

PACS: 82.20.Wt

## RADIATION STABILITY OF BITUMINOUS OILS AND ITS TAR FRACTION

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**Abstract:** The radiation-chemical transformation of bituminous oil from Balakhani oil deposit and its tar fraction have been studied.

The mechanism of radiation-chemical transformation of bituminous oil and its tar fraction have been established by methods of mass-spectrometry, IR-spectroscopy and chromatography. It has been shown that bituminous oils has a high radiation stability at the temperature under 50<sup>0</sup>C. The ratio of radiation stabilities of oil and tar fraction is 4 : 1. The radiation-chemical yield of decomposition of polycyclic aromatic compounds in the tar fraction changes in limits 10<sup>-2</sup>-10<sup>-3</sup>.

It was concluded that high radiation stability of bituminous oil and its tar fraction, allows to use them as a initial raw material for production of the hydroisolation material, which can be used in conditions of influence of radiation.

**Keywords:** *bituminous oils, tar fraction,  $\gamma$ -radiation, gas, PAH, polycondensation*

### 1. Introduction

In the context of the limited reserves of conventional crude oils, high rate of oil consumption and the price appreciations in the world market, pilot commercial development on the use of bituminous oils are conducted. Bituminous oils (BO) are suitable for power-generating fuel production, road bitumen, different dyestuff, plastics, surfactants, lubricants or their components, and other building and finishing materials [1].

At the same time, their recycling is power-consuming and multi-stage process that requires the use of extreme conditions for maximum recovery of valuable components from the BO [2].

The use of bituminous oils and their tar fractions as raw material for the production of building materials used in conditions of ionizing radiation also requires the study of their radiation stability [3-4].

This paper presents the results of the study of the radiation chemical transformations of bituminous oils and their tar fractions.

### 2. Experimental

The investigated bituminous oil have been taken from the Kirmaky oil field with the depth of over 100 m. The tar fraction has been separated from bituminous oil in accordance with the GOST-11858-66.

As a source of ionizing radiation, the isotopic source of  $\gamma$ -radiation <sup>60</sup>Co “MRX- $\gamma$ -30” has been used. The power of the radiation source is 0.27 Gy/sec, and the studies have been carried out at the range of absorbed dose of 34,5-216 kGy .

To determine the structural-group composition of the components, the IR spectroscopy has been used by application of the Spectrophotometer M-80. The gas products have been analyzed by the gas chromatography method. Liquid products have been identified by the IR-spectrometry and chromato- mass-spectrometry apparatus GMS Trace DSQ (Thermo Electron, Finnigan, USA, 2005).

### 3. Results and discussions

In determining the radiation stability of bituminous oils and their tar fractions, one of the important indicator is the study of the kinetics of gas generation in the process of their radiolysis [4-5].

The generation rate and the radiation-chemical yields formed in the result of  $\gamma$ -radiolysis of bituminous oil and its tar the gases ( $H_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $\Sigma C_1-C_7$ ) have been identified. The samples of the studied oils have been exposed to radiation in vacuum and air conditions at wide time intervals.

As an example, the kinetics of generation of  $H_2$  from BO is shown in Figure 1.

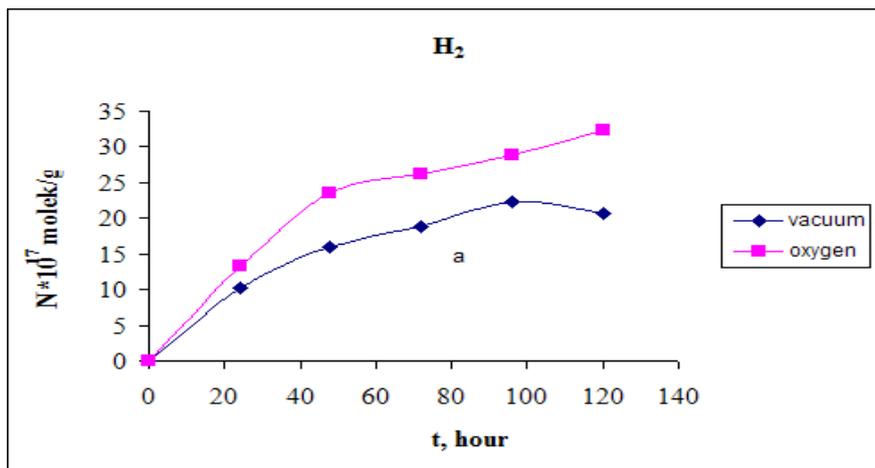


Fig.1. Kinetics of formation of  $H_2$  in the radiolysis of bituminous oil in the vacuum and oxygen medium

The kinetics of formation of gases at the radiolysis of tar fraction shown in fig. 2-3.

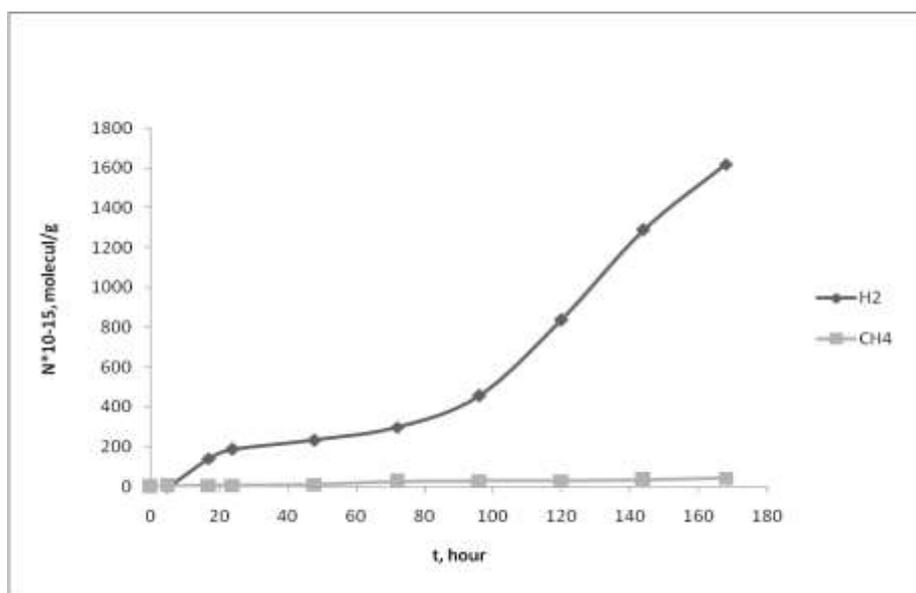


Fig.2. Kinetics of formation of  $H_2$  and  $CH_4$  in the radiolysis of tar fraction of bituminous oil in the vacuum

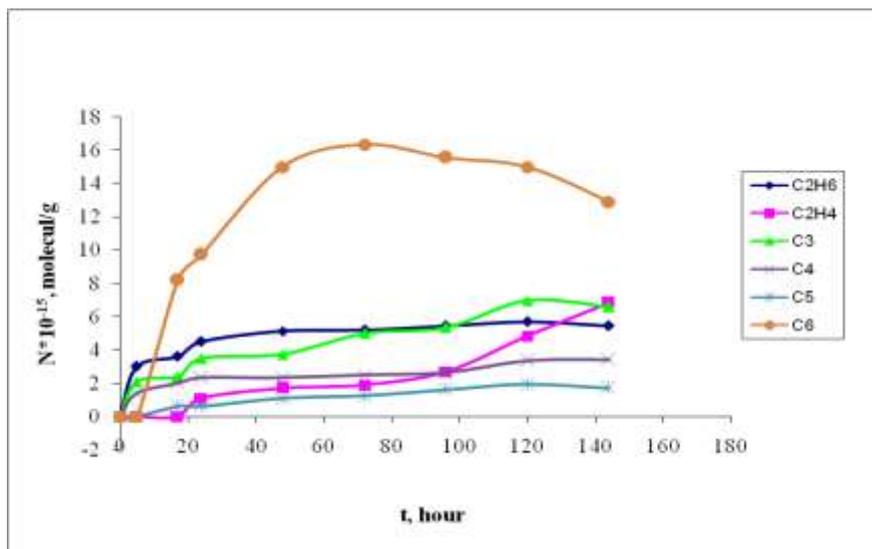


Fig. 3. Kinetics of formation of hydrocarbons of C<sub>2</sub>-C<sub>6</sub> in the radiolysis of tar fraction of bituminous oil in the vacuum

The table 1 shows the average values of the radiation-chemical yields of gases at  $\gamma$ -irradiation of bituminous oil and its tar fraction. Fig. 2-3 shows the kinetic gas generation curves in the tar fraction of Balakhani oil. Compared with the data in Figure 1, it can be seen that the average value of radiation-chemical hydrogen yield in tar is 4 times lower than in crude oil. The yields of other gases in the oil and its tar fraction are also shown in the table. With the exception of the formation of benzene, in all cases, the radiation-chemical decay with the generation of light products in the oil is faster than in the tar fraction. Due to the fact that the tar fraction is rich in aromatic compounds, the benzene formation is faster than in the oil.

Table 1 The average values of the radiation-chemical yields of gases at  $\gamma$ -irradiation of bituminous oil and its tar fraction

Bituminous oil									
H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	$\Sigma$ C <sub>3</sub>	$\Sigma$ C <sub>4</sub>	$\Sigma$ C <sub>5</sub>	$\Sigma$ Gas
0,256	0,057	0,234	0,0122	0,0052	0,00204	0,00432	0,0122	0,0252	0.608
Tar of bituminous oil									
0,092	0,043	0,005	0,0036	0,00082	0,0018	0,0015	0,0003	0,0056	0.153
Goil/Gtar									
2.7	1.3	46.8	3.4	6.3	1.1	2.88	40.6	4.5	4

As seen in the table data the total yield of gaseous products don't exceeds  $\Sigma$ Gas < 0.60 molec/100 eV from BO and  $\Sigma$ Gas < 0.15 molec/100 eV from tar, that connected with high radiation stability of BO, especially its tar fraction.

The effect of the  $\gamma$ -irradiation on the structural-group composition of BO has been studied. By IR spectroscopic analysis, the structural-group composition of bituminous oil

samples has been identified [6]. From the comparative analysis of the IR spectra of the original and irradiated under different conditions of  $\gamma$ -irradiation the BO samples, it follows that in bituminous oil (original sample) occur intense absorption bands at  $740\text{ cm}^{-1}$ , which cause pendulum oscillations of  $\text{CH}_2$  groups, as well as the deformation bands at  $1380\text{ cm}^{-1}$  and the valence vibrations at  $2860, 2960\text{ cm}^{-1}$  characteristic to the  $\text{CH}_3$  methyl groups. The absorption bands of bending at  $1460\text{ cm}^{-1}$  and valence vibrations at  $2840, 2920\text{ cm}^{-1}$  correspond to the  $\text{CH}_2$  methylene groups. The spectrum contains out-of-plane ( $960, 995\text{ cm}^{-1}$ ) and plane ( $905\text{ cm}^{-1}$ ) deformation and valence ( $1640\text{ cm}^{-1}$ ) vibrations, which are characteristic, for the groups of  $=\text{CH}_2$  and  $\text{C}=\text{C}$  bonds of unsaturated (alkene) hydrocarbons, respectively. The spectrum contains the absorption bands with the peak values at  $920, 980\text{ cm}^{-1}$ , responsible for the deformation fluctuations in  $\text{C}=\text{C}$ -bonds of unsaturated hydrocarbons. Also, absorption bands with the peak value  $805$  and  $880\text{ cm}^{-1}$  occur, which correspond to non-planar bending vibrations of substituted benzene (aromatic) rings and the absorption band with a maximum at  $1605\text{ cm}^{-1}$  and cause the valence fluctuations -  $\text{C}=\text{C}$  bonds of benzene (aromatic) rings. The absorption bands at  $1720\text{ cm}^{-1}$  complies with the carbonyl group  $\text{C}=\text{O}$ . In addition, absorption bands occur in the realm of the  $1020\text{-}1160\text{ cm}^{-1}$  with peaks at  $1025, 1070, 1120, 1160\text{ cm}^{-1}$ , corresponding to the oxygen group ( $\text{C}-\text{O}$ -,  $\text{C}-\text{O}-\text{O}$ ,  $\text{O}-\text{H}$ ).

The comparison of the IR spectra of the source and irradiated in air absorbed doses of the  $129.6$  and  $216\text{ kGy}$  BO samples shows that the intensity of the absorption bands, which cause paraffin, unsaturated, and oxygen-containing compounds significantly decrease in the following sequence: initial > air-irradiated dose of  $129.6\text{ Gy}$  > air-irradiated dose of  $216\text{ kGy}$ .

Similar results have been obtained for the vacuum-irradiated samples: initial > vacuum-irradiated dose of  $129.6\text{ Gy}$  > vacuum-irradiated dose of  $216\text{ kGy}$ .

The spectroscopic studies of bituminous oil samples irradiated in air and in vacuum are conducted. In the IR spectra of the  $\gamma$ -rays-irradiated BO samples, the optical density of some groups has been determined. The dependency of the content of these groups on the irradiation time is shown in the Table 2 and Table 3.

Table 2 IR spectroscopic analysis of the air-irradiated samples

Name	$D_{1380}(\text{CH}_3)$	$D_{1460}(\text{CH}_2)$	$D_{1610}(\text{C}=\text{C}$ benz.rings)	$D_{1610}(\text{C}=\text{C}$ unsat.H/C)	$D_{1720}(\text{C}=\text{O})$
Initial	0.74	0.97	0.14	0.13	0.21
Air, $129,6\text{ kGy}$	0.23	0.39	0.06	0.06	0.05
Air, $216\text{ kGy}$	0.20	0.34	0.05	0.05	0.04

Table 3 IR spectroscopic analysis of the vacuum-irradiated samples

Name	$D_{1380}(\text{CH}_3)$	$D_{1460}(\text{CH}_2)$	$D_{1610}(\text{C}=\text{C}$ benz.rings)	$D_{1610}(\text{C}=\text{C}$ un sat.H/C)	$D_{1720}(\text{C}=\text{O})$
Initial	0.74	0.97	0.14	0.13	0.21
Vacuum $129,6$ $\text{kGy}$	0.44	0.84	0.09	0.08	0.09
Vacuum $216\text{ kGy}$	0.32	0.60	0.07	0.05	0.06

Consequently, it can be assumed that as a result of irradiation of the samples both in air and in vacuum, occurs a decrease of optical density both in aliphatic groups  $-\text{CH}_2-\text{CH}_3$  and the double bonds  $\text{C}=\text{C}$ . This shows that the formation of hydrogen and hydrogen-containing gases is the result of the decay in the  $-\text{CH}_2-\text{CH}_3$  groups, while the decrease in density of double bonds occurs due to radiolytic breakdown. Depending on the absorbed dose, the high concentration of broken double bonds may cause polycondensation processes. In these circumstances, the bituminous oil obtains high radiation resistance and can be used as original stock in the production of construction materials with specified properties to use in extreme conditions.

Fig. 4 shows the mass spectra of the initial and irradiated bituminous oil samples.

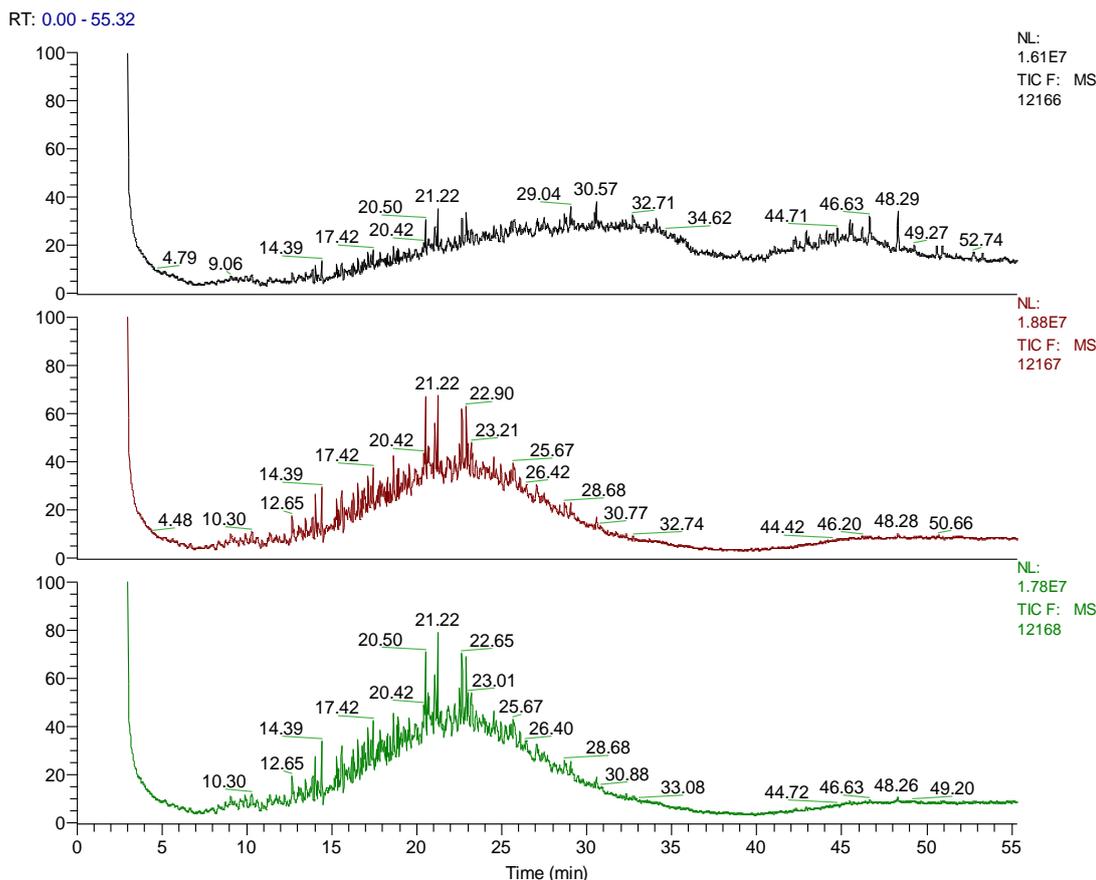


Fig. 4 Mass spectra of the initial (1) and vacuum-irradiated (2) and air-irradiated (3) BO samples,  $D=172.8$  kGy.

By the mass spectra, the components in the initial and irradiated bituminous oil samples have been identified. The identified oil components are given in Table 4.

As can be seen from the mass-spectra, both the air and vacuum irradiation, leads to increase in the content of relatively low-molecular hydrocarbons  $\text{C}_{10}-\text{C}_{13}$ , while the content of high-molecular-weight components of bituminous oil decreases under irradiation. This is explained by the characteristics of the radiation effects on polycyclic aromatic compounds with functional groups. At relatively low irradiation dosage ( $172.8$  kGy), the destructive processes in the polycyclic structures lead to the formation of low molecular weight compounds, which can be observed in the mass spectra. The breakage of high-molecular BO fractions leads to reduction of its concentration, as also seen in mass spectra.

Table 4 The identified bituminous oil components

Time, min	Components	Chemical formula
12.65	Naphthalene, decahydro-	C <sub>10</sub> H <sub>18</sub>
13.46	Adamantane	C <sub>10</sub> H <sub>16</sub>
14.03	trans-Decalin, 2-methyl-	C <sub>11</sub> H <sub>20</sub>
14.39	trans-4a-Methyl-decahydronaphthalene	C <sub>11</sub> H <sub>20</sub>
15.61	Decalin, anti-1-methyl-, cis-	C <sub>11</sub> H <sub>20</sub>
17.13	Cyclohexane, 1,2-diethyl-3-methyl-	C <sub>11</sub> H <sub>22</sub>
17.42	Cyclopentane, 1-butyl-2-pentyl-	C <sub>14</sub> H <sub>28</sub>
18.63	5,6,7,8,9,10-Hexahydrobenzocyclooctene	C <sub>12</sub> H <sub>16</sub>
20.5	Decahydro-4,4,8,9,10-pentamethylnaphthalene	C <sub>15</sub> H <sub>28</sub>
21.22	1H-Indene, octahydro-2,2,4,4,7,7-hexamethyl-, trans-	C <sub>15</sub> H <sub>28</sub>
21.45	2-Oxabicyclo[4.4.0]dec-3-en-10-ol, 5-methylene-1,3,7,7-tetramethyl-, acetate	C <sub>16</sub> H <sub>24</sub> O <sub>3</sub>
22.65	Naphthalene, 2,3,6-trimethyl-	C <sub>13</sub> H <sub>14</sub>
22.9	Naphthalene, 1,6,7-trimethyl	C <sub>13</sub> H <sub>14</sub>
23.01	Azulene, 4,6,8-trimethyl-	C <sub>13</sub> H <sub>14</sub>
23.47	9-Methoxycalamenene	C <sub>16</sub> H <sub>24</sub> O
24.51	Fluoroacetic acid, dodecyl ester	C <sub>14</sub> H <sub>27</sub> FO <sub>2</sub>
24.95	Azulene, 7-ethyl-1,4-dimethyl-	C <sub>14</sub> H <sub>16</sub>
25.73	(2,3-Diphenyl-aziridin-1-yl)-(1-methyl-7-oxa-bicyclo[4.1.0]hept-2-ylidene)-amine	C <sub>21</sub> H <sub>22</sub> N <sub>2</sub> O
26.42	1,1'-Biphenyl, 2-ethyl	C <sub>14</sub> H <sub>14</sub>
29.04	Anthracene, 2-methyl-	C <sub>15</sub> H <sub>12</sub>
30.57	Phenanthrene, 2,7-dimethyl-	C <sub>16</sub> H <sub>14</sub>
42.9	Cholestane	C <sub>27</sub> H <sub>48</sub>
43.7	15-Isobutyl-(13 $\alpha$ H)-isocopalane	C <sub>24</sub> H <sub>44</sub>
44.71	Stigmastane	C <sub>29</sub> H <sub>52</sub>
	28-Nor-17 $\alpha$ (H)-hopane	C <sub>29</sub> H <sub>50</sub>
48.29	5-(7a-Isopropenyl-4,5-dimethyl-octahydroinden-4-yl)-3-methyl-pent-2-enal	C <sub>20</sub> H <sub>32</sub> O
50.56	Lup-20(29)-en-28-ol	C <sub>30</sub> H <sub>50</sub> O

This dependence of the BO content on the absorbed dose is also associated with the structural features of BO [8]. Apparently, higher molecular-weight fractions are in branched functional groups, and when exposed to radiation this fraction resolves more than low-molecular-weight ones.

The tar fractions of bituminous oils are an important component of it, and this fraction can generate in a large measure during thermal processing of crude oils. Therefore, the study of radiation-chemical transformations of this fraction is of separate interest. The patterns of the conversion of the different hydrocarbon groups in radiation and chemical exposure have been studied. Such oil groups are usually separated when considering the environmental impacts of oils, as they have similar environmental effects. These groups are: total petroleum hydrocarbons, non-resolvable systems of oil hydrocarbons, polycyclic aromatics compounds with the rings number of 2-6, polycondensed systems, 16EPA polycyclic aromatic compounds, NFD-naphthalene-phenanthrene-dibenzothiophene. The concentration changes patterns of these compounds groups when exposed to radiation have been identified.

In ecological perspective, the occurrence of the polycyclic aromatic hydrocarbons in the oil and its fractions and their conversion at the radiation and chemical exposure are of particular interest. Fig. 4 shows the shifts in the concentration of general hydrocarbon tar fraction with exposure to gamma-irradiation. It can be seen that at the irradiation of 163 kGy (144 hours), the concentration decrease from 567 mg/g to 412 mg/g, which is apparently due to the behaviour of polycondensation processes.

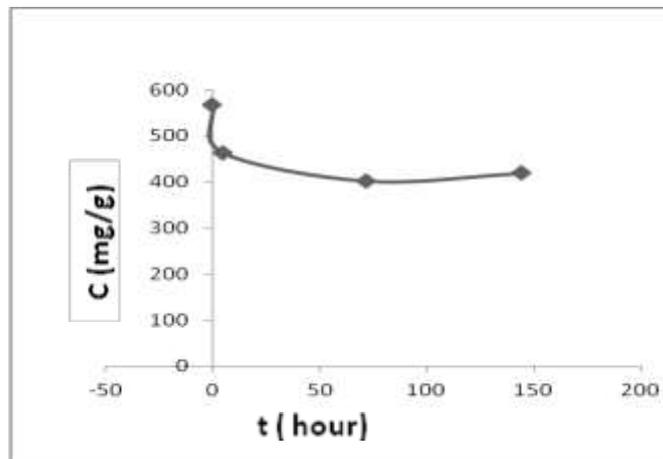


Fig. 4 The dependency of the concentration of the total hydrocarbons in tar fraction on the irradiation time.

Experimentally, the kinetics of changes in the concentration generated in fractions under the influence of the irradiation of compounds - total hydrocarbons, polycyclic aromatics compounds with the number of oscillations from 2 to 6, 16 PAH, naphthalen-phenanthrene-dibenzothiophenesystems in the tar fraction. So, in the range of absorbed dose of gamma irradiation up to 163 kGy, the following decreasing have been observed in concentrations of tar compounds: general hydrocarbons - 27% , 16EPA - 64%, 2-6PAH - 59%, NPD -61%.

The difference in the concentrations changes in these fractions of the oil can be explained by the peculiarities of radiation energy distribution in the composition of polycyclic aromatic compounds

Fig. 5 shows the dependency of the concentration of the three groups of polycyclic aromatic hydrocarbons on the irradiation time.

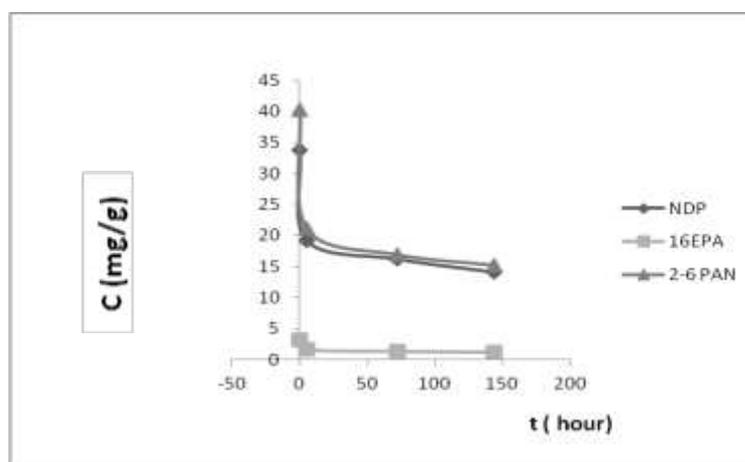


Fig.5 The dependency of the concentration of the three groups of polycyclic aromatic hydrocarbons on the irradiation time

The figure shows that for all groups of polycyclic aromatic hydrocarbons (PAH), the reduction of the concentration on the irradiation time is observed. The preliminary estimates of radiation-chemical yield of the degradation of individual PAHs have been made, which equals to  $G(-) = 0.00137$  molec./100 eV for pyrene,  $G(-) = 0.0117$  molec./100 eV for anthracene and  $G(-) = 0.0037$  molec./100 eV for naphthalene. This testifies the high radiation stability of PAHs included in the tarry compound of the oil. The difference in radiation stability of PAH due to the number of aromatic nuclei, as well as the structure of the compounds.

#### **4. Conclusion**

The effect of gamma radiation on the fractions of heavy bituminous oils and their tars has been studied. With respect to the gas formation processes, the radiation stability of the studied fractions of bituminous oils changes in the following ratio: tar/oil = 4/1. The obtained experimental data shows that the radiation resistance of petroleum fractions is associated with their structural group composition and concentration in their composition of polycyclic aromatic compounds. In systems with condensed aromatic rings, the distribution of absorbed radiation energy is a result of delocalization of  $\pi$ -electrons, which leads to dissipation processes and the occurrence of radiation stability.

It's been found that at the gamma-irradiation of petroleum fractions in bituminous oil the value of up to 160 kGy absorbed radiation dose, in the tar fractions the decrease in the concentrations of all PAHs, i.e. 16EPA, 2-6-ring polycyclic aromatic compounds, NPD with radiation yields of  $10^{-2}$ - $10^{-3}$  molec./100 eV is observed. This is due to ongoing polycondensation processes that increase the radiation stability of the tarry fractions in the oil.

The high radiation stability of bituminous oils allows the use of it as a raw material for water proofing material, applied in terms of radiation influence.

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