

Influence of Radiation on Resinous Fractions of the Degraded Oil

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Abstract: *The process of formation of gases under the influence of gamma radiation from oil and degraded in water oil fractions has been investigated at $D = 0-110$ kGy dose at temperature $35-40$ °C. As gas products H_2 , CO , CH_4 , C_2H_6 , C_2H_4 , ΣC_3 , ΣC_4 and ΣC_5 gases have been identified.*

Key words. *Tar, degradation, oil, ecology*

Oil products today occupy one of the leading places among the most common sources that pollute not only land, but also water. According to UNESCO statistics, all chemical compounds that are derived from petroleum or petroleum gases are classified as the most dangerous environmental pollutants on the planet [1].

Oil trapped in groundwater, begins to destroy their normal composition changing the ratio of mineral components. The ingress of petroleum products into drinking water is a major risk factor in the development of cancer. That is, oil is capable of damaging both to the person himself and the environment, so the purification of water from oil products is simply necessary for modern society.

Purification of water from petroleum products can consist of physical, chemical, mechanical and biological methods. The use of each method depends on the scale and source of pollution, the volume of oil emissions. 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 study of changes in 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 oil-containing wastewaters and for selecting methods for purifying water from oil products.

To assess the role of radiation in the process of detecting oil on the surface of water bodies and to identify the possibilities of using radiation-chemical technology in cleaning water from oil contamination, some regularities in the radiation-chemical transformations of resinous oil fractions after a long stay on the water surface have been investigated [2].

The studies were carried out for samples of Surakhani oil of Azerbaijan, taken from the well, from the water surface under the influence of environmental factors and ionizing radiation. The contents of the main components - hydrocarbons, resins and asphaltenes were determined in isolated oil samples in accordance with GOST 1158-66.

The source of ionizing radiation was an isotope gamma source of ^{60}Co -MPX- γ -30 with a dose rate of $P = 0.21$ Gy/s. Absorbed doses varied in the interval $D = 3.8 - 110$ kGy. Gas products were analyzed by gas chromatography on devices "AgilentGC 7890 A" and "Gasochrom-3101".

The formation of gases

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35-40 °C. As gas products H₂, CO, CH₄, C₂H₆, C₂H₄, ΣC₃, ΣC₄ and ΣC₅ gases have been identified.

Average radiation-chemical yields of gases are shown in Table 1.

Table 1

Radiation-chemical yields of gases (molec/100 eV)

	H ₂	CO	CH ₄	C ₂ H ₄	C ₂ H ₆	ΣC ₃	ΣC ₄	ΣC ₅
Resinous fraction of crude oil	0,98	-	0,036	0,05	0,045	0,01	0,01	0,011
Resinous fraction of degraded oil	0,14	0,043	0,012	0,015	0,26	0,01	0,008	0,0095

As seen, the largest radiation-chemical yield ($G_{H_2} = 0.94$ molec/100 eV) has hydrogen, and 90% of the resulting gases consist of hydrogen, and the radiation-chemical yields of gases in residual fractions in the degraded oil are much smaller than for crude oil. This is due to the high concentration of high radiation-resistant polycyclic compounds in the resinous fraction.

The formation kinetics of gases are shown in Figures 1-7.

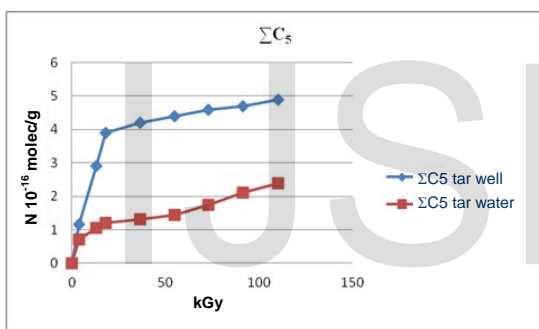


Fig. 1. The formation kinetic of ΣC₅ hydrocarbons in the radiolysis of resinous fraction of crude oil and degraded oil; P = 0.22 Gy/s, T = 30 °C.

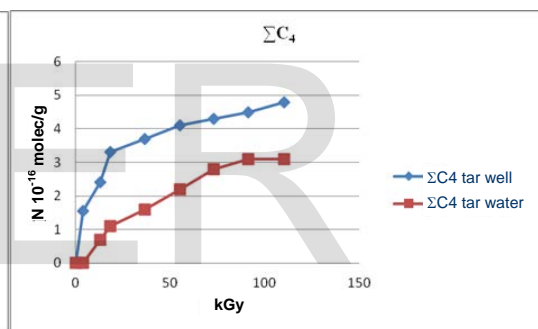


Fig. 2. The formation kinetic of ΣC₄ hydrocarbons in the radiolysis of resinous fraction of crude oil and degraded oil; P = 0.22 Gy/s, T = 30 °C.

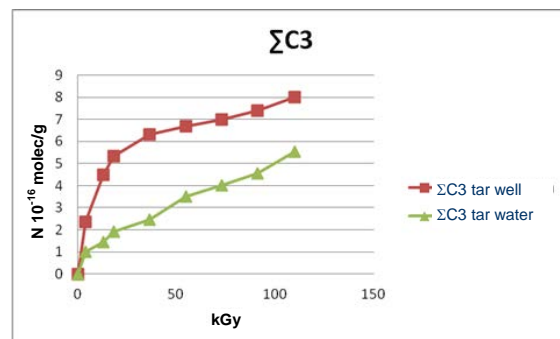
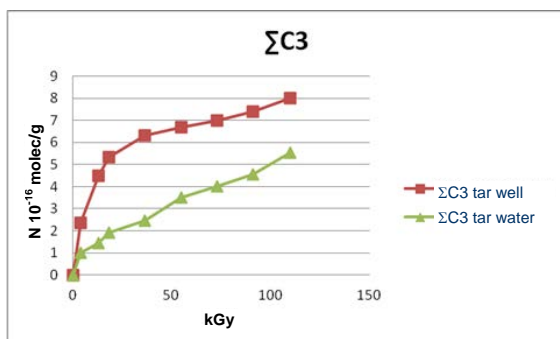


Fig. 3. The formation kinetic of ΣC_3 hydrocarbons in the radiolysis of resinous fraction of crude oil and degraded oil; $P = 0.22 \text{ Gy/s}$, $T = 30 \text{ }^\circ\text{C}$.

Fig. 4. The formation kinetic of ethylene in the radiolysis of resinous fraction of crude oil and degraded oil; $P = 0.22 \text{ Gy/s}$, $T = 30 \text{ }^\circ\text{C}$.

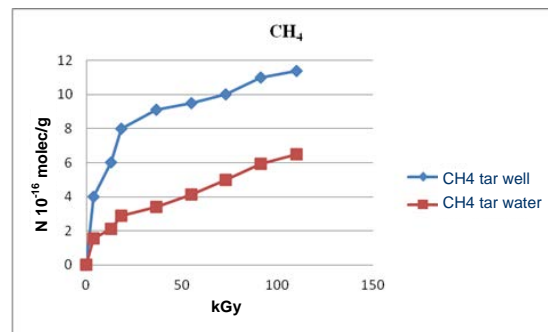
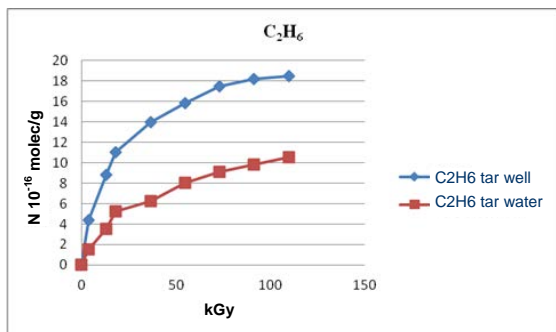


Fig. 40. The formation kinetic of ethane in the radiolysis of resinous fraction of crude oil and degraded oil; $P = 0.22 \text{ Gy/s}$, $T = 30 \text{ }^\circ\text{C}$.

Fig. 38. The formation kinetic of methane in the radiolysis of resinous fraction of crude oil and degraded oil; $P = 0.22 \text{ Gy/s}$, $T = 30 \text{ }^\circ\text{C}$.

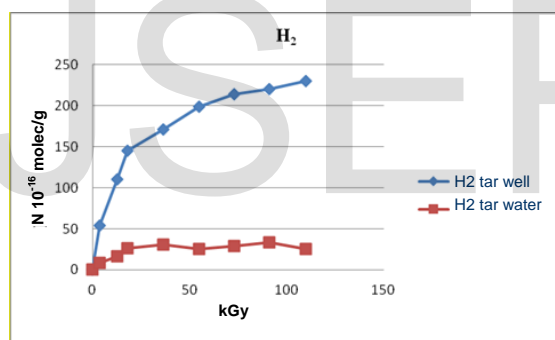


Fig. 37. The formation kinetic of hydrogen in the radiolysis of resinous fraction of crude oil and degraded oil; $P = 0.22 \text{ Gy/s}$, $T = 30 \text{ }^\circ\text{C}$.

As seen, if the kinetic curve for hydrogen is close to the straight line, for other gases, these tendencies tend to have saturation at doses greater than 40 kGy. The saturation state in these curves may be due to opposing reactions or limitations of the initial hydrogen resources. Studies show that the concentration of these gases in the reaction zone is not more than 10^{15} - 10^{17} molec/ml, and probability of the occurring the opposite radiation-chemical reactions is low. With great probability, the saturation state in the kinetic curves is due to the limitations of hydrogen resources. As the molecular mass of the originated gas increases, their rate of formation and, consequently, their radiation-chemical yields decreases.

As seen, the concentration of separate gases in gases formed from both crude oil and degraded oils vary with the following sequence: $\text{H}_2 > \text{CH}_4 > \text{C}_2\text{H}_4 > \text{C}_2\text{H}_6 > \Sigma\text{C}_3 > \Sigma\text{C}_4 > \Sigma\text{C}_5$. It should be noted that in contrast to crude oil, degraded oils in addition to hydrogen and hydrocarbons also produce carbon monoxide.

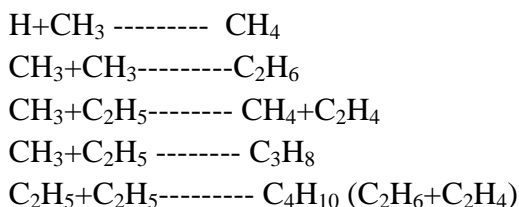
It is known from the literature that the formation of gases during the decomposition of hydrocarbons occurs through the following reactions [3].

1. $M \rightarrow H, CH_3, CO$ radiolytic decomposition
2. $H+H \rightarrow (CH_3+H)$ recombination
3. $R + M \rightarrow H_2, CH_4 + M^*$ detachment
4. $R + R=M \rightarrow R-R- M^*$ composition

There is a classic mechanism for the formation of gases from oil hydrocarbons under the influence of radiation. According to this mechanism, the formation of hydrogen in cyclic compounds of oil, high molecular weight alkanes and other components is due to originating hydrogen atoms under radiation effects and their subsequent recombination.

Most likely, hydrogen abstraction under the influence of radiation occurs in functional groups. Decreasing of $-CH_2-$, $-CH_3$ groups in the IR-spectrum of irradiated samples is observed, and this indicate that the formation of hydrogen and other gases is due ^{to} radiolitic decomposition occurring in functional groups.

The formation of other, heavier gases also is due to the reactions of H, CH_3 and C_2H_5 radicals



Values $G = 0.01-0.24$ mol /100 eV for radiation-chemical yields of gases are characteristic for polycyclic aromatic hydrocarbons with high radiation resistance. Apparently, when the polycondensation processes occur in the degradation process, the rigid structure of oil is formed, and the radiolitic decomposition occurs only in functional groups.

Radiation-chemical processes are carried out at room temperature and therefore the process of gas production is even more complicated by the difficulty of diffusion. As a result, very small values of radiation-chemical yields given in the table are observed.

Note that in the radiolysis of the resinous fraction of the degraded oil carbon monoxide gas is formed along with hydrogen and hydrocarbons (Table 1). This is most likely due to the formation oxygen contained components such as $-CO-$, $-CHO-$ and so on in the oil functional groups during the degradation process, and these groups form CO molecules when they decompose under the influence of radiation.

Such yields and speeds in the formation of gases are characteristic for radiation-resistant polycyclic aromatic compounds. The degraded oils have the same properties. For example, in the radiolysis of naphthalene, anthracene, phenanthrene and other polycyclic aromatic hydrocarbons formation of gases having the same order of yields and speeds have been observed. Linear part in the initial stages of gases yields in the investigated dose range, succeeded by the saturated state is explained by the radiation-chemical reactions of groups that differently resistant to radiation in degraded oils with complex structure.

Thus, it is possible to change the productivity of radiation-chemical processes by changing the dose power at the fixed temperature and this feature can be used for the development of radiation-chemical technology.

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