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THE IMPACT OF IONIZING RADIATION ON DIESEL FUEL

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Abstract: The samples of diesel fuel from natural oils of Azerbaijan were used as the research object. Laboratory studies were conducted on Co⁶⁰ gamma-source at dose rate of P= 0,18 Gy/s at different absorbed doses D=15-153kGy. The results of chromatographic, IR-spectroscopic studies are given. Concentrations, radiation-chemical yields of the obtained gases are established. Density of fuel samples before and after irradiation was determined at different absorbed doses and estimated their radiation resistance.

Key words: fuel, radiolysis, IR-spectrum, gases

1. Introduction

Diesel oil with a boiling temperature 180-360 °C, density of 0.790-0.860 g/cm³ is obtained from virgin oil followed by hydrotreating and dewaxing. The best diesel oil is considered light engine fuel with boiling temperature 230-350°C, consisting of 60% kerosene fractions boiling up to 300°C and 40% heavier – straw fractions boiling at the range of 290-350°C. The ability of fuel components to keep its chemical composition under operating conditions within temperature change, radiation, under metal influence is of important practical significance. Radiation influence can be accompanied by chemical transformations: break, displacement of chemical bonds, formation of free radicals, gas release, formation of double bonds and polymerization. The materials resistant to radiation influence must have the ability to absorb energy without excessive ionization.

We studied the effect of radiation on operational performance of diesel under static conditions in the usual manner before and after irradiation. Earlier, the results of experimental studies of radiation-chemical transformation of synthetic oil of oil-bituminous breed were presented (1).

The aim of the work is the study of radiation resistance of diesel oil from the oil of Azerbaijan. The results of such research allow estimating the radiation resistance of fuel, revealing the influence of irradiation on the overall composition of fuel and the possible changes in the quality of fuel.

1. Methodology

The samples of diesel oil in 1 ml placed in ampoules and sealed in vacuum were irradiated at room temperature on Co⁶⁰ gamma-source at dose rate P=0,18 Gy/s at various absorbed doses: within 15-153 kGy in vacuum for tracing the kinetics of the occurring processes. As an ionizing radiation it was used Co⁶⁰ γ -radiation source of MPX γ -30 type. The influence of absorbed doses of radiation on the change of properties and some operational performance of diesel oil was studied.

IR absorption spectra of the studied samples were recorded on the spectrometer VARIAN 640-IR (the Company of VARIAN) at the wavelength range (4000-400cm⁻¹). The samples were recorded in the form of film with thickness of d=1. Assignment of bands of the obtained spectra

was carried out as described in [2,3]. Gas products were analyzed by gas chromatography. Density was determined by a pycnometer in accordance with GOST 3900 - 85.

2. Experiments and results

The kinetic curves of accumulation of gases at gamma-radiolysis of diesel fuel are presented below (fig.1-2).

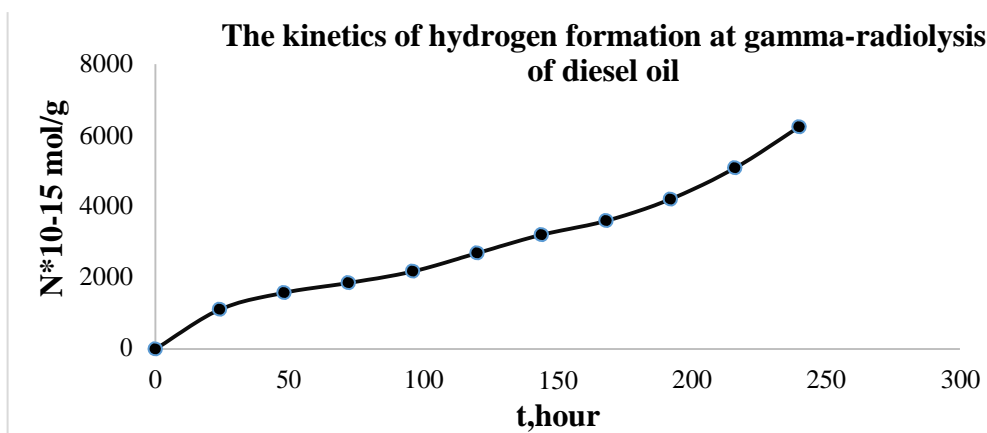


Fig.1. Kinetics of hydrogen formation at gamma-radiolysis of diesel oil

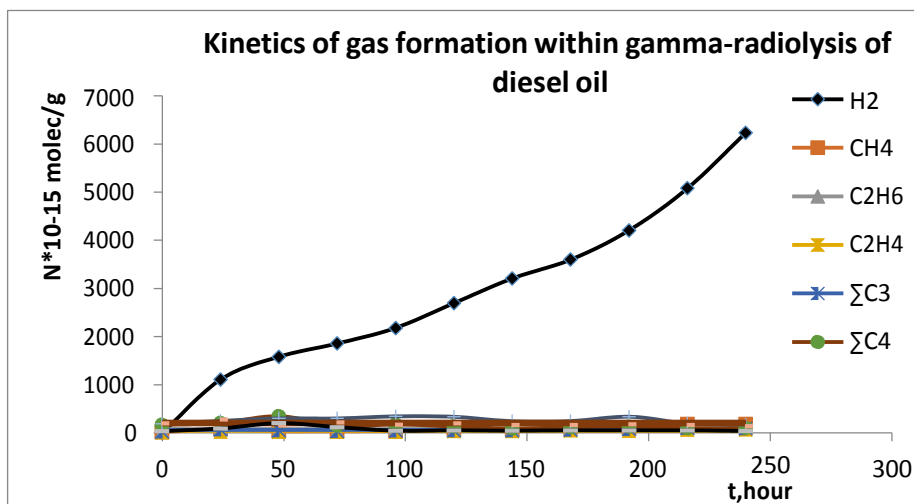


Fig. 2. Kinetics of gas formation within gamma-radiolysis of diesel oil

The influence of absorbed radiation dose on the change of fuel density was studied. The change of density of diesel oil within radiation is given in Table 2.

Table 1. Determination of density of diesel oil by pycnometer in accordance with GOST 3900-85

Determination of density of diesel oil by pycnometer at 20°C, kg/m ³		
№ ampoules	Duration of irradiation	Density at 20°C, kg /m ³ , P ₄ ²⁰
Original D ₀		851
after irradiation D ₁₃	24	853
after irradiation D ₁₁	48	854
after irradiation D ₁₂	72	855
after irradiation D ₁₄	96	856
after irradiation D ₁₅	120	857
after irradiation D ₁₆	144	858
after irradiation D ₁₇	168	859
after irradiation D ₁₈	192	862
after irradiation D ₁₉	216	863
after irradiation D ₂₀	240	867

As it is seen from table 1, fuel density increases with the increase of absorbed dose. Density indirectly characterizes the chemical properties, fraction composition and volatility of fuel. The more heavy fractions in the fuel, the higher its density. The fuel with high density falling to the bottom of piston and cylinder mirror promotes the increase in carbon-deposition and heat stress. The efficiency of purification from water in separators decreases in fuels with a density close to the unity.

The results of IR-spectroscopic studies of samples are shown below in Figure 3-4.

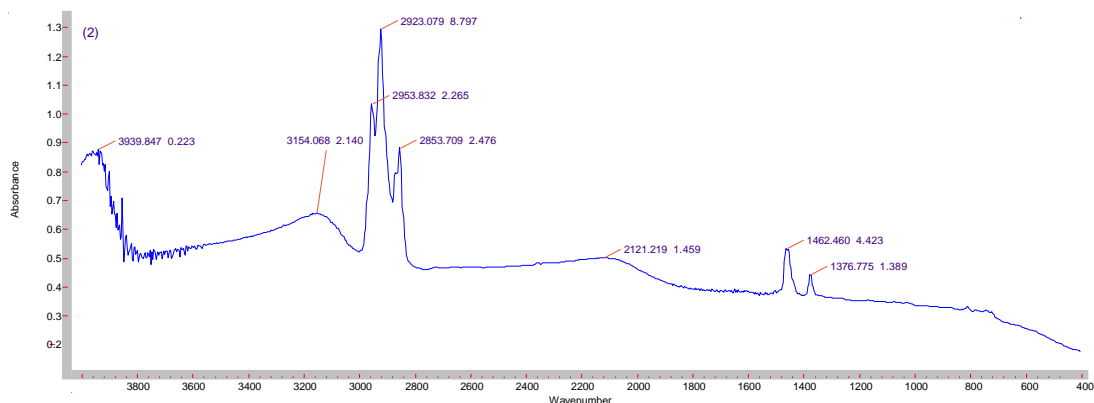


Fig. 3. IR -spectra of original diesel fuel

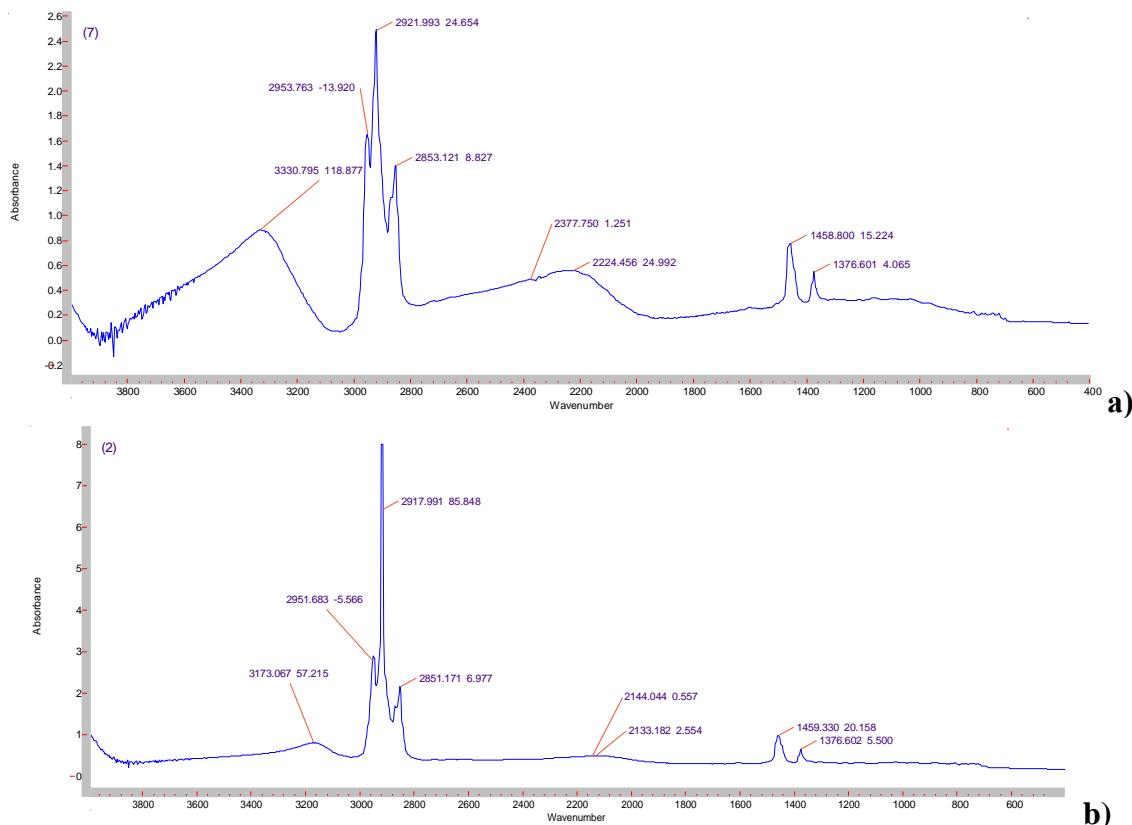


Fig. 4. IR -spectra of irradiated diesel fuel (a-120 hours, b- 240 hours irradiation)

Bands of deformation oscillation of $-\text{CH}_3$ ($1376\text{-}1380\text{ cm}^{-1}$) groups and oscillation of C-H bonds in alkanes ($1470\text{-}1435\text{ cm}^{-1}$) are observed in the original diesel fuel. Cumulated double - N_3 ($2160\text{-}2120\text{ cm}^{-1}$) bonds and an aldehyde $\text{C} = \text{O}$ ($2880\text{-}2650\text{ cm}^{-1}$) group attached to $-\text{CH}_3$ heteroatoms are observed. Significant valence oscillation of N-H groups (3154 cm^{-1}) -thiophene, furans and valence methylene $-\text{CH}_2-$ ($2940\text{-}2915\text{ cm}^{-1}$) oscillation are also observed.

After 120 hours irradiation (76 kGy), it is observed a 2 times increase in intensity of cycles (2920 cm^{-1}) of valence methylene $-\text{CH}_2-$ groups, and O- CH_3 groups attached to heteroatoms, as well as valence oscillation $-\text{CH}_3$ (2853 cm^{-1}). ($3400\text{-}3200\text{ cm}^{-1}$) - intra- and intermolecular H- bonds appear in the dimers and polymers. The intensity of valence oscillation of NH (primary amine $-\text{NH}_2$) is also increasing. There appears aryl nitrile (2224 cm^{-1}).

After 240 hours of irradiation (153 kGy), there occurs a sharp increase in cycles of valence methylene $-\text{CH}_2-$ (2917 cm^{-1}) groups by 8 times, and the intensity of the valence oscillation of $-\text{CH}_3$ - groups ($2860\text{-}2960\text{ cm}^{-1}$) by 2-3 times.

3. Discussion of the results

All fuels are organic compounds, therefore different radiation lead to chemical degradation and formation of new chemical structures. Study of the irradiation influence on the composition of oil fuel, establishment of link between the demand for fuel composition and its radiation resistance is of practical importance. Unstable fuel are those which have unsaturated compounds and tar. Sunlight and radiation significantly increase the rate of tar formation in diesel oil. Within radiolysis of hydrocarbon mixtures the initial impact energy is rapidly absorbed by liquid and chemical changes occurring under radiation influence are caused by the effect of electrons with the energy less than 100 eV. As a result of γ -radiation in the irradiated medium fast electrons occur, which have high energy and are capable to change the chemical

properties of molecules. In this case chemical bonds are broken and free radicals, ions are formed which have free valences and excess energy. Simultaneously with the low molecular compounds of fragmental character, dimers and polymers are formed as the products of recombination of radicals and ions as a result of cracking, dehydrogenation, isomerization and polymerization of hydrocarbons. Radiolysis of alkanes leads to some of their dehydrogenating with disengagement of free hydrogen, radicals and ions. Secondary, especially tertiary and quaternary C-C bonds and secondary C-H bonds easily burst under radiolysis influence. The yield of gaseous products, including hydrogen is reduced within the irradiation of ethylenes. Total yield of radiolysis products, in which polymers are dominant, increases. More stable ones to radiation effect are polynuclear aromatic hydrocarbons, consisting of 2-4 rings, which were the basis to recommend this class of compounds for using as hydraulic fluid and lubricants working under the conditions of relatively high temperatures and radioactive radiation influence. Such compounds showed high radiation resistance even under intense γ -radiation (4-5).

4. Results

Conducted studies showed that chemical processes, density change occur in diesel oil within the absorbed doses 15-153 kGy. The effect of radiation influence on hydrocarbons of fuel depends on chemical structure, fuel composition. Within the combustion the hydrocarbons are oxidized so fast that the radiation influence is negligible. When the formation of radicals slow down at low temperatures, a small amount of seal products are formed in hydrocarbon medium as a result of radiation. The processes occurring due to radiolysis can continue long after the termination of irradiation which leads to the change of fuel composition. As a result, the operating ability of oil fuel deteriorates at an ambient temperature. The negative effect of fuel irradiation which is in contact with atmospheric oxygen is more at higher temperatures. In the future, it will be able to select such composition of oil fuel which will withstand the effect of radioactive irradiation at high temperatures by changing hydrocarbon composition of oil products due to minor changes in the composition and introduction of additives.

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ВОЗДЕЙСТВИЕ ИОНИЗИРУЮЩЕГО ИЗЛУЧЕНИЯ НА ДИЗЕЛЬНЫЕ ТОПЛИВА

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Резюме: В качестве объекта исследования использовались образцы дизельного топлива из природных нефтей Азербайджана. Лабораторные исследования проводились на гамма-источнике Co^{60} при мощности дозы $P=0,18$ Гр/с при различных поглощенных дозах $D=15-153$ кГр. Представлены результаты хроматографического, ИК-спектроскопического исследований. Установлены концентрации, радиационно-химические выходы полученных газов. Определены

плотность до и после облучения при различных поглощенных дозах образцов топлив и оценена их радиационная стойкость.

Ключевые слова: топливо, радиолиз, ИК-спектры, газы

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Xülasə: Tədqiqat obyektı kimi Azərbaycanın təbii neftindən alınan dizel yanacaq nümunələri istifadə edilmişdir. Laboratoriya tədqiqatları $D=15-153\text{kGr}$ müxtəlif udulma dozalarında $P=0,18$ Gr/s doza intervalında Co^{60} gamma-mənbəyi üzrə aparılmışdır. Xromatoqrafik, İQ-spektroskopik tədqiqatların nəticəsi verilmişdir. Əldə edilmiş qazların konsentrasiyaları, radiasiya-kimyəvi çıxımları müəyyən edilmişdir. Yanacaq nümunələrinin sıxlığı şüalanmadan əvvəl və sonra müxtəlif udulma dozalarında təyin edilmiş və onların radiasiya davamlılığını ölçülmüşdür.

Açar sözlər: yanacaq, radioliz, İQ-spektrlər, qazlar