the resinous fraction the values of these PAHs increase, respectively, by 37.8%, 44.4% and 48.3%. It should be noted that these changes refer to the PAHs, measured in the oil composition.

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The concentration of individual PAHs of the 16EPA group varies in different ways in the degradation processes on the water surface, depending on the group fraction. It should be noted that as expected, the concentrations for all individual hydrocarbons of this group, except naphthalene in the resinous fraction, are much higher than in the oil fraction. This difference is wide, ranging from 20% to 35 times. Only the content of naphthalene in the oil fraction is 47% higher than in the resinous fraction. These regularities are most likely associated with specific processes of formation of various groups of compounds in the genesis and metamorphism of the oil.

The process of oil degradation also significantly affects the concentrations of individual PAHs in both oil and resin. Despite the fact that the total

concentration of 16 EPA does not change in the oil fraction, significant changes occur in its composition. In the resinous fraction during degradation, the concentration of naphthalene increases by more than 2 times.

The ratio of the concentrations of individual hydrocarbons in resin and oil, as well as in fresh and degraded petroleum, depends on the number of benzene rings in their composition. It can be seen from Fig. 3 that these ratios increase with increasing K for both fresh and degraded oil, and this effect is more pronounced for fresh oil, where the ratio C_{tar}/C_{oil} reaches 13 for $K = 6$. There is also a tendency to increase the content of these groups of hydrocarbons with an increase in the number of benzene rings in their composition.

Table3. The effect of oil degradation in the aquatic environment on the PAH content of the 16 EPA group in its composition

Name of the PAH	Oil from degraded petroleum	Resin from fresh petroleum	Resin from degraded petroleum
Total EPA 16	962	1 286	1 908
Naphthalene	562	421	975
Acenaphthylene	38	35	68
Acenaphthene	25	52	43
Fluorene	89	203	200
Phenanthrene	202	404	511
Anthracene	9,2	22,8	16,2
Fluoranthene	3,1	8,2	9,2
Pyrene	8,2	27,6	17,9
Benzo(a)anthracene	4,0	17,5	11,7
Chrysene	18,1	73,7	46,3
Benzo(b)fluoranthene	1,4	11,2	5,9
Benzo(k)fluoranthene	0,3	1,5	1,1
Benzo(a)pyrene	0,2	1,7	0,4
Indeno(123cd)pyrene	0,7	0,6	0,5
Benzo(ghi)perylene	0,3	5,1	1,6
Dibenzo(ah)anthracene	0,5	0,7	0,1

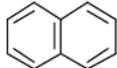
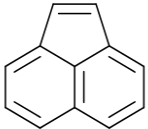
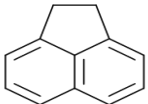
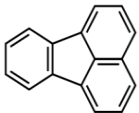
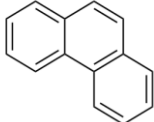
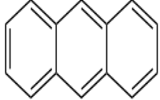
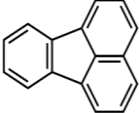
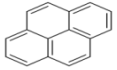
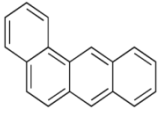
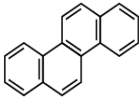
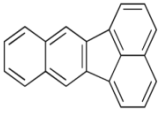
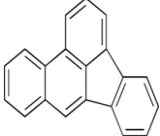
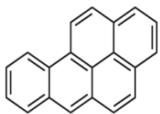
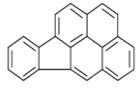
Due to the fact that polycyclic compounds are the most toxic from the ecological point of view, it is interesting to study their changes in the course of oil degradation processes in the

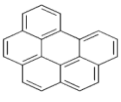
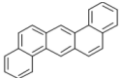
environment. The toxicity of individual PAHs (especially benzocompounds) is a thousands times greater than the toxicity of others (see Table 4).

Table4. Basic characteristics of PAH 16ERA

Name	Molecular mass, g/mole	Chemical structure	Chemical formula	Number of benzene rings	The toxicity factor	MAC
Total EPA 16						

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Naphthalene	128		$C_{10}H_8$	2	0.001	
Acenaphthylene	152.2		$C_{12}H_8$	3	0.001	
Acenaphthene	154.2		$C_{10}H_{10}$	3	0.001	
Fluorene	166.2		$C_{13}H_{10}$	4	0.001	
Phenanthrene	178.23		$C_{14}H_{10}$	3	0.001	
Anthracene	178.23		$C_{14}H_{10}$	3	0.01	
Fluoranthene	202.26		$C_{16}H_{10}$	4	0.001	
Pyrene	202.26		$C_{16}H_{10}$	4	0.001	
Benzo(a)anthracene	228.29		$C_{18}H_{12}$	4	0.1	
Chrysene	228.29		$C_{18}H_{12}$	4	0.01	
Benzo(k)fluoranthene	252.32		$C_{20}H_{12}$	5	0.1	
Benzo(b)fluoranthene	252.32		$C_{20}H_{12}$	5	0.1	
Benzo(a)pyrene	252.3		$C_{20}H_{12}$	5	1	10^{-9} g/m^3 0,02 mg/kg
Indeno(123cd)pyrene	276.3		$C_{22}H_{12}$	6	0.1	9

Benzo(ghi)perylene	276.3		$C_{22}H_{12}$	6	1	3
Dibenzo(ah)anthra-cene	278.3		$C_{22}H_{14}$	5	5	0,007 mg/m ³

Therefore mutual transformations of these PAHs is important from the environmental point of view, and the study of these processes under the influence of various factors has great practical and scientific interest.

Fig. 3 shows dependencies of individual PAHs concentrations in resinous (Ctar) and oil (Coil) fractions on the number of aromatic rings (K) for fresh (a) and degraded petroleum (b). It can be seen from the figure that with an increase in the number of benzene rings from 2 to 6, the ratio Ctar / Coil increases for both fresh and degraded petroleum. Moreover, in freshly extracted petroleum this value grows faster than in the degraded petroleum, and at $K > 3$ this ratio becomes 13.5 ($K = 6$). In degraded petroleum, this ratio does not exceed 3 for all values of K. This indicates that in degraded oils the distribution of 16ERA with different numbers of benzene rings between the fractions is closer to uniform than in fresh oils.

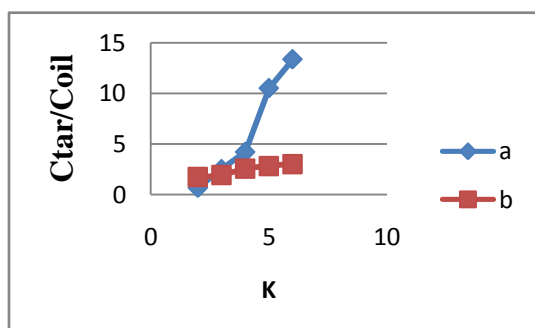


Figure3. Dependences on the number of benzene rings: (a) – the ratios of the content of individual PAHs in the tar and oil fractions of freshly produced petroleum; (b) – the ratios of the content of individual PAHs in resinous and oil fractions of degraded petroleum

Fig. 4 shows dependencies of individual PAHs concentration ratios in degraded and fresh fractions on the number of benzene rings. With the growth of K in the resinous fraction, this ratio is reduced by 4 times, and the oil fraction, on the contrary, increases by only 60%. This shows that degradation has a greater effect on the concentration of individual PAHs in the resinous fraction, which is apparently associated with rapid conversions of light PAHs with the

formation of heavier PAHs. Degradation processes affect light PAHs more than heavy PAHs, which is associated with their relatively high reactivity with respect to environmental factors.

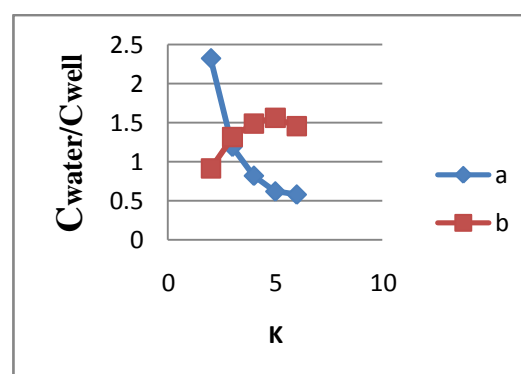


Figure4. Dependences on the number of benzene rings: (a) – the ratios of the content of individual PAHs in resins of degraded and freshly produced petroleum; (b) - ratios of the content of individual PAHs in oils of degraded and freshly produced petroleum

Represented data show that after a long stay of the oil on the water surface under the influence of natural factors the material composition of the oil changes - a content of hydrocarbons decreases, and a content of resins and asphaltenes increases. This is explained by the influence of solar radiation, atmospheric oxygen and radiations of various origin on destructive transformations of oil components [6]. Moreover, the more the molecular mass and the number of aromatic rings, the process of poly condensation occurs more rapidly than in light PAHs. It is seen that with an increase in the number of rings, the ratio Ctar/Coil increases, which indicates the occurrence of poly condensation processes. At the same time, these processes occur faster in the oil fraction, and PAH content decreases in lighter fractions of the petroleum. On the other hand, with smaller amounts of aromatic rings, PAHs are more soluble in water, and respectively, they are more exposed to biodegradation by microorganisms. The dissolution process is also positively influenced by the salt content of the water.

It should be taken into account that our analytical methodology identifies only PAHs with the number of aromatic units up to 6. Therefore, it should be taken into account that a part of PAH can be converted to PAH with a number of aromatic nuclei greater than 6, which we can not to identify. As the content of asphaltene increases dramatically during the degradation process, it can be assumed that part of PAH is released together with asphaltenes.

CONCLUSION

1. The ratio of the contents of individual PAHs in the resinous and oil fractions of the petroleum (Ctar/Coil) strongly depends on the number of benzene rings, and reaches up to 13.6 at K=6 in freshly produced petroleum. In degraded petroleum, this dependence is relatively weak, and the value of Ctar/Coil does not exceed 3 at K = 5-6. This indicates a relatively uniform distribution of individual PAHs in tar and oil fractions of degraded petroleum.
2. With the degradation of petroleum in water, light PAH content is strongly transformed both in oil and resin, the content of relatively heavy PAH with K = 4-6 changes by no more than 50%, and in the resinous fraction this process proceeds with a higher speed. The faster degradation of relatively light PAHs with K = 2-3 is associated with their high reactivity to environmental factors.

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ACKNOWLEDGEMENT

This work was carried out under the financial support of the Science Development Foundation under the President of the Republic of Azerbaijan.

Grant No. EIF-KETPL-2-2015-1 (25) - 56/23/4No. EIF-KETPL-2-2015-1 (25) -56/23/4

Citation: S. Hajiyeva, A. Samadova, N. Guliyeva and I. Mustafayev, "Transformations of Various Hydrocarbon Groups in Oil Degradation on the Water Surface", *International Journal of Research Studies in Science, Engineering and Technology*, vol. 5, no. 1, pp. 25-31, 2018.

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