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INFLUENCE OF GAMMA-RADIATION ON OIL FRACTION OF PETROLEUM DEGRADED IN SOIL

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Abstract: The regularities of gas formation, changes in molecular structure and content of polycyclic aromatic hydrocarbons (PAH) at the influence of gamma-radiation on oil fraction degraded in soil of Surakhani oil field have been studied. It has been established that, within the range of absorbed dose D = 0-109.2 kGy the total radiation-chemical yield of H_2 gases and hydrocarbons C_1-C_5 does not exceed 1.67 molec/100 eV. In molecular structure of oil fraction there are no substantial changes, although minor changes in IR-spectra are observed in the wavelength range of ν= 870-2960 cm^{-1}, corresponding to the groups $–CH_2$, $-CH_3$, C=O, C =C, C-H.

The influence of gamma-radiation on 16EPA – groups of polycyclic aromatic hydrocarbons has been studied. It is shown that, within the radiation-chemical transformations of oil fraction up to absorbed dose 109.2 kGy the content of the group 16 EPA in PAH increases by 5.3%, content of some individual benzo compounds decreases from 2.3 to 100 times. The conventional radiolysis mechanism of PAH explains the observed experimental laws.

Keywords: gamma-radiation, oil, environment, water.

1. Introduction

As a result of industrial production of oil in Absheron peninsula, tens of million tons of petroleum have been dumped in the environment more than 160 years /1/. These discharges were carried out in the processes of extraction, release from water, storage, transport and use of oil. Oil and products of its degradation, especially polycyclic aromatic hydrocarbons, create serious ecological problems in the environment, negatively affect human health and the ecosystem as a whole /2,3/.

Over the past 35-40 years it has been carried out extensive researches on purification of lands and water resources from oil pollution. However, the issues on oil degradation in soil and water medium haven’t been studied enough. At the same time, the degree of oil degradation significantly affects the efficiency of the processes of purification from oil pollution. The study of radiation-chemical transformations of oil is essential for both assessment of radiation role in degradation processes in the environment, and development of radiation-chemical technology for processing of degraded oil /4/. This issue is of interest for gathering oil products from the environment, as well.

2. Research methodology

Oil samples were taken from the contaminated soil in the areas of Surakhani oil fields. After purification from impurities, the oil samples were divided into three fractions: oil, tar and asphaltenes in accordance with GOST 1158-66.

Table 1. Fractional composition (wt %) of oil samples taken from wells and soil

Sample	**Oil**	**Tar**	**asphaltene**
Oil from soil	71.1	22.4	6.5
Oil from well	90.9	9.0	0.1

As it is seen from table, the content of oil fraction in the composition of degraded oil taken from soil, was found to be significant in comparison with the oil samples from well – less by 20%. Radiation-chemical studies were conducted on oil fractions of freshly produced and degraded oil.

Isotopic source of γ-radiation Co^{60} – «MPX-γ-30» was used as a source of ionizing radiation. Gas products were analyzed by gas chromatography method on devices “Tsvet-102” and “Gazoxrom-3101”. IR-spectra were measured by Fourier method applying spectrophotometer “Varian 640-IR” in the wavelength range of 600-4000 cm^{-1}.

For analyzing the products in liquid phase, it was used chromate-mass spectrometric method. Chromatograph GCFİD (GS-450, Varium-2010 USA) and mass-spectrometer GC/MS Trace DSQ (Thermo Electron, Finngan USA, 2005) were used. The oil samples were dried with dry Na_2SO_4, then diluted with dichloromethane (CH_2Cl_2) for chromatographic analysis. The analyses were carried out on device GC/MS Trace DSQ (Thermo Electron, Finngan USA, 2005) within m/z =35-400 (m/z - mass-to-charge ratio), and the components of the products were identified on the base of mass-spectra.

3. Results and discussion

Figures 1 and 2, as an example show the formation kinetics of hydrogen and ethylene within radiation-chemical decomposition of oil fraction of freshly produced and degraded in soil oil.

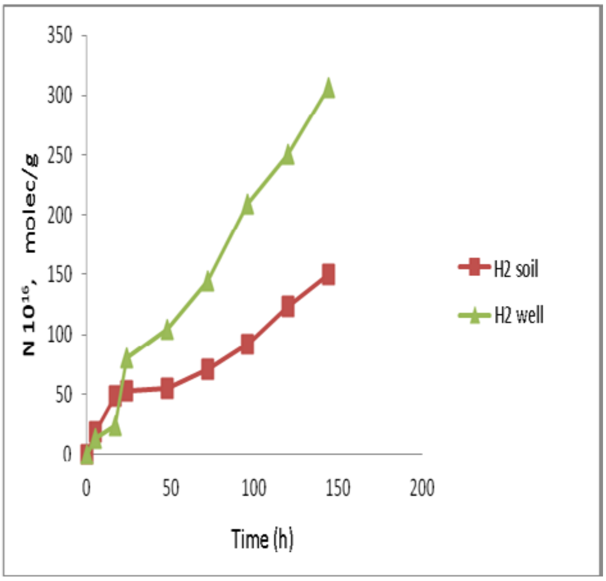

Fig.1. Kinetics of hydrogen formation at radiolysis of oil fraction of petroleum

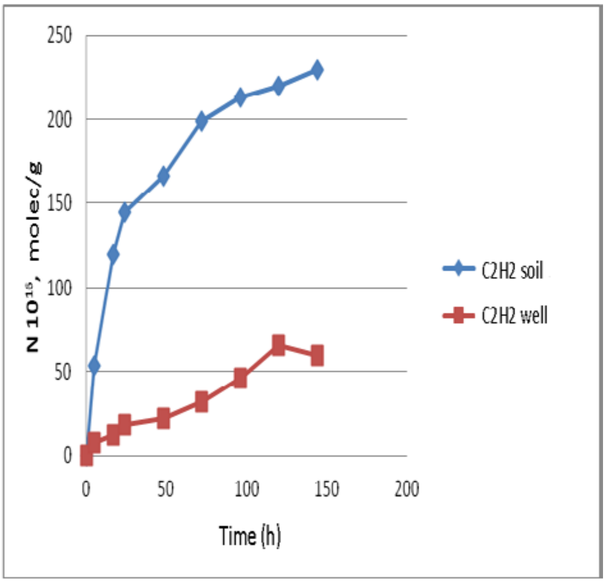

Fig.2. Kinetics of ethylene formation at radiolysis of oil fraction of petroleum

Table 2. Average values of radiation-chemical yields of gases at radiation-chemical transformations of oil fractions of freshly produced and degraded in soil oil.

Gases	**H_2**	**CH_4**	**C_2H_6**	**C_2H_4**	**$\sum C_3$**	**$\sum C_4$**	**$\sum C_5$**	**$\sum$gases**
Freshly produced oil	0.67	0.45	0.26	0.11	0.05	0.08	0.05	1.67
Oil degraded in soil	0.50	0.43	0.36	0.09	0.04	0.06	0.03	1.51

As can be seen from figures 1-2 and table 2, the radiation resistivity of oil fraction significantly increases at degradation with respect to gas formation. This, apparently, is associated with the decay of easily related functional groups in the course of degradation. These groups are the source of gas products in the oil composition /5/. In degradation process the formation of oxygen-containing functional groups may occur, which decompose rapidly at low doses and at the initial stage of kinetic curves in some cases higher gas yields are observed in degraded oil than in freshly produced.

Molecular structures of oil fractions of degraded oil in all cases have been measured by applying Fourier-spectroscopy method (fig.3).

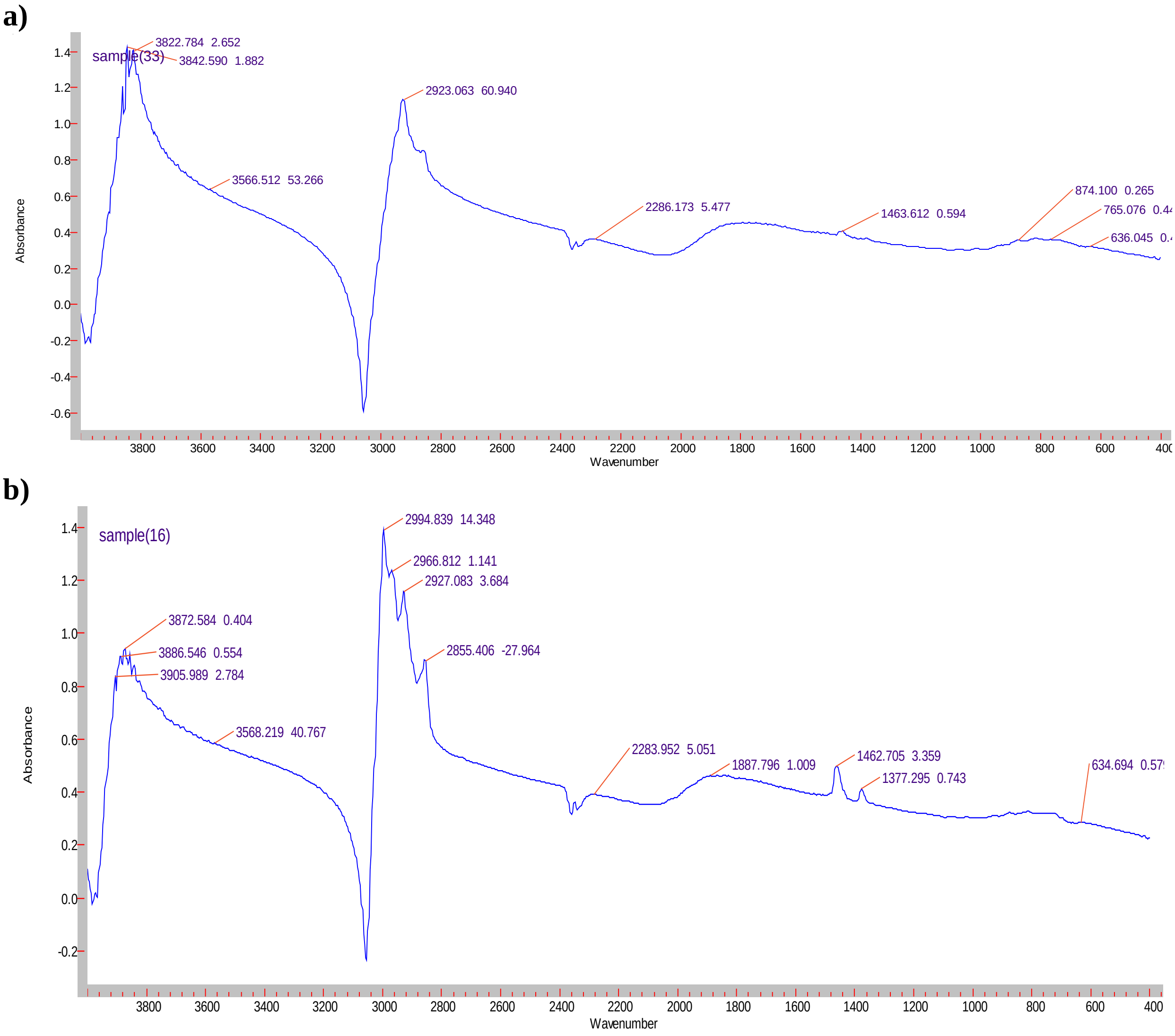

Fig.3. IR-spectra of the initial (a) and irradiated at D=109,2 kGy (b) of oil fractions of degraded in soil oil

The comparative analysis of IR spectra of the studied fractions show that, significant changes in molecular structure under gamma-radiation occur mainly at absorbed doses 91,2 and 109,2 kGy. At wavenumbers 1460 cm^{-1} and 1370 cm^{-1} there is observed a growth in absorption bands of deformation vibrations of $-CH_2-$ and $-CH_3$ group. In non-irradiated samples at wavenumber 870 cm^{-1} it is observed the absorption bands of deformation vibrations of C-H group of benzene ring, and at 1885 cm^{-1} stretching vibrations of C=O and C=C groups. At irradiation dose of 109,2 kGy it is observed the absorption bands $-CH_2-$ and $-CH_3$ groups at 2850 cm^{-1} and 2960 cm^{-1} are observed, and at 870 cm^{-1} there is a decrease in absorption bands, corresponding to deformation vibrations of C-H group of benzene ring. In the irradiated samples within the wavenumbers 2960 cm^{-1} there is an increase in absorption bands, corresponding to $-CH_3$ group.

From the environmental point, the most important oil components are polycyclic aromatic hydrocarbons (PAH). The environmental impact of PAH are much higher than the influence of other groups of hydrocarbons due to the possibility of their accumulation in oil-contaminated soils and sea-floor sediments of basins, as well as the toxicity of their influence on living organisms /6/.

Toxicity of individual PAH may differ from one another thousand of times, for example PAH with benzocompounds are much more toxic than the normal ones.

For instance, the ratio of toxicity in PAH anthracene:benzoanthracene:dibenzoanthracene = 1:10:50, which indicates the high environmental impact of benzogroup. Therefore, mutual transformations of these PAH in degradation processes and within the influence of various factors, including ionizing radiation are essential. In figures 4(a,b,c,d) it is depicted the dose dependences of changes in concentrations of polycyclic aromatic hydrocarbon groups, having important environmental value.

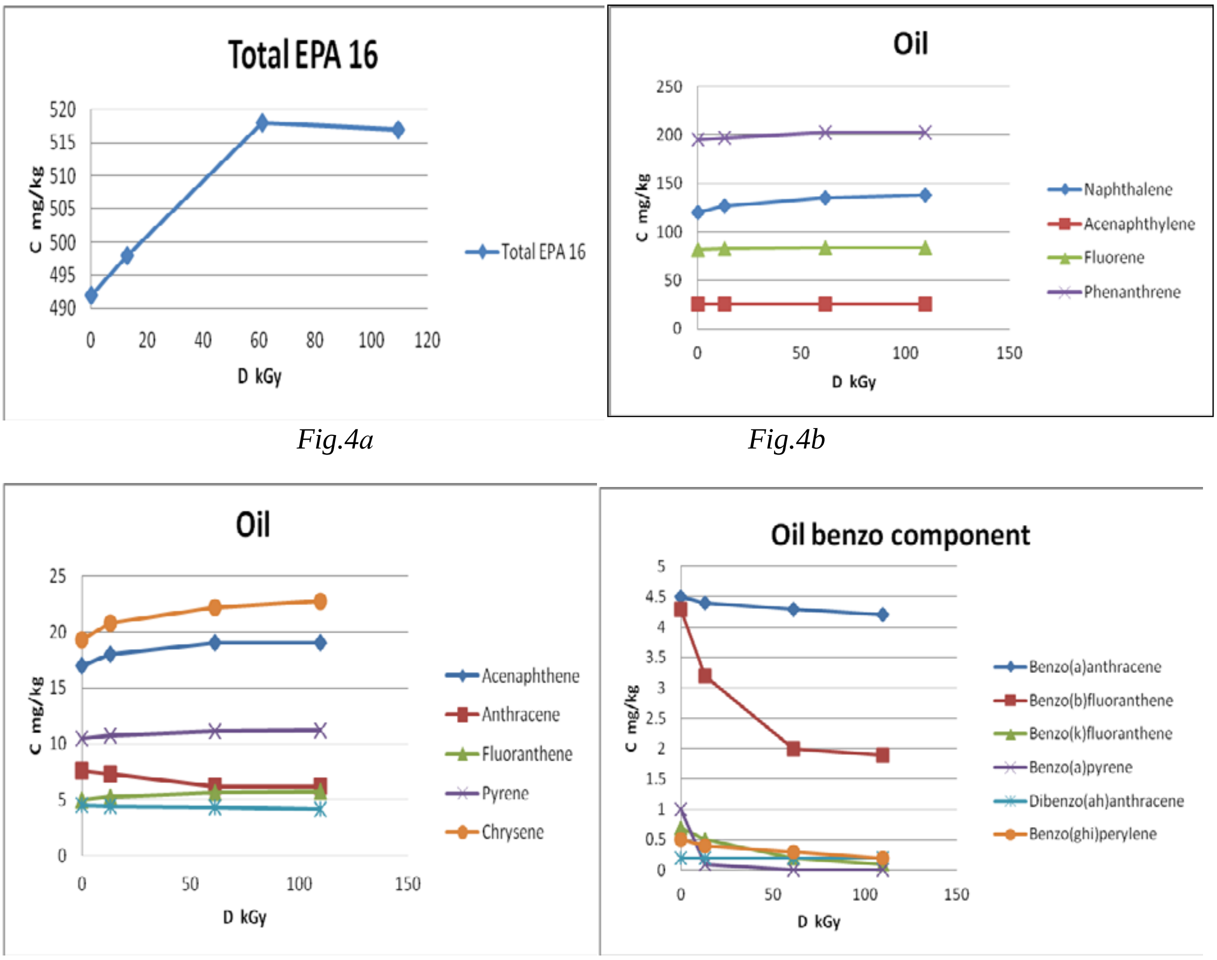

Fig.4a *Fig.4b*

Fig.4c *Fig.4d*

Fig.4. Dependences of concentrations of individual PAH on irradiation dose of oil fraction of degraded oil

Measurements show that, within the irradiation of oil fraction of degraded oil at dose of 109 kGy the total concentration of 16EPA (fig.4a) slightly increases – from 492 mkg/kg to 517 mkg/kg. This seems to be associated with the occurrence of radiation-stimulated processes of aromatization of linear hydrocarbons which is well studied in /7/.

As it is seen from figures 4b, 4c, 4d, the radiation differently affects the individual PAH. Some PAH benzocompounds decompose quickly (fig.4d) and their concentration decreases to 10 times at doses up to 109 kGy. It leads to reduction in toxicity of the entire mass of degraded hydrocarbons. Average values of radiation-chemical yields of concentration changes in PAH in oil fraction have been given in table 3. As it is seen from table, these values (molec/100 eV) correspond to the values of radiation-chemical yields of PAH in various environments.

Table 3. Average values of radiation-chemical yields of concentration changes of PAH-16EPA group

16EPA	M, g/mol	Chemical formula	Radiation-chemical yield, molec/ 100eV	Toxicity
Naphthalene	128	$C_{10}H_8$	0.012	0.001
Acenaphthylene	152.2	$C_{12}H_8$	0	0.001
Acenaphthene	154.2	$C_{10}H_{10}$	0.0011	0.001
Fluorene	166.2	$C_{13}H_{10}$	0,0011	0.001
Phenanthrene	178.23	$C_{14}H_{10}$	0.004	0.001
Anthracene	178.23	$C_{14}H_{10}$	-0.007	0.01
Fluoranthene	202.26	$C_{16}H_{10}$	0.0003	0.001
Pyrene	202.26	$C_{16}H_{10}$	0.0003	0.001
Benzo(a)anthracene	228.29	$C_{18}H_{12}$	-0.0001	0.1
Chrysene	228.29	$C_{18}H_{12}$	0.0013	0.01
Benzo(k)fluoranthene	252.32	$C_{20}H_{12}$	-0.0008	0.1
Benzo(b)fluoranthene	252.32	$C_{20}H_{12}$	-0.00021	0.1
Benzo(a)pyrene	252.3	$C_{20}H_{12}$	-0.00035	1
Indeno(123cd)pyrene	276.3	$C_{22}H_{12}$	0.0001	0.1
Benzo(ghi)perylene	276.3	$C_{22}H_{12}$	-0.0001	1
Dibenzo(ah)anthracene	278.3	$C_{22}H_{14}$	0	5

The sign (-) indicates decomposition

It should be noted that, within the irradiation of oil fraction of the freshly produced (non-degraded) oil at dose up to 91.2kGy the total concentration of PAH, on the contrary, decreases from 962 to 867 mkg/g. It is connected with the features (molecular structure, potential ionization, degree of conjugacy and etc.) of irradiation environment, as well as with the values of the initial concentrations of individual components.

It should be noted that, our analytical method identifies only PAH with the number of aromatic units up to 6. Therefore, the reduction in the content of these PAH groups is, apparently, associated with polycondensation of PAH with the number of aromatic nuclei less than 6, and with formation of heavier PAH which we can’t identify. As far as the content of asphaltenes increases dramatically in degradation process, it can be assumed that, the part of PAH is released along with asphaltenes.

4. Conclusion

1. Gas formation at the irradiation of oil fraction of degraded oil occurs with the average radiation-chemical yield – 1.67 molec/100eV, and the degraded fraction exhibits higher radiation stability than the freshly produced one.
2. As the total concentration of polycyclic aromatic hydrocarbons of 16 EPA groups, the concentration of most individual PAH also, slightly increases within the irradiation dose from 110 kGy (by 5-15%). In this case, the concentrations of PAH benzocompounds decrease from 2.3 (Benzo(b)fluoranthene) to 100 times (Benzo(a)pyrene). On the whole, the radiation influence leads to a decrease in toxicity of oil contamination.

References

1. Mir-Babayev M.F. Protection of the environment of Caspian Sea. Azerbaijan oil industry, №10,2010.p.77-79
2. F. Valerio & A. Lazzarotto (1985) Photochemical Degradation of Polycyclic Aromatic Hydrocarbons (PAH) in Real and Laboratory Conditions, International Journal of Environmental Analytical Chemistry, 23:1-2, 135-151.
3. L.Desiree Plata, Charlesm Sharpless and Christopherm Reddy. Photochemical Degradation of Polycyclic Aromatic Hydrocarbons in Oil Films *Environ. Sci. Technol.* 2008, *42,* 2432–2438
4. I.I. Mustafayev, A.P.Mamedov, S.F. Aliyeva, R.A.Jafarova. Degradation of Absheron oil in the environment. Ecology of industrial production. 1(85) 2014.p.71-74
5. I. Mustafayev, K.Yakubov, N.Guliyeva “Radiation-chemical transformations of oil degradated on water surface and in the soil”. 5-th Eurasian Conference on Nuclear Sciences and Applications. p.164-165, 14-17 Oct. 2008, Ankara – Türkiye.
6. Tsimbalyuk K.K., Denga Y.M., Antonovich V.P. Determination of PAH in objects of the environment. (Review). Methods and objects of chemical analysis. 2013.8, №2,p.50-62.
7. Svollou A. Radiation chemistry of organic compounds. M.: ATOMIZDAT 1978.p.278.

ВЛИЯНИЕ ГАММА-ИЗЛУЧЕНИЯ НА МАСЛЯНУЮ ФРАКЦИЮ ДЕГРАДИРОВАННОЙ В ПОЧВЕ НЕФТИ

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Резюме: Изучены закономерности образования газов, изменения молекулярной структуры и содержания полициклических ароматических углеводородов при воздействии гамма излучения на масляную фракцию деградированной в почве Сураханской нефти. Установлено, что в интервале поглощенной дозы в пределах D = 0-109.2 кГр суммарный радиационно-химический выход газов – Н2 и углеводородов С1-С5 не превышает 1.67 молек/100 эВ. В молекулярной структуре масляной фракции существенные изменения не происходят, хотя незначительные изменения в ИК-спектрах наблюдаются в интервале длин волн ν= 870-2960 см-1, соответствующих группам –СН2, -СН3 , С=О, С =С, С-Н.

Изучено воздействие гамма-излучения на 16ЕРА -группы полициклических ароматических углеводородов. Показано, что при радиационно-химических превращениях масляной фракции до поглощенной дозы 109.2 кГр содержание в ПАУ группы 16 ЕРА возрастает на 5.3%, содержание некоторых индивидуальных бензосоединений уменьшается от 2.3 до 100 раз. В рамках общепринятого механизма радиолиза ПАУ объясняются наблюдаемые экспериментальные закономерности.

Ключевые слова: гамма-излучение, нефть, окружающая среда, вода

QAMMA ŞÜALANMANIN TORPAĞINDA DEQRADASİYAYA UĞRAMIŞ NEFTİN YAĞ FRAKSİYASINA TƏSİRİ

İ.İ. Mustafayev, N.A. İbadov, N.K. Quliyeva, Ş.H. Hacıyev

Xülasə: Qaz əmələgəlmə qanunauyğunluqları, molekulyar quruluşdakı dəyişikliklər və politsiklik aromatik karbohidrogenlərin tərkibi qamma şüalanmanın Suraxanı torpağında deqradasiyaya uğramış neftin yağ fraksiyasına təsiri zamanı tədqiq olunmuşdur. Müəyyən olunmuşdur ki, D = 0-109.2 kQr udulma dozası aralığında H_2-qazlarının və C_1-C_5 karbohidrogenlərin ümumi radiasiya-kimyəvi çıxımı 1.67 molek/100 eV-ni keçmir.–CH_2, -CH_3, C=O, C =C, C-H qruplarına xas dalğa uzunluğunun ν= 870-2960 sm^{-1} aralığında İQ spektrlarda kiçik dəyişikliklərin müşahidə olunmasına baxmayaraq, yağ fraksiyasının molekulyar quruluşunda əsaslı dəyişikliklər baş vermir.

Qamma şüalanmanın politsiklik aromatik karbohidrogenlərin 16EPA-qrupuna təsiri öyrənilmişdir. Göstərilmişdir ki, yağ fraksiyasının radiasiya-kimyəvi çevrilmələri zamanı 109.2kQr udulma dozasına qədər PAK-ın tərkibində 16 EPA qrupunun miqdarı 5.3%-ə qədər artır, bəzi fərdi benzo-birləşmələrin miqdarı isə 2.3-dən 100 dəfəyə qədər azalır. Müşahidə olunan təcrübi qanunauyğunluqlar PAK radiolizinin ümumi qəbul olunmuş mexanizması çərçivəsində izah olunur.

Açar sözlər: qamma-şüalanma, neft, ətraf mühit, su