

Influence of Radiation on the Structure and Properties of the Oil Degraded on the Water Surface

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Abstract. The oil degradation of the Surakhani deposit of the Azerbaijan in the environment have been investigated. Samples of the oil were taken from the well and from the surface of the water reservoir. It was shown that the content of tar and asphaltenes increases due to natural factors and radiation on the surface layer of water in the degraded oil composition. Radiolysis of oil fractions, composition and dynamics of changes in physical parameters of oil - density and oil viscosity have been investigated.

Keywords: oil, degradation, tar, asphaltene, radiation, viscosity, density

1 INTRODUCTION

Most of the oil pollution of the ocean is caused by the following factors: transportation, catastrophes, natural sources, industrial waste, waste from coastal oil refineries / 1 /. Oil is a complex mixture consisting of aliphatic and naphthenic hydrocarbons, aromatic compounds, asphalt-tar substances, whose behavior in the aqueous medium is different.

Annually in the World Ocean from various sources as a result of human activity about 5 million tons of oil fall. Since 1 ton of the oil, spreading over the surface of the ocean, occupies an area of 12 km², the World Ocean probably already is covered with a thin surface film of hydrocarbons / 2 /.

In the environment due to the processes of evaporation, filtration and degradation of oil change its physico-chemical properties. All types of the oil contain low-boiling components that evaporate quickly from the water surface, and low-molecular components are removed from the oil stain, mainly as a result of dissolution, settling to the bottom or wash ashore.

Current methods of water and wastewater treatment used now often do not provide full-fledged treatment and do not meet modern environmental requirements. In this regard, the use of advanced technologies for water purification from oil is very important / 3-4 /. One of the promising and ecologically modern methods of water and sewage treatment is radiation technology. It is based on reducing the concentration of contaminants in the water under the influence of ionizing radiation.

In order to assess the role of radiation in the process of detecting oil on the surface of the water bodies and to identify the possibilities of using radiation-chemical technology in cleaning water from oil pollution, certain regularities in the radiation-chemical transformation of oil samples after a long stay on the water surface in natural conditions have been studied.

2 EXPERIMENTAL TECHNIQUE

The contents of the main components - hydrocarbons, tar and asphaltenes groups of petroleum 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 of 4000-600 cm⁻¹. Indication of the bands of the spectra obtained was carried out in accordance with / 5 /. A source of ionizing radiation was isotope gamma source ⁶⁰Co- MPX-30 with a dose rate P = 0.21 Gy/s, as well as a linear electron accelerator ELU-4. Kinematic viscosity was determined in accordance with GOST 33-82, density - according to GOST-3900-85. Absorbed doses varied in the interval D = 3.8 -109.5 kGy (gamma irradiation) and 1170-3120 kGy (accelerated electrons). Gas products were analyzed by gas chromatography on the devices "Цбер-102" and "Газохром-3101" .

3 EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The investigated oil samples were separated from water by extraction. Benzene was used as the extractant. For comparison, oil samples taken directly from a nearby well were used. Table 1 gives the content of the main components of oil taken from the well and from the water surface - hydrocarbons, resins and asphaltenes.

Table 1
 Fractional composition of samples of oils taken from the well and 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

Represented data show that after a long stay of oil on the water surface under the influence of natural factors, the material composition of the oil changes - the content of hydrocarbons decreases, whereas the content of resins and asphaltenes increases. This is due to the influence of solar radiation, atmospheric oxygen and radiations of various origins on the destructive transformations of heavy oil components / 6 /.

The character of the change in the properties of oil taken from the water surface was traced by the IR-spectra of oil fractions, the kinetics of gas formation during the radiolysis of oil petroleum fractions, and by the change of physical characteristics of the samples under study.

The formation of more condensed aromatic rings in the oil structure after a long stay in water is indicated by the results of IR-spectroscopy of samples of the degraded oil. Figures 1-2 show IR-spectra of initial samples of tar fractions of petroleum from the well and from the water surface.

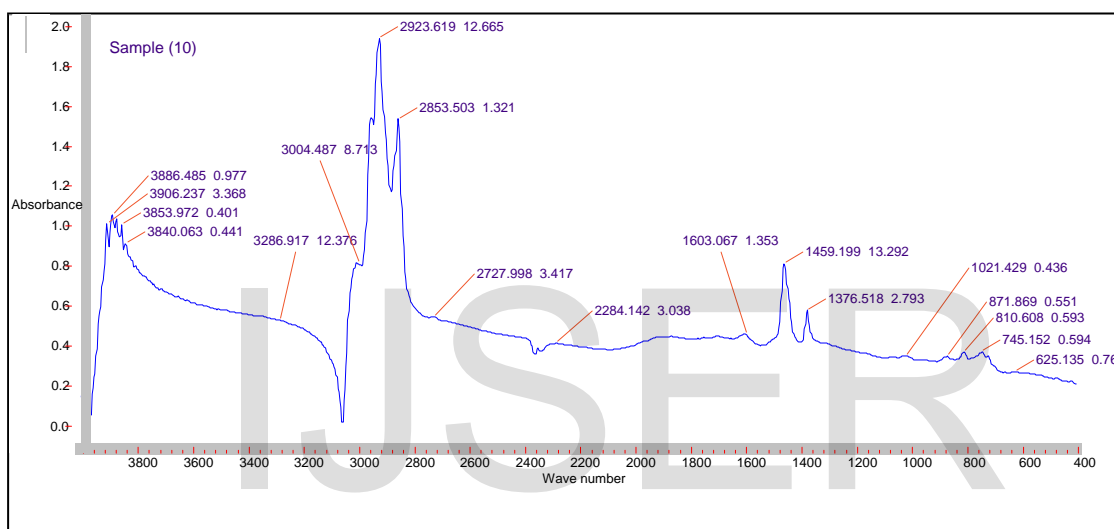


Fig.1. IR-spectrum of tar fraction of the petroleum from the well

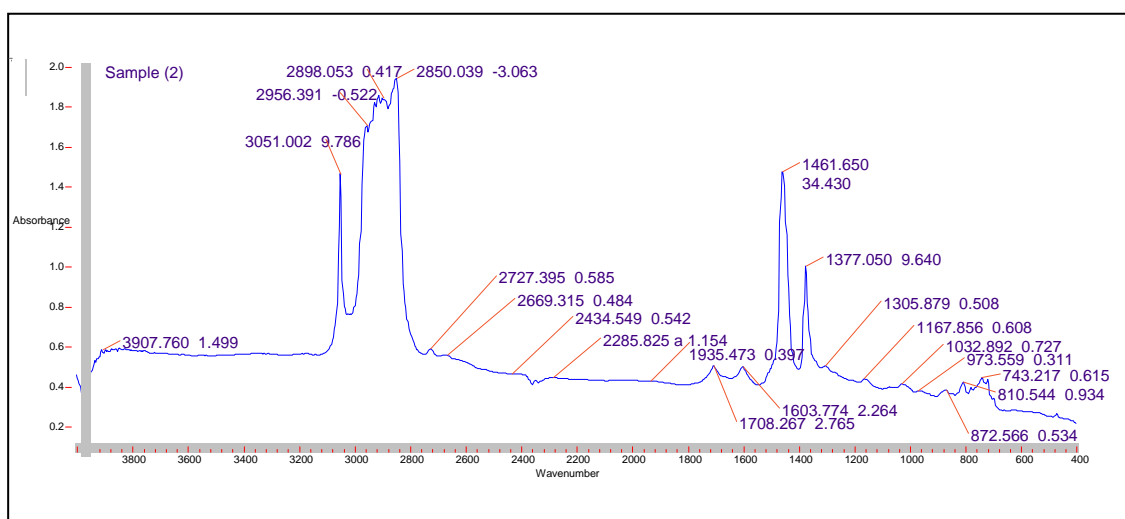


Fig. 2. IR-spectrum of the tar fraction of the petroleum from the water surface

Comparative analysis of IR-spectra of initial samples of the tar fraction of the petroleum showed that the process of tar oxidation occurs after a prolonged stay of oil on the water surface as a result of decomposition, from which the appearance of bands at 1708 cm^{-1} belonging to C=O groups is indicative. This absorption band is an objective criterion for the accumulation of oxygen-containing products. Intensive absorption bands are also observed at 3051 and 1603 cm^{-1} ,

characteristic for the stretching vibrations of the C=C bond of a cyclic or benzene (aromatic) ring, at 1030 cm^{-1} appear bands corresponding to polynuclear aromatic structures. Strong accumulation of the condensed aromatic rings - 3-4 times as compared to samples from the well is observed. Also, absorption bands appear in the wavelength interval $600\text{--}1000\text{ cm}^{-1}$, corresponding to deformation vibrations of CH_2 and CH_3 groups, and in the range of 1461 cm^{-1} and 1377 cm^{-1} - a strong increase of these groups. The data obtained indicate significant changes in the composition of the oil due to environmental factors / 9 /.

The dynamics of the change in composition of the tar fraction of the petroleum after being on the water surface is also observed from the presented chromatograms (Fig. 3-4). Reducing the height of peaks of n-alkanes, shifting their maximum toward heavier hydrocarbons is one of the results of the oil degradation.

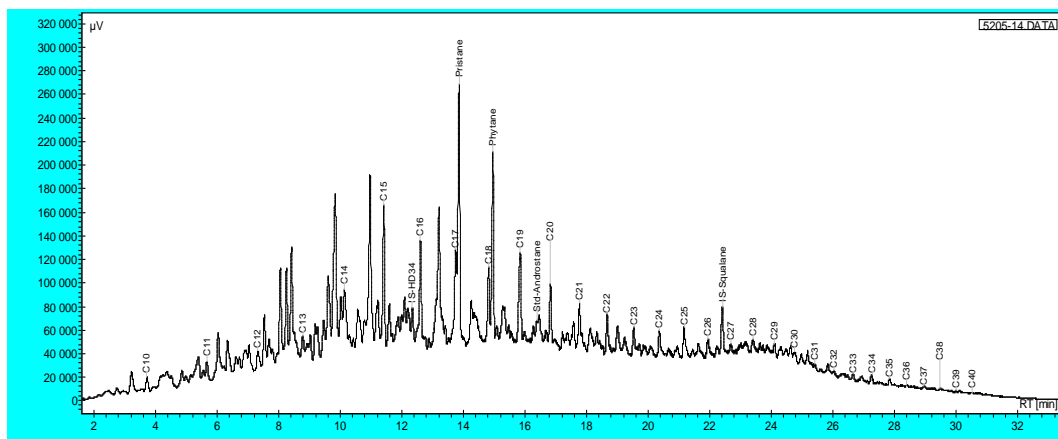


Fig. 3. Chromatogram of the tar fraction of the petroleum from the water surface

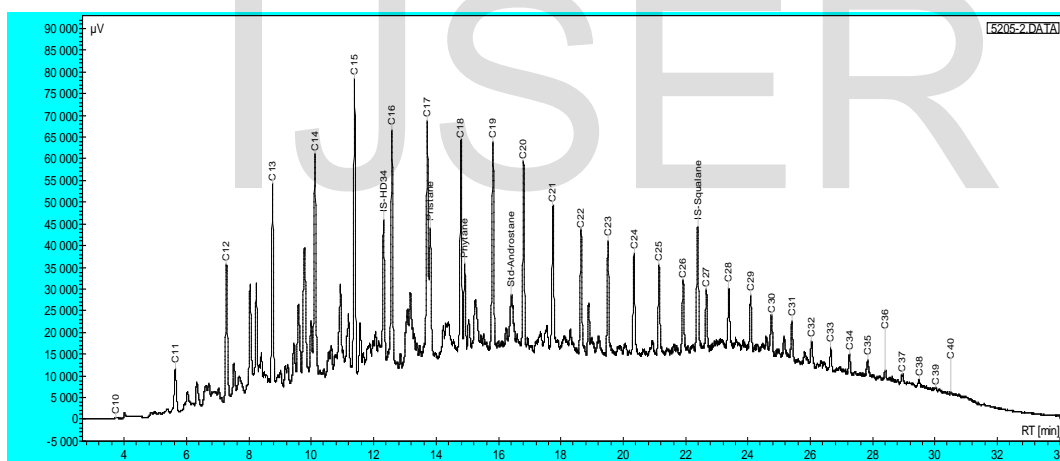


Fig. 4. Chromatogram of the tar fraction of the petroleum taken from the well

Changing of radiation stability of the oil group fractions under radiation were investigated. The radiolysis of petroleum fractions and the effect of the absorbed dose of gamma radiation on the yield of gas products during radiation-chemical transformations of oil and tar fractions of the petroleum have been studied. The formation rate and the radiation-chemical yields of gases formed as a result of gamma-radiolysis of the fractions were determined: H_2 , CO , CH_4 , C_2H_4 , C_2H_6 , $\Sigma\text{C}_3\text{--C}_6$.

Figures 5-6 show the kinetic curves of the formation of hydrogen in the radiolysis of the oil and tar fractions of the oil taken from the well and from the water surface.

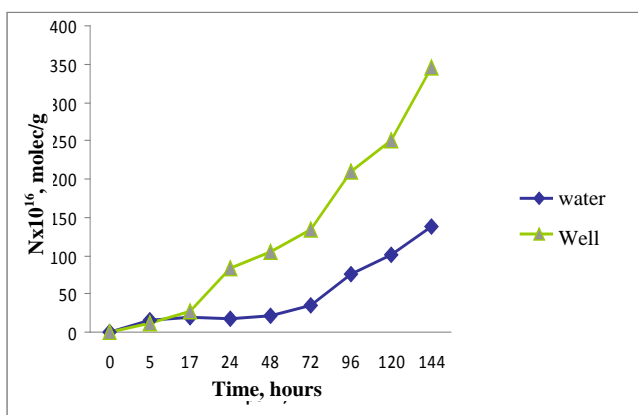


Fig. 5. Kinetics of the formation of hydrogen in the radiolysis of oil fractions of petroleum

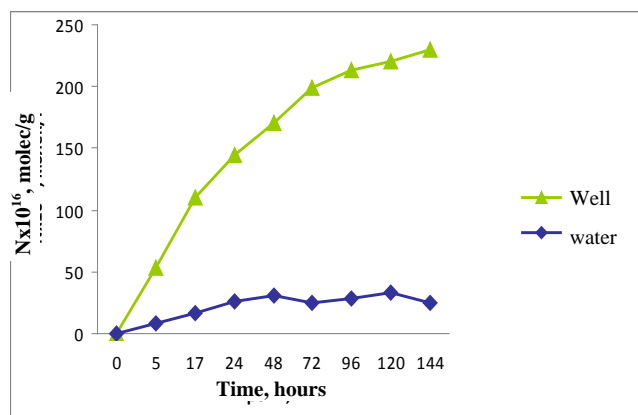


Fig. 6. Kinetics of the formation of hydrogen in the radiolysis of the resinous oil fractions

From the kinetics of the formation of hydrogen as a result of radiolysis of the oil samples in the range of absorbed dose of gamma irradiation up to 110 kGy (144 hour) it is evident that the greatest yield of hydrogen is observed in the samples of the oil from the well. Samples of the oil taken from the water surface are characterized by low hydrogen yields, i.e. they have high radiation resistance. This regularity is explained by the structural changes in oil during the process of being on the water surface, namely, with the increase in their composition of radiation-resistant tars and asphaltenes / 7 /. This is especially observed in the radiolysis of the resinous fraction, which differs from the oil with a low content of functional groups and a higher content of condensed aromatic compounds.

In a wide range of the absorbed dose (1170-3120 kGy) of accelerated electrons, the dynamics of the change in the physical parameters of the oil - kinematic viscosity and density was studied. It is established, that under the influence of radiation the kinematic viscosity and density of the oil samples increase by almost 50%. Fig. 7 shows the change in the density of oil samples from the well (No.0) and from the water surface (No.1a) upon irradiation with accelerated electrons.

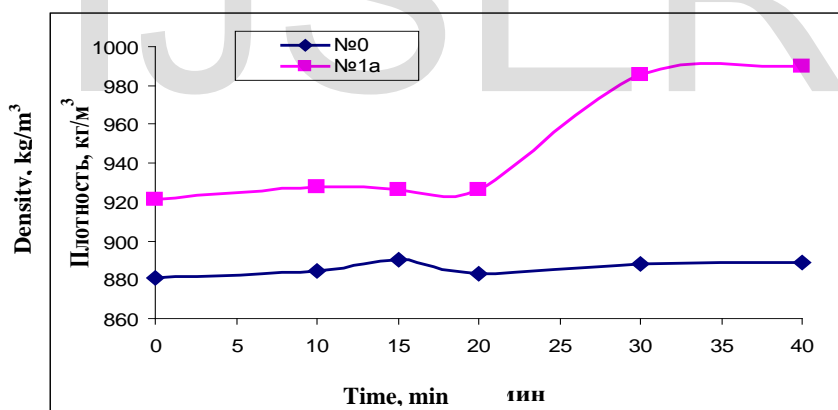


Fig. 7. Dependence of the density of the oil samples irradiated with accelerated electrons on the irradiation time.

As can be seen from Fig. 7, for non-irradiated samples the density of the oil from the water surface exceeds the density of the oil from the well. After irradiation a significant increase in the density of samples from the water surface is observed, which is due to polycondensation processes, while the density of the oil from the well is almost unchanged.

In determining the kinematic viscosity (Fig. 8 - a, b) the following phenomena were observed. Prior to irradiation, the viscosity of samples from the well (Fig. 8-a) is almost 5 times higher than the viscosity of the samples from the water surface (Fig. 8-b). This is due to the degradation processes occurring with oil on the water surface under the influence of various factors / 8 /. For a long time, being on the surface of the water, oil undergoes significant changes, namely, heavy fractions gravitate to the bottom or, being displaced to the shore, are bitumenized.

(a)

(b)

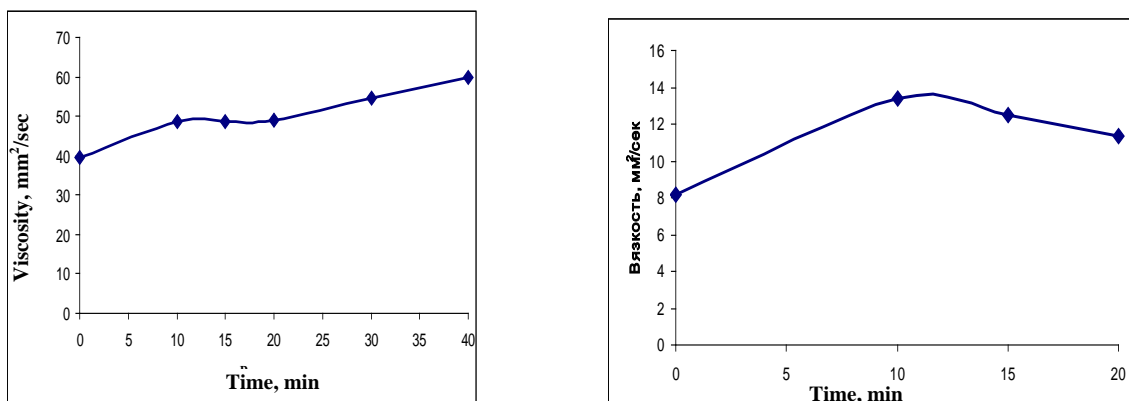


Fig. 8. Dependence of kinematic viscosity of the oil from well (a) and from the water surface (b) on the time of irradiation

Relatively light oil fractions remaining on the water surface are characterized by low viscosity (8 mm²/s). Under the influence of irradiation the viscosity of both samples increases as a result of polycondensation processes to almost 50%.

The results of IR-spectroscopy of the samples indicate changes in the structural-group composition of resinous oil fractions under the influence of irradiation. IR-spectra of irradiated samples of the resinous oil fractions taken from the water surface are presented in Figures 9-10.

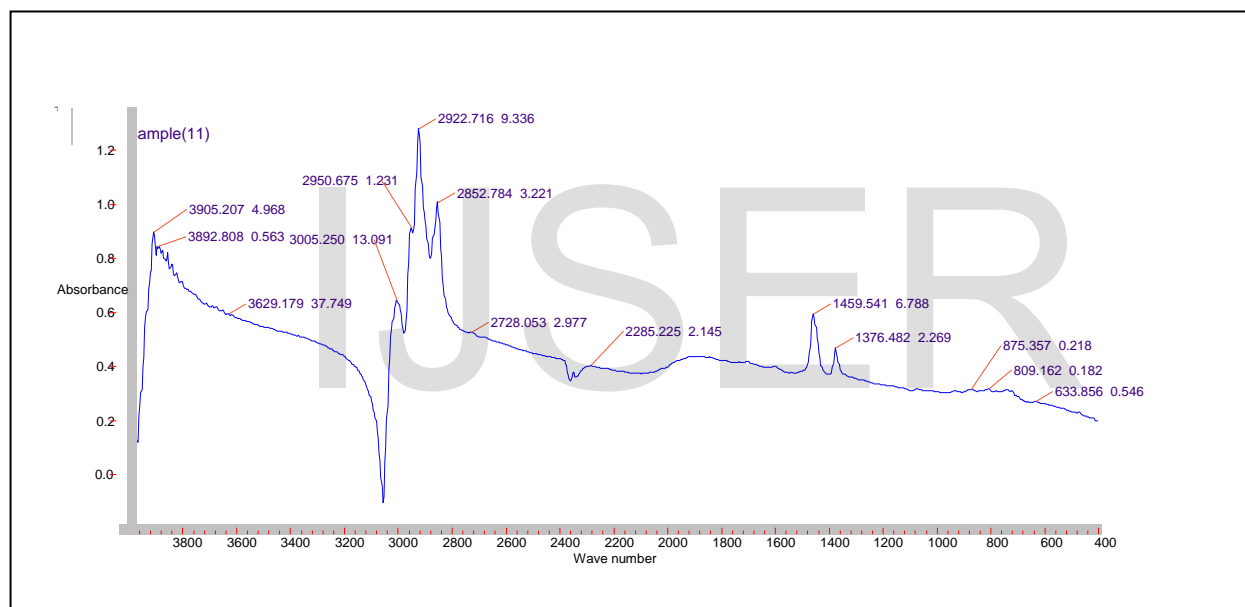


Fig. 9. IR-spectrum of the irradiated tar fraction of the petroleum from the water surface (D = 54.7 kGy)

As can be seen from Fig. 9, during 72 hours (54.7 kGy) of irradiation of the samples from the water surface, the IR-spectra show the highest intensity of absorption bands at 3005 cm⁻¹, corresponding to the polycondensation processes. After 144 hours of irradiation (109.5 kGy) of the samples, bands disappear indicating destructive processes.

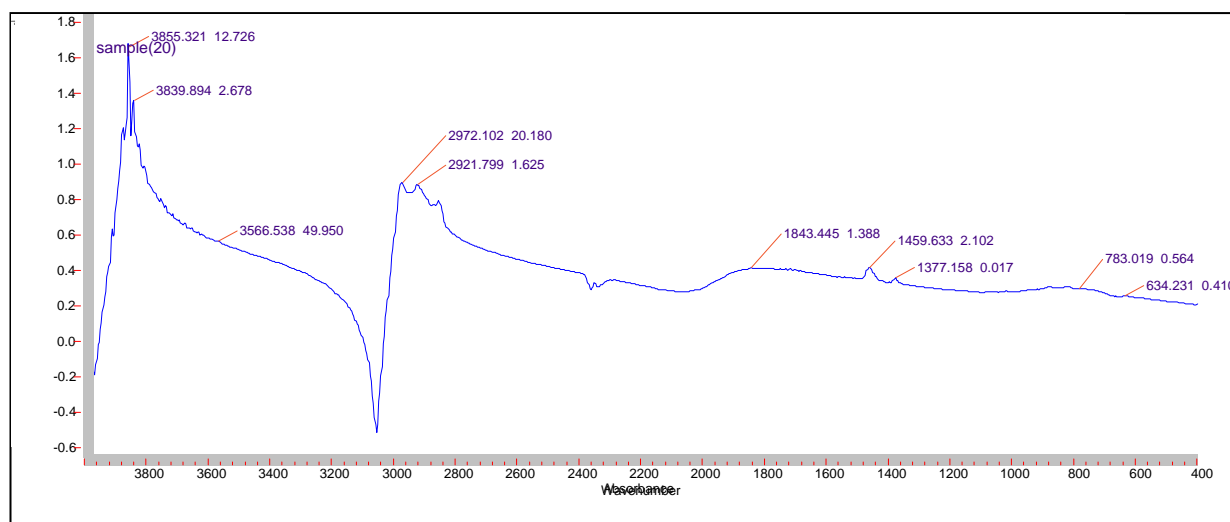
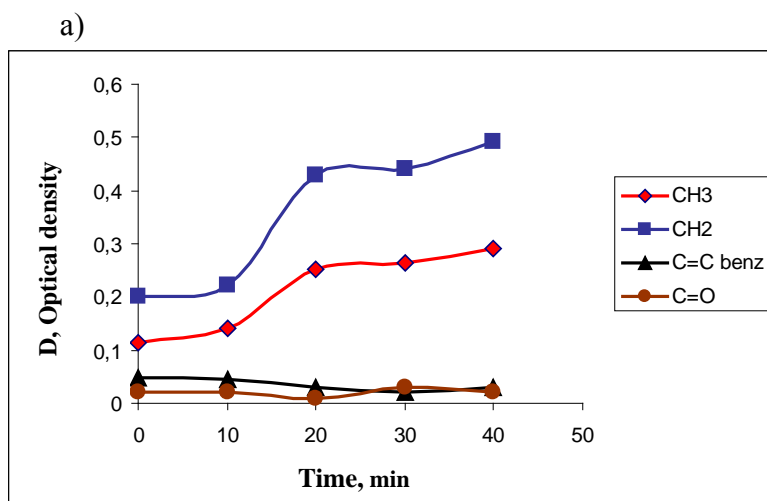


Fig. 10. IR-spectrum of the irradiated sample of tar fraction of the petroleum, taken from the water surface ($D = 109.5$ kGy)

Changes in absorption bands are observed in the 2920 and 2860 cm^{-1} range, which corresponds to stretching vibrations of $-\text{CH}_3$ and $-\text{CH}_2$ -groups, and this is due to the scattering of radiation energy in functional groups (Fig. 10). At the same time, the absorption bands of 1708 and 1603 cm^{-1} , corresponding to the $\text{C}=\text{C}$ bonds of the aromatic ring, and the carbonyl bonds of $\text{C}=\text{O}$ disappear in the IR-spectra after irradiation, which is apparently related to condensation of the aromatic rings after irradiation.

Compared to samples of resinous fraction, in the samples of the oil fractions there are no strong changes in the absorption bands corresponding to aromatic rings. In the composition of resinous fractions there are hydrocarbons in the form of condensed aromatic rings with a large number of paraffin side chains. In IR-spectra of samples of oil fraction after irradiation exists only a redistribution of intensity of $-\text{CH}_2$ - and $-\text{CH}_3$ groups.

From the IR-spectra of samples of the oil irradiated with accelerated electrons, at wavelength 1380 cm^{-1} ($-\text{CH}_3$) and 1480 cm^{-1} ($-\text{CH}_2$) the optical densities of the corresponding groups were determined. Dependences of the content of these groups on the irradiation time are shown in Fig. 11.



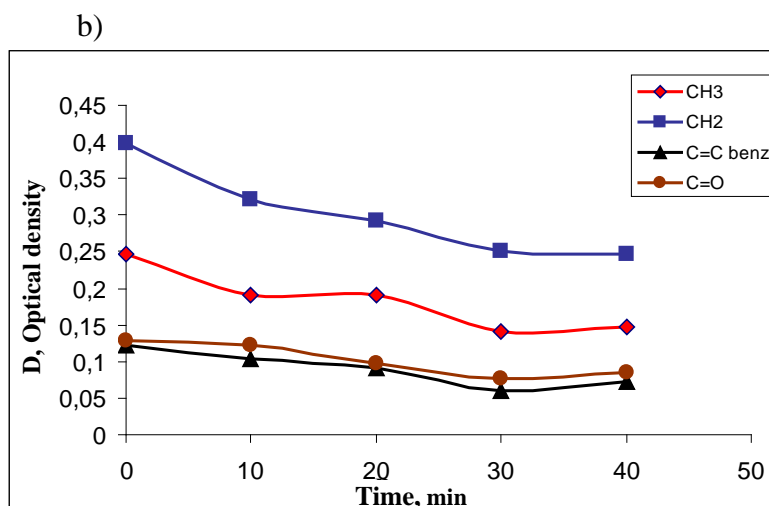


Fig. 11 Kinetic curves of the change in the optical density of various groups in the IR-spectra of the oil from the well (a) and from the water surface (b) at the radiolysis of oil.

As can be seen from Fig. 11 (a), the optical density corresponding to -CH₂- and -CH₃ groups in oil samples from the well as a result of irradiation increases, which is due to the formation of a liquid fraction from the fragmentation radicals rich in hydrogen. The content of oxygen containing and C=C-benzene groups decreases due to the binding of these groups and their transition upon irradiation into a heavy fraction. The pattern changes when the oil samples from the water surface are irradiated. In this case, oil is relatively homogeneous, and as a result of polycondensation processes it is condensed and accordingly the number of -CH₂- and -CH₃ groups decreases.

It is evident from the presented IR-spectra of the samples that during the long stay of oil on the water surface, as well as under the influence of radiation, the structural-group composition of the degraded oil changes.

CONCLUSION

1. Polycondensation processes occur in the environment due to oil degradation, which leads to a decrease in the amount of hydrocarbons and a corresponding increase of tar and asphaltene group fractions in its composition.

2. The effect of ionizing radiation (gamma radiation, accelerated electrons) leads to an increase in the viscosity and density of oil samples, which is the result of radiation-stimulated polycondensation processes.

3. For a long time, under the influence of natural factors, oil, being in the environment is degraded and structural changes take place in it.

The above data indicate that the study of changes in the oil from water surfaces under the influence of natural factors, as well as under the influence of radiation, knowledge of the composition of oil contamination in water bodies is one of the conditions for extracting additional oil resources from oily waste waters and for selection methods of water purification from oil products.

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