

UDC: 541.15

## STUDY OF PHOTOCHEMICAL TRANSFORMATION OF OIL AND ITS COMPONENTS (SUMMARY)

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**Abstract:** This work is devoted to the analysis of literature data on the photo resistance of crude oil and its main components when exposed to visible and UV radiation. Photochemical oxidation of oil and oil products plays an important role in the transfer of organic matter from oil to water. The resulting products have a great impact on the physical and chemical properties of the oil, its viscosity, foaming and aeration. Some products of the photo oxidation process can be dissolved in water that increases the solubility of crude oil in water under the influence of UV and sunlight.

**Keywords:** hydrocarbons, photo oxidation, degradation, crude oil, UV photolysis, gas chromatography

### 1. Introduction

Among the environmental problems of the oil industry, the dangers posed by offshore oil spills pose serious risks to human health through marine biodiversity and the food chain. For this reason, the development of scientific bases for the transformation of hydrocarbons as a result of various physical, physicochemical and biological processes on the surface and inside the sea during oil spills is an urgent scientific issue. It is known that crude oil falling into the sea is subject to various effects - physical, chemical, biological, etc. exposed. As a result, the final stage is formed by the final effect of the above factors that simultaneously affect. Because the final mechanism of action of these factors is complex, the study of these effects separately is studied by mathematical modeling in model systems and under certain conditions.

### 2. Analyses of literature data on the impact of UV radiation on crude oil and its components under UV radiation

The dependence of the optical density of samples on the wavelength of heavy and light oils under the influence of UV rays of the mercury lamp DRSH-500 was studied [2-4]. In [2] Oil samples with a thickness of 0.5 mm and an area of 80 cm<sup>2</sup> were irradiated in the form of thin layers. Optical density values were measured in control and irradiated samples. The spectra of the samples were taken on a Specol-11 spectrophotometer in the range of 350-800 nm. The power of the UV radiation source was 500 W and chloroform and benzene were taken as solvents. The obtained results are shown in table 1.

**Table 1**

Results of light (1) and heavy (2) oil irradiation

$\lambda$ , nm	Control sample		UV irradiated sample	
	Optical density			
	<i>1</i>	<i>2</i>	<i>1</i>	<i>2</i>
350	9,99	9,99	-	-
400	9,99	1,41	3,23	2,53
450	2,56	0,68	2,99	1,27
500	1,31	0,40	1,53	0,73
550	0,72	0,26	0,84	0,46
600	0,41	0,17	0,49	0,30
650	0,24	0,13	0,29	0,23
700	0,15	0,10	0,185	0,17
750	0,09	0,09	0,12	0,14
800	0,06	0,07	0,08	0,11

Experiments with heavy and light oils have shown that UV radiation causes to shift of absorption spectra over large wavelengths. Such a shift in the spectrum in heavy oil is due to the predominance of high molecular weight components in the samples.

From the expression for the rate of reversible photochemical reactions the dependence of the reactions, yield on the intensity of radiation during a photochemical reaction was calculated. In general, the following expression is obtained for the time dependence of the product concentration:

$$dC_2/dt = \gamma \cdot m \cdot E_e \cdot C_1 - k \cdot C_2$$

Where,  $\gamma$  and  $k$  are the rate constants of the reaction in light and dark,  $C_1$  and  $C_2$  are the concentration of the initial component and the reaction product, respectively,  $E_e$  is the intensity of radiation [2, 4].

The kinetic regularities of the oxidation of resin and asphaltene fractions under the influence of UV rays were studied in [5-9]. It is shown that the oxidation process during the irradiation of resin and asphaltene fractions goes through 3 stages. The change occurs in the presence of dissolved oxygen in the fraction. Adsorbed by the fraction atmosphere oxygen is involved in the oxidation process in the second stage. The final stage covers the negative effects of radiation on the oxidation of phenol, quinones and ester molecules. Alcohols, aldehydes, ketones, acids, etc. are formed as a result of the conversion of the hydrocarbon part of the resin-asphaltene fraction arises. Radiation produces also gas products -  $H_2$ , CO,  $CO_2$ ,  $CH_4$ , ethane, propane, butane.

The obtained results were confirmed by various methods as chromatography and spectroscopy. The mechanism of oxidation processes is discussed in general.

The effect of UV rays on Surakhani oil residues extracted from the soil was studied in [10,11]. It has been shown that during UV irradiation, the concentration of oxygen-containing compounds in the extract - alcohols, ketones, aldehydes, acids, esters, quinones, hydroquinones increases. Saturated hydrocarbons are dehydrogenated and successively condensed. The obtained results show, that the formation of alkyl radicals as a result of energy transfer and the formation of peroxide radicals as a result of their combination with oxygen takes place by the 2 quantum absorptions of photons, which confirmed by luminescence, photoluminescence, thermochemical

luminescence and IR methods.

In this study, the degradation processes of PAHs under the influence of  $\gamma$  rays were studied, which differs from the results of photon irradiations. However, in this case, the formation of vinyl-aromatic esters, oxy-ethers, dimeric carbonic acids and alcohols, as well as carbonyl compounds are observed during the irradiation of the extract. During  $\gamma$  radiation, the presence of PAHs in the extract has a radiation protection effect.

[12-15] studied the elementary stages and mechanisms of photophysical and photochemical processes in petroleum phosphors. The studied "Shirvanol NL", consisted of 30-35% PAH, 65-66% naphthen-paraffin hydrocarbons, 1-2% olefin hydrocarbons. It has been shown that when a sample is heated by polychromatic light at a temperature of  $-196^{\circ}\text{C}$ , elementary particles in the presence of molecular oxygen -  $e^-$ , H- atoms,  $R^{\cdot}$ ,  $\text{HO}_2^{\cdot}$ ,  $\text{RO}_2^{\cdot}$ ,  $\text{RO}_2^-$ ,  $\text{HO}_2^-$ ,  $\text{PAH}^{**}$  are formed and participates in recombination processes as the temperature rises. As a result of these processes, endoperoxides, tetraoxides and dioxetans are formed, and when the temperature rises, they are converted into acids, ketones, esters and alcohols. It has been shown that photosensitizers have an effect on the decomposition of petroleum phosphors and the decomposition of aliphatic alcohols. PAH molecules in NL play the role of photosensitizers in this process. The ionization potential of paraffin hydrocarbons is  $\geq 9\text{eV}$ , aromatic compounds 7-10eV, aliphatic alcohol 6-7 eV. Therefore, the cleavage of these compounds occurs in the presence of triplet states of PAH molecules. Since the approach time in the triplet case is long (for example, naphthalene - 2.5 s., phenanthrene - 3.5 s., Etc.), they can decompose aliphatic alcohols and paraffin by receiving a second light quantum. For aliphatic alcohols, decomposition occurs by the  $\text{C}\alpha\text{-H}$  bond, and for paraffins by the C-H bond (methylene group).

The mechanism of conversion of heavy oil residues under the influence of UV rays by IR, UV and EPR spectroscopy methods was studied in [15-17]. Physico-chemical studies have identified important differences between the generation and destruction of free radicals during photovoltaicization: free radicals are generated in resin and luminescent concentrate, and destroyed in heavy oil residues and asphaltenes. It has been shown that the photochemical and photo oxidative processes that occur in heavy oil residues depend on the sensitizing properties of their main components.

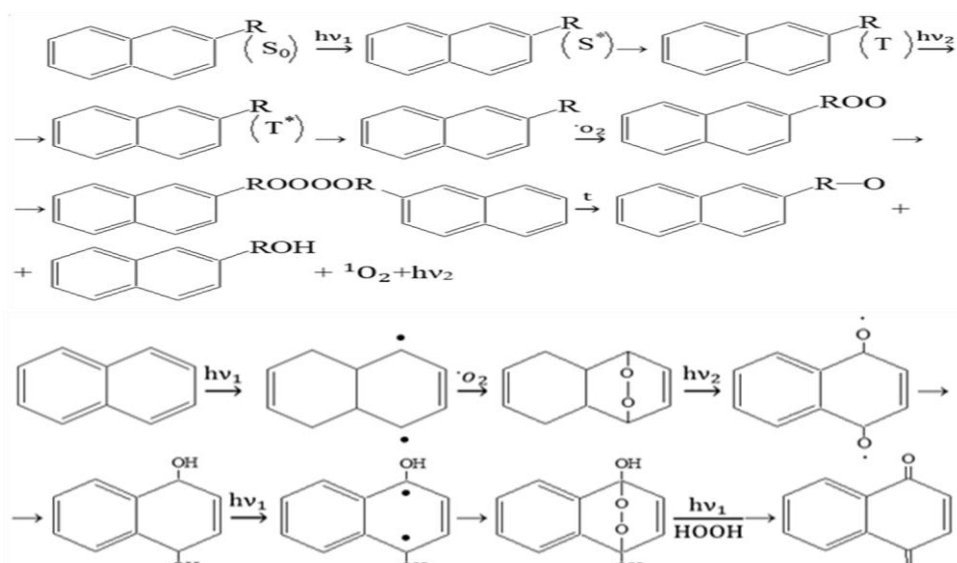
The photosensitizing properties of polycyclic aromatic hydrocarbons present in luminescent concentrates of catalytic cracking heavy oil, heavy pyrolysis resin, paraffin oil tar in the process of decomposition of aliphatic alcohols and saturated hydrocarbons were studied by the EPR method. It has been established that PAHs are also involved in the photosensitizing degradation of naphthen-paraffin hydrocarbons extracted from the heavy gas oil of catalytic cracking. It has been shown that the effective sensitization of photo particles of organic compounds requires a certain difference in the composition of the luminescent concentrates studied, depending on their molecular weight. It was found that the triplet-excited state of PAH is involved in these processes, and the photo hydrogenation of substrates occurs mainly by a two-quantum mechanism due to low-molecular-weight PAH with a large approach time, such as naphthalene, phenanthrene, anthracene.

The initial and intermediate stages in photosensitive decomposition of organic compounds have been studied over a wide temperature range ( $-196 \div 25^{\circ}\text{C}$ ). When PAH ( $10^{-7}$  mol/l) was added to all the binary solutions studied, several types of primary alcohols, hydrocarbon radicals, and atomic hydrogen were detected in the EPR spectra at  $-196^{\circ}\text{C}$ . These radicals are formed as a result of the hydrogen atom breaking away from the carbon atoms in the molecule. PAHs have also been shown to photosensitize photo oxidation processes. In these matrices, molecular oxygen was shown to form an intermediate  $\text{ROO}^{\cdot}$  peroxide radical at minus

133 °C.

The photosensitizing properties of asphaltenes separated from tar were studied at room temperature and they were proposed as photosensitizers. It was found that the addition of small amounts of weakly hydrogen-related organic substances (alcohols, isoparaffins) to the benzene solution of asphaltenes leads to a significant reduction in the concentration of free radicals in them during irradiation. Studies have shown that one of the modifications in preparation for the recycling of heavy oil residues is exposure to UV light. In this case, the atomic hydrogen formed in the photosensitization decomposition of weakly hydrogen-bonded organic compounds deactivates the paramagnetic nucleus of colloidal particles of asphaltenes, and in this case, the surrounding layers collapse, resulting in increased yield of low molecular weight open petroleum products.

The physicochemical properties and structural parameters of Surakhani oil and its hydrocarbon composition and changes in its parameters when irradiated with UV rays were studied [18,19]. Paraffin-naphthene, aromatic hydrocarbons groups I, II, III and resin groups of hydrocarbon content were studied in the taken samples. It has been shown that aromatic hydrocarbons include mono- and bicyclic compounds. The amount of these compounds varies depending on the group. The amount of monocyclic aromatic compounds are highest in group I, he and the amount of bicyclic compounds is highest in group III. UV spectroscopic method measured the values of optical density at different wavelengths. During UV radiation (15 minutes), the maximum value of absorption of the optical density corresponding to 266 nm decreases. Maximum new absorption bands (250 nm and 255 nm) are observed at larger irradiation times (240-260 nm), and these bands are referred to as quinones. At higher dose values, the maximum absorption of the optical density at wavelengths of 250 and 255 nm is observed. In contrast to group I, 1 maximum (252 nm) is observed in group II for 1 hour. The maximum absorption band corresponding to 226.3 nm (naphthalene-containing hydrocarbons) decreases after irradiation, but the optical density increases according to the boundary of the absorption band at a wavelength of 200 nm. In group III aromatic hydrocarbons, in addition to the maximum absorption bands corresponding to 203.4 and 208 nm, individual absorption bands are observed (262, 285, 295 nm). With the exception of optical densities corresponding to absorption maxima at 250 nm, variations are also observed at maxima at other wavelengths. The results show that in all groups of aromatic hydrocarbons, oxidation of hydrocarbons with naphthalene nuclei occurs as a result of radiation:



The results were also confirmed by IR spectroscopy. Thus, in all groups of irradiated aromatic hydrocarbons, absorption bands due to the formation of quinones are observed. Maximum values of optical density corresponding to 250-255 nm are observed in group I hydrocarbons, 250, 251, 252 nm in group II aromatic hydrocarbons and 250 nm in group III aromatic hydrocarbons.

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## **ИЗУЧЕНИЕ ФОТОХИМИЧЕСКИХ ИЗМЕНЕНИЙ НЕФТИ И ЕГО ПРОДУКТОВ (ОБЗОР)**

**Т.С. Идрисов, М.А. Курбанов, У.А. Кулиева**

**Резюме:** Настоящая работа посвящена анализу литературных данных о фотоустойчивости сырой нефти и ее основных компонентов при воздействии видимого и УФ-излучения. Фотохимическое окисление нефти и нефтепродуктов играет важную роль в переносе органических веществ от нефти к воде. Полученные продукты оказывают большое влияние на физические и химические свойства нефти, его вязкость, пенообразование и аэрацию. Некоторые продукты процесса фотоокисления содержат токсичные компоненты, которые могут растворяться в воде. Под воздействием ультрафиолета и солнечного света растворимость сырой нефти в воде увеличивается.

**Ключевые слова:** углеводороды, фотоокисление, разложение, сырая нефть, УФ-фотолиз, газовая хроматография.

## **NEFT VƏ ONUN MƏHSULLARININ FOTOKİMYƏVİ ÇEVİRİLMƏLƏRİNİN TƏDQIQI (İCMAL)**

**T.S. İdrisov, M.A. Qurbanov, Ü.Ə. Quliyeva**

**Xülasə:** Baxılan iş görünən və ultrabənövşəyi şüaların təsiri altında xam neftin və onun əsas komponentlərinin foto davamlılığına aid ədəbiyyat məlumatlarının təhlilinə həsr edilmişdir. Neft və neft məhsullarının fotokimyəvi oksidləşməsi üzvi maddələrin neftdən suya keçməsində mühüm rol oynayır. Yaranan məhsullar neftin fiziki-kimyəvi xassələrinə, onun özlülüyünə, köpüklənməsinə və aerasiyasına böyük təsir göstərir. Fotooksidləşmə prosesinin bəzi məhsullarında suda həll oluna bilən zəhərli komponentlər var. Ultrabənövşəyi işığın və günəş işığının təsiri altında xam neftin suda həllolma

qabiliyyəti artır.

**Açar sözlər:** karbohidrogenlər, fotooksidləşmə, parçalanma, xam neft, UB- fotoliz, qaz xromatoqrafiya