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RADIATION RESISTANCE OF TAR FRACTIONS OF BITUMINOUS OIL

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Abstract: The results of studies of radiation-chemical transformations of Balakhani bituminous oil of Azerbaijan are adduced. The IR spectra of initial and irradiated samples of tar fractions of bituminous oil are compared. The kinetics of radiation-chemical yields of gas products at the irradiation of bituminous oil and its tar fraction have been investigated. Irradiation were conducted in the gamma-ray source of isotope ^{60}Co at the dose rate of $P = 0.27 \text{ Gy/s}$ and absorbed doses $D = 5\text{-}163 \text{ kGy}$. It was found that in comparison with oil fraction, tar fraction of bituminous oil has a high resistance to radiation.

Keywords: Bituminous oil, tar fraction, γ -radiolysis, radiation resistance, IR- spectra, Chromatography, gas products.

1. Introduction

Petroleum fractions are widely used as a chemical components in the preparation of materials, in particular lacquers, paints and finish coatings. There are widespread use is bitumen, which is also a product derived from the crude oil. The main difference of bituminous oils from traditional low viscosity oil is low content of light fractions and high content of asphalt-tar components, which is the reason for their high density. Quality of bitumen intended for road construction, depending on the content of the various resinous substances.

One of the most important quality characteristics of materials intended for use in industrial production is their radiation resistance - the ability to withstand the effects of radiation and preserve the original properties [1]. From this point of view the study of radiation resistance of bituminous oils and derived petroleum fractions has a practical interest and in connection with this process of radiation-chemical transformations studied petroleum fractions require investigation of the mechanism occurring destructive and polycondensation processes during their radiolysis to obtain radiation-resistant products refining.

This paper presents the results of the study of radiation resistance of tar fraction of Balakhani bituminous oil of Azerbaijan. The content of tar-asphaltene compounds of oil was determined according to QOST 11858- 66.

2. Experimental

As the main indicators of the radiation resistance were studied kinetics of gases formation in the γ -radiolysis of fractions of heavy bituminous oil and change of concentrations of the various categories of oil compounds (total petroleum hydrocarbons, polycyclic aromatic compounds with the number of rings from 2 to 6, 16EPA, NPД) and also change of structural-group composition of liquid products of the radiolysis.

To study the material composition of the oil, namely oil- tar-asphaltenes fractions and the filtrate obtained after the precipitation of oil samples with n-heptane the asphaltene content was determined. The tar dissolved in the filtrate were adsorbed on silicagel and then stripped of alcohol-benzene mixture and quantified after distillation of the solvent is determined [2].

The source of ionizing radiation used isotope gamma radiation source ^{60}Co "MRX - γ - 30". The dose rate of the radiation source is 0.27 Gy/sec, the absorbed doses of 5 - 163 kGy. Gas

products were analyzed by gas chromatography, liquid products were identified by chromatography-mass spectrometry for the apparatus GC / MS Trace DSQ (Thermo Electron, Finnigan USA 2005). To determined the structural-group composition of the components used by Fourier IR- spectroscopy.

3. Results and discussion

Radiation resistance of organic materials made to determine the magnitude of the radiation-chemical yield of radiolysis products.

One of the essential indicators of radiation resistance of petroleum fractions is the radiation-chemical yields of gases in the processes of radiolysis [3]. They were identified and the rate of formation of radiation-chemical yields of gases formed as a result of γ -radiolysis oil fractions: H_2 , CO , CH_4 , C_2H_4 , C_2H_6 , ΣC_3-C_6 (Σ means the total number of gas yield with the same amount of carbon -simply, propane + propylene). As an example, figure 1 shows the kinetics of hydrogen formation in the radiolysis of bituminous oil fractions.

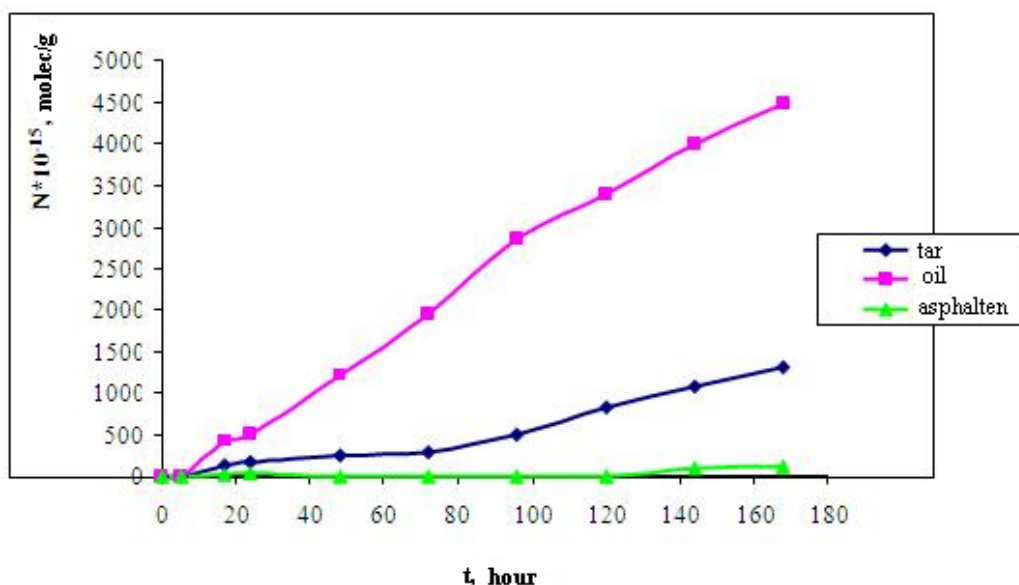


Fig.1 The kinetics of hydrogen formation in the radiolysis of oil, tar and asphaltene fractions of bituminous oil of Balakhani oil-field.

From the kinetics of formation of gas calculated mean values (at different times of exposure) radiation-chemical yields of gases (Table 1).

Table 1 The average values of radiation-chemical yields of gases

Fractions	G, molec/100 eV								
	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	ΣC ₃	ΣC ₄	ΣC ₅	ΣC ₆	Σ
Oil	0.452	0.014	0.011	0.0028	0.0068	0.0027	0.00072	0	0.49
Tar	0.092	0.005	0,0036	0.00082	0.0018	0.0015	0.0003	0.0056	0.11
Asphaltene	0.0195	0.0031	0.0048	0.0011	0.0043	0.003	0.0006	0	0.036

Σ - The amount of radiation-chemical yields of gas oil fractions in the radiolysis

As seen from the table, the most resistant to radiation during formation of gases have asphaltenes, tar and oils further. Radiation resistance of petroleum fractions according to the gas formation in the studied conditions is following ratio: asphalt: tar: oil = 13: 5: 1. A significant difference in the radiation resistance of these fractions is due to their composition and structure are very difference. So the content of the tar and asphaltene there are more conjugated double bonds and aromatic rings and heterocyclic condensed polycyclic component, that increases its resistance to radiation.

In order to determine the mechanism of physical and chemical processes occurring in the radiolysis of various factions of bituminous oil the radiation-chemical transformations of liquid fractions were studied.

Molecules of polycyclic components studied tars constructed from blocks in which include the identical structural types homo- and heteroaromatic rings, polinaftenoaromatic and polycyclic systems.

The results of the mass-spectrometric investigation of the aromatic part of Balakhani bituminous oil showed that in the all heavy fractions are present various PAHs - naphthalene, acenaphthene, phenanthrene, pyrene, chrysene and fluorite [4]. The kinetics of changes of concentrations of the compounds - total hydrocarbons, polycyclic aromatic (with the number of rings from 2 to 6), 16EPA, NPD and individual polynuclear hydrocarbons in the fractions by irradiation were experimentally established.

Fig. 2 shows the kinetics of changes in the concentration of polycyclic aromatic compounds (number of rings 2-6) in the radiolysis of tar fraction.

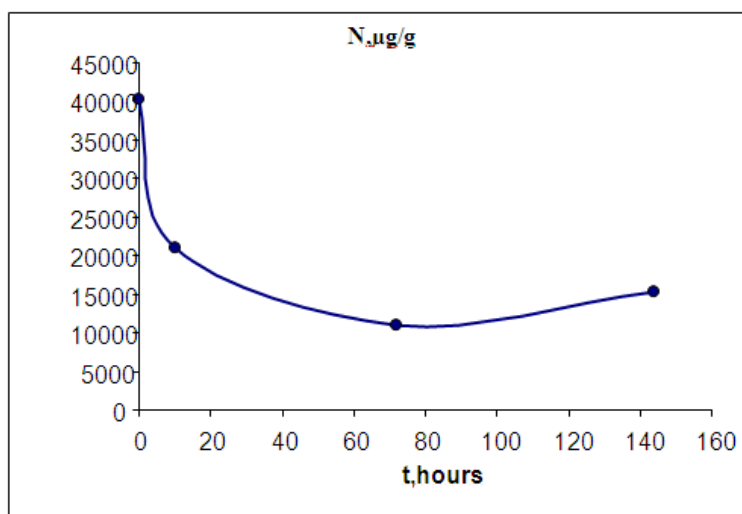


Fig. 2. Kinetics of changes in the concentration of 2-6 ring polycyclic aromatic hydrocarbons in the radiolysis of tar fraction of bituminous oil.

In contrast to oil fractions, which even in irradiating the samples to 163 kGy changes were not observed, radiolysis of petroleum tar leads to significant changes in the concentration of polycyclic aromatic compounds. This can be explained, apparently splitting and dehydration cyclic structures tar by means of radiation [5].

For example, in the range of absorbed dose of gamma irradiation of tar fraction to 163 kGy reduce concentrations observed following compounds: common hydrocarbons - 26%, 16 PAH - 78%, 2-6 aromatic rings - 70%, the phenanthrene-naphthalene-dibenzothiophene -71%.

The difference in change in concentration of these oil compounds is explained by characteristics of distribution of radiation energy between the polycyclic aromatic compounds. Aromatic hydrocarbons are very stable to the effects of radiation. This is due to the fact that the excitation energy originally arising in the primary act of ionization and excitation in any

particular fragment of the aromatic molecules due to the presence π -bonds are delocalized in the aromatic ring. As a result, none of the vibration degrees of freedom, does not get enough energy to break the chemical bond, and the gap of the ring becomes unlikely.

In order to explain the mechanism of these processes the kinetics of changes of concentrations of the individual components with fused aromatic rings in the oil at the radiation impact has been studied.

Fig. 3 shows the kinetics of changes the concentration of polynuclear compounds - fluorine, phenanthrene, chrysene in the tar composition.

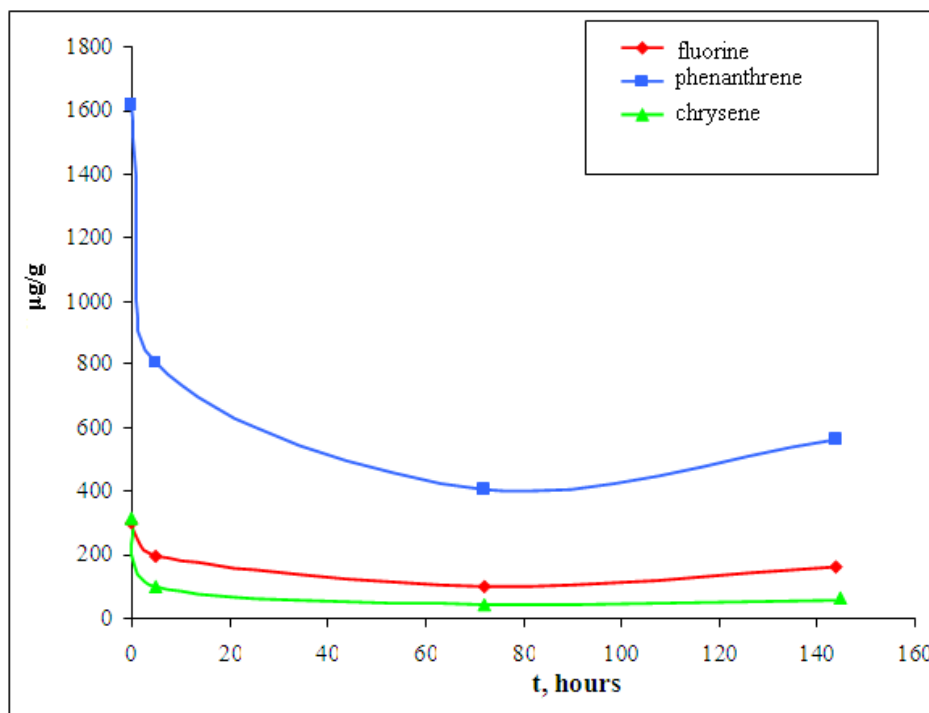


Fig. 3. Kinetics of changes of the concentration of fluorene, phenanthrene, and chrysene in the radiolysis of tar fraction of Balakhani bituminous oil.

The observed significant changes in the concentrations of these compounds in the radiolysis of the tar fraction as follows: fluorene - 50%, chrysene - 90%, fenantren - 69%.

The effects of gamma irradiation on the structural-group composition of tar fraction has been studied by the IR- spectroscopy [6]. In the Figure 4 shown IR- spectra of initial and irradiated samples of tar fraction.

The high content of aromatic rings in the tar fraction confirmed appreciable intensity band 1600 cm^{-1} . Analysis of IR - spectra showed that, under the influence of gamma-radiation observed changes in the intensity of the absorption bands at wavelengths $2852 - 2964\text{ cm}^{-1}$, responsible for the valence fluctuations groups $=\text{CH}_2$ and $-\text{CH}_3$ corresponding fused aromatic rings, and these strips deformation vibrations groups at $1376 - 1457\text{ cm}^{-1}$. The reduction of intensities of the absorption bands of deformation vibrations of $-\text{CH}_3$ at wavelength 1457 cm^{-1} , and deformation vibrations of $-\text{CH}$ mono- aromatic rings and substituted polynuclear structures at a wavelength 811 cm^{-1} after irradiation happens due to dissipation of radiation energy in the functional groups.

Furthermore, in the tar fraction 1707 cm^{-1} - the band intensity responsible for stretching vibrations $\text{C} = \text{C}$ bond of the benzene (aromatic) ring, decreases under the influence of irradiation, due to the increasing degree of condensation of aromatic rings.

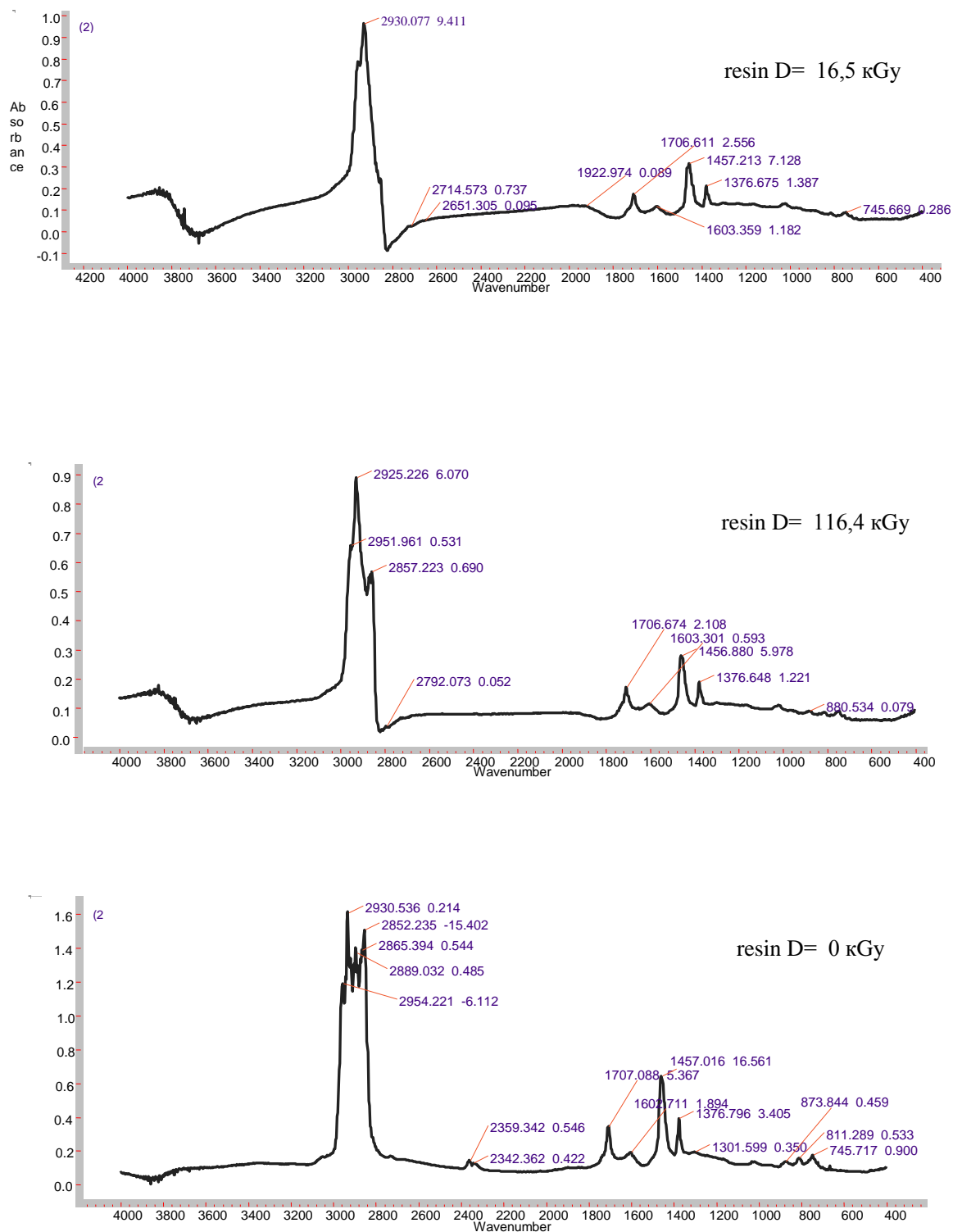


Fig. 4. IR spectra of the initial and irradiated samples of tar fraction of bituminous oil.

Thus, the absorption spectra of the tar obvious that their containing saturated hydrogen carbon atoms, aromatic ring, carbonyl group. The specific properties of the tar, compared with oil fractions is increased content of the multiblock molecules with a large number of aromatic rings [7]. High intensity of the band 1380 cm^{-1} corresponding to the methyl groups, indicating a

relatively high molecular branching. The hydrocarbon tar are in the form of aromatic rings with more paraffinic side chains. They are flat fused systems containing 5-6 aromatic rings, naphthenic and heterocyclic structure connected means aliphatic structures. In aromatic compounds in the transition from mono to poly-cyclic aliphatic chains are shortened. The tar are macromolecular organic compounds and heterocyclic structure has a high degree of condensation interconnected aliphatic chains.

4. Conclusion

In recent years there has been an increase of heavy oil production, natural bitumen and growing interest in their high molecular weight component -tar and asphaltenes because of their potential qualities as a raw material products. Face the task of control to optimize technological processes of preparation, transportation and refining.

The effect of gamma radiation on the fractions is heavy oil bitumen, oils, tars and asphaltenes.

The experimental data showed that the radiation resistance of petroleum fractions associated with their structural-group composition, and increased radiation resistance observed in tar fractions of oil, as a complex system of hydrocarbons of various structures, requires a detailed study of radiation-induced transformations of petroleum fractions, the establishment of the mechanism occurring destructive and polycondensation processes at its radiolysis. This mechanism explains the radiation-chemical transformations of these aromatic polyconjugated systems. The high radiation resistance feature of all cyclic compounds with unsaturated conjugated bonds. Irradiation molecules containing a benzene ring, the unpaired electron is located on the ring. In such systems with condensed aromatic rings distribution of absorbed radiation energy is a result of delocalization of π -electrons, which leads to the dissociation process and thereby expression of the radiation resistance [8].

It was found that the gamma-radiolysis of petroleum fractions bituminous oil at values of absorbed radiation dose to the $D = 160$ kGy only in fractions of tar was observed a decrease in the concentrations of 2-6- ring polycyclic aromatic compounds with radiation-chemical yields 10^{-2} - 10^{-3} molecules/100 eV because of an increase in polycondensation processes, increases the radiation resistance of the oil fractions. The absorbed dose range studied the compounds of hydrocarbon oil fractions do not undergo changes.

A significant difference in radiation resistance due to the presence of oil fractions in the composition of the fractions of tar compounds with condensed polycyclic structures. Greater stability to radiation aromatics condensed structure compared with hydrocarbons of different structure determined by the arrangement of the alkyl chains on the aromatic ring. More stable to the action of radiation is composed of polynuclear aromatic hydrocarbon fraction of bituminous oil that can serve as a basis to recommend this class of compounds for use as a raw material in the production of building materials, as well as hydraulic fluids and lubricants even working under the action of radiation (nuclear reactors, radionuclide installation, electron accelerators, etc).

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РАДИАЦИОННАЯ СТОЙКОСТЬ СМОЛИСТОЙ ФРАКЦИИ БИТУМИНОЗНОЙ НЕФТИ

Н.Г. Гулиева, Н.А. Ибадов, С.Ф. Алиева-Чичек, С.М.Алиев

Резюме: Приведены результаты исследований радиационно-химических превращений смолистой фракции битуминозной нефти Балаханского месторождения Азербайджана. Сопоставлены ИК-спектры исходных и облученных образцов смолистой фракции, Определены концентрации входящих в состав смолистой фракции полиароматических соединений, кинетика радиационно-химических выходов газовых продуктов радиолитических фракций нефти. Исследования проводились на гамма-источнике при мощности дозы $P=0,27$ Гр/с и поглощенных дозах $D=5-163$ кГр. Установлено что в сравнении с другими фракциями, смолистая фракция битуминозной нефти обладает повышенной радиационной стойкостью.

Ключевые слова: Битуминозная нефть, радиолит, смола, радиационная стойкость.

BİTÜMLÜ NEFTİN QƏTRAN FRAKSİYASININ RADİASİYAYA DAVAMLIĞI

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Xülasə: Azərbaycanın Balaxanı mədəninədən götürülmüş bitumlu neftin qətran fraksiyasının radiasiya-kimyəvi çevrilmələri tədqiq edilmişdir. Qətran fraksiyasının şüalanmış və şüalanmamış nümunələrinin İK-spektrləri müqaisə olunmuş, radioliz nəticəsində alınmış qazların kinetikasi, tərkibində olan poliaromatik birləşmələrin qatılıqları müəyyən olunmuşdur. Tədqiqatlar qamma şüalanma mənbəyində ($P=0.27$ Gr/s) udulan dozanın $D= 5-163$ kGy intervalında aparılmışdır. Müəyyən edilmişdir ki, neftin qətran fraksiyası digər fraksiyalarla müqaisədə daha yüksək radiasiya stabilliyinə malikdir.

Açar sözlər: Bitumlu neft, radioliz, qətran, radiasiya stabilliyi.