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HIGH-TEMPERATURE RADIOLYSIS OF MOTOR PETROL AI-92

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Abstract: As a research object, samples of AI-92 petrol from Azerbaijan oil were used. Laboratory studies were carried out on the gamma source of Co^{60} at a dose rate of P = 0.18Gy/s and an absorbed dose of D=0.64 kGy at different temperatures (50-250°C). Combined effect of radiation and temperature on AI-92 motor petrol under static conditions was investigated by the usual method before and after irradiation. The methods used to determine the radiation stability are based on the irradiation of the product and the subsequent determination of the changes that occurred therein. Radiation oxidations of processes were considered in the high-temperature region, when chain processes occur. The results of chromatographic, IR-spectroscopic studies are presented. Concentrations, radiation-chemical yields of the produced gases of petrol samples after irradiation at different temperatures were established and their radiation resistance is estimated.

Keywords: fuel, radiolysis, IR-spectrum, gases, petrol

1. Introduction

While choosing fuel for the use in irradiation conditions, it is necessary to know whether the fuel has sufficient radiation resistance, whether it is possible to increase their stability due to small changes in composition or introduction of additives. In connection with the opportunity to develop new technological processes with the use of radioactive energy, it is necessary to study the effect of various types of radiation on hydrocarbons and oil products. Stability is understood as the ability of a fuel to maintain its chemical structure under operating conditions with a change in temperature, ionizing radiation and under the influence of metals. It is necessary to provide a radiation resistance in the physical and chemical properties of the fuel. The methods used for determining radiation stability are based on the irradiation of fuel and the subsequent determination of the changes occurred in it. These changes can vary widely - from the changes in individual working properties of fuel to its complete destruction.

The effect of radiation on the performance characteristics of AI-92 motor petrol under static conditions was investigated by the usual method before and after irradiation at different temperatures. Low-temperature radiolysis of various hydrocarbon fuels was previously presented in [1-3]. Also, the results of experimental studies of the radiation-chemical transformation of synthetic oil from petroleum bituminous rock and oil fractions were cited [4,5]. Gradually focused on the combined effect of radiation and heating. Since organic fuels and lubricants are particularly sensitive to the effects of radiation when heated, it should be taken into account not only radiation, but also temperature conditions in calculations. Radiation-thermal cracking is a chain process including the splitting of amyl radicals formed by heating or irradiation. Since the development of the chain process is carried out by the same type of radical splitting, the cracking products in both modes should be the same. The key products of all experiments were hydrogen, methane, ethane, propane, ethylene, butylene, pentane, and hexane.

The purpose of this work is to study the effect of radiation on the quality of petrol AI-92 at high temperatures. The results of such studies allow estimating the radiation stability of AI-92 petrol, determining the effect of irradiation on fuel composition and possible changes in its quality.

2. Methodology

Samples of petrol AI-92 (0.5 ml), placed in ampoules and sealed in vacuum, were irradiated at different temperatures (50-250°C) on MPX γ-30 type gamma-source Co^{60} at dose rate P=0.18 Gy/s within absorption dose of 0,64 kGy in vacuum with the purpose of tracing the kinetics of the proceeding processes. The influence of temperature and radiation on the change of properties and some performance characteristics of petrol was investigated. IR-absorption spectra of the studied samples were registered on spectrometer VARIAN 640-IR (VARIAN company) in the wavelength range (4000-400cm^{-1}). Samples were taken in the form of films with thickness d=1. The assignment of the bands of the obtained spectra was carried out as described in [6]. Gas products were analyzed by gas chromatography

3. Experiments and Results

Chemical method is used together with IR spectroscopy while determining the uncertainties. The results of IR spectroscopic studies of petrol samples AI-92 are presented below.

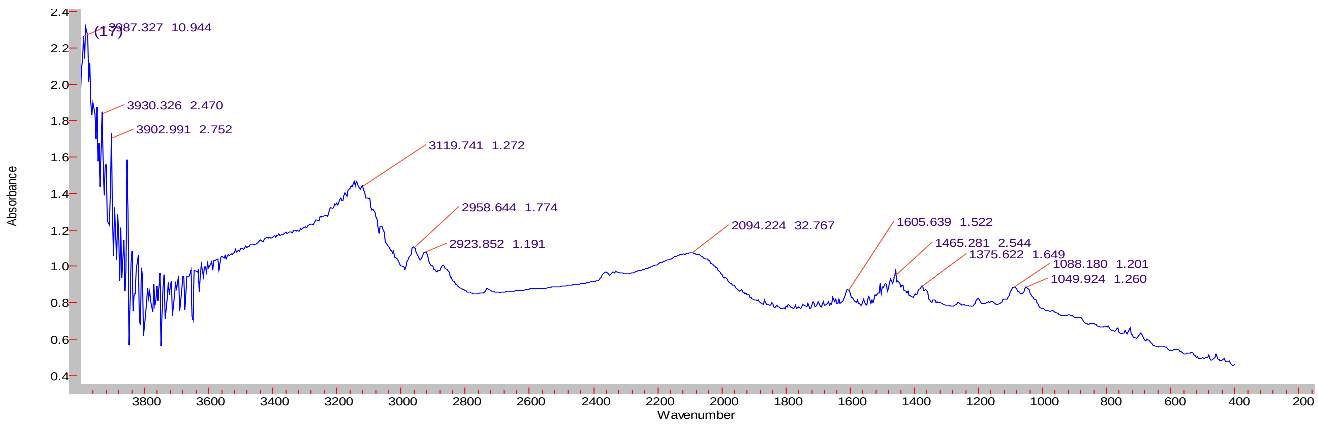
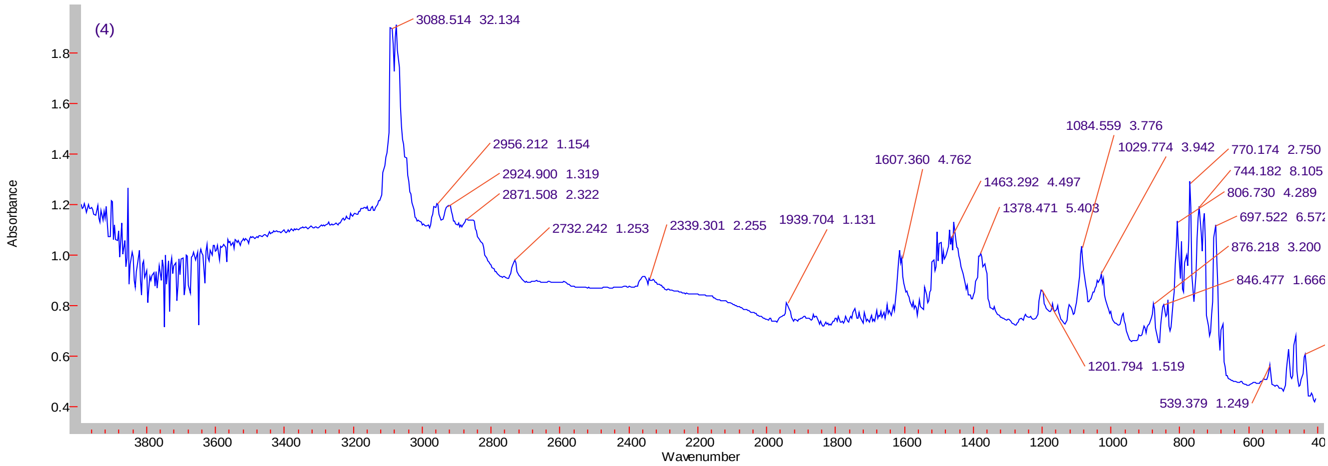


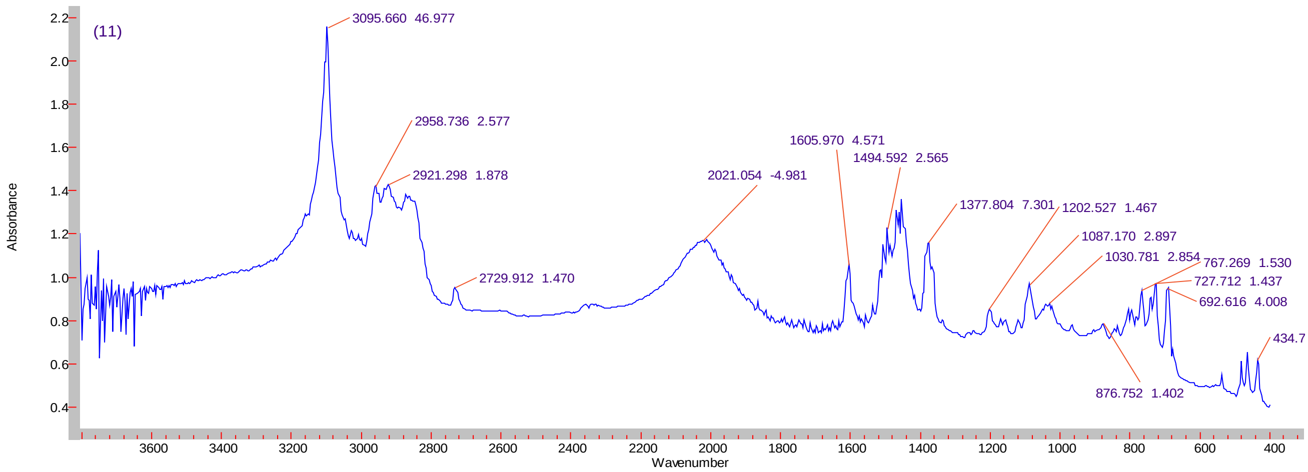
Fig.1 IR spectra of the original petrol

Plane deformation vibrations C-H are observed in the region (1225-950) cm^{-1}. (1080-1090) cm^{-1} - organophosphorus compounds. (1370-1380) cm^{-1} - deformation vibrations $-CH_3$-g, 1470-1435 cm^{-1} vibration of bond $-CH_3$-, 1606-cm^{-1} C=C valence vibration of aromatic ring, 2140-2080 cm^{-1} vibrations of CO_2 groups, 2940-2915 cm^{-1} vibration of CH_2 bonds in alkenes, 2975-2950 cm^{-1} vibration of CH_3 bonds in alkenes, 3130-3030 cm^{-1} -deformation vibration of NH_2 group of amino acid.



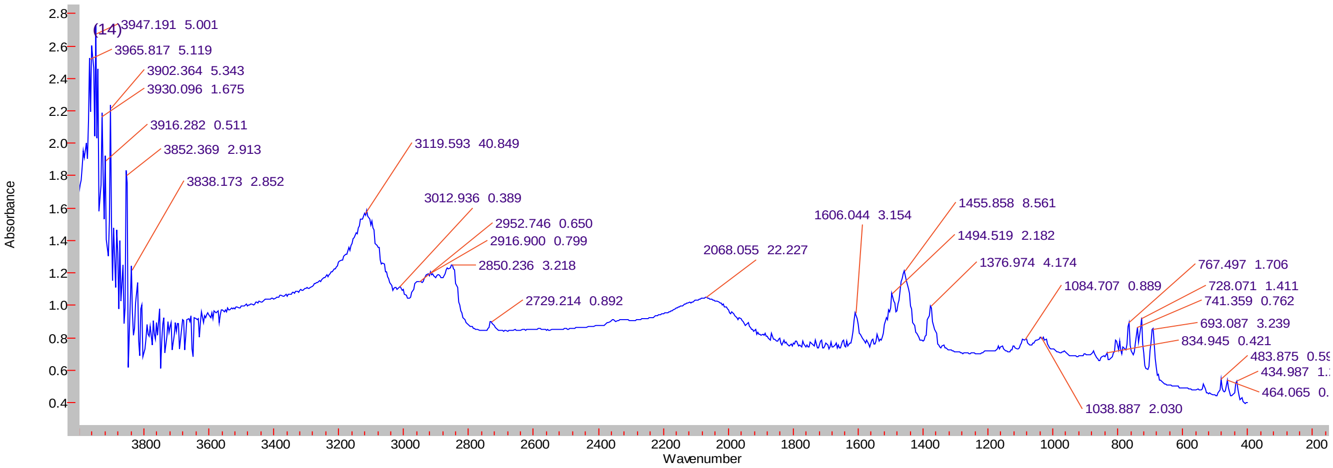
(a)

After irradiation at temperature of 50°C, the intensity of the bands of deformation vibrations of C-H bonds in alkenes increases in the range 730-665 cm^{-1}, 770-730, 806.876 cm^{-1}. Out of plane deformation vibrations of C-H bonds appear in the region 1000-650 cm^{-1}, 1080-1090-organophosphorus compounds. (1370-1380) cm^{-1}-deformation vibrations of -CH_3- groups increase slightly. 1606-cm^{-1} C=C valence vibrations of aromatic ring increase, 1075-1000 cm^{-1} plane deformation vibrations of C-H bonds, 1410-1310 cm^{-1} -vibrations of C-O-H bonds, 1930-1970 cm^{-1} - cumulated double bonds, 2732-2339 cm^{-1} -group of bands of o amine salts, 2,923 cm^{-1} vibrations of CH_2 bonds in alkenes increase with the increase of irradiation temperature. 2975-2950 cm^{-1} vibrations of CH_3 bonds in alkenes increase. 3095-3075 cm^{-1} - valence vibrations of C-H bonds in alkenes increase sharply.



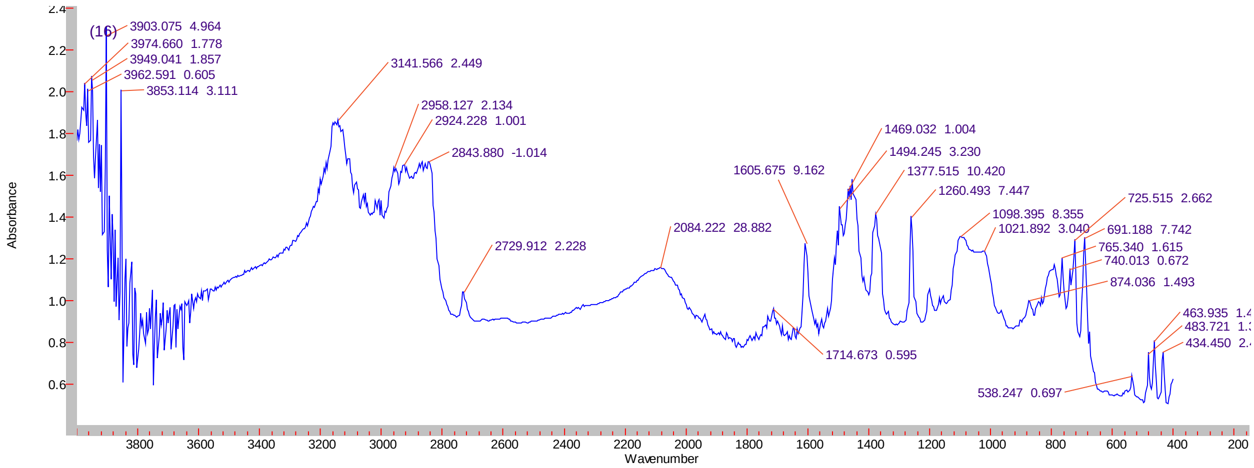
(b)

After irradiation at the temperature of 100°C, the intensity of bands 730-665 cm^{-1} - deformation vibrations of C-H bonds is observed in the alkenes. 770-730, 806.876 cm^{-1} - out of plane deformation vibrations of C-H bonds in the range of 1000-650cm^{-1}. 1410-1310 cm^{-1} - vibrations of C-O-H bonds. 1600-1494 cm^{-1} N=N azocompounds, 1606 cm^{-1} C=C valence vibrations of aromatic ring, 2030-2000 cm^{-1} - cumulative double bonds C=C=N. 2921cm^{-1} vibrations of CH_2 bonds in alkenes. 2975-2950cm^{-1} vibration of CH_3 bonds in alkenes and 3095-3075cm^{-1}- valence vibrations of C-H bonds in alkenes grow sharply with the increase of irradiation temperature.



(c)

The intensity of the bands 485-610 cm^{-1}-halogenated organic compounds is observed after irradiation at the temperature of 150^{0}C. 700-600 cm^{-1} -alkynes and triple bonds C≡ N, 690-615 cm^{-1} - nitrites, 770-730, 806,876 cm^{-1} -out of plane deformation vibrations of C-H bonds in the range of 1000-650 cm-^{1}, 1410-1310 cm^{-1} -vibrations of C-O-H bonds. 1606 cm^{-1} C=C valence vibrations of the aromatic ring, 1494 cm^{-1} N=N azocompounds, 2732-2339 cm^{-1} a group of bands of amine salts. 2923 cm^{-1} vibration of CH_2 bonds in alkenes, 2975-2950 cm^{-1} vibrations of CH_3 bonds in alkenes increase, 3130-3030 cm^{-1} - deformation vibrations of NH_2 of amino acid group are formed.



(d)

Fig. 2. (a,b,c,d). IR spectra of irradiated petrol AI-92 at various temperatures (a-50^{0}C, b-100^{0}C, c-150 ^{0}C, d - 200 ^{0}C).

After irradiation at the temperature of 200°C, intensity of the bands 485-610 cm^{-1} -halogen derivatives of organic compounds is observed, 700-600 cm^{-1}-alkynes and triple bonds C≡ N, 690-615 cm^{-1} -nitrite, 770-730 cm^{-1}, 806.876 cm^{-1}- out of plane deformation vibration of C-H bonds in the range of 1000-650cm^{-1}. (1020-1075) cm^{-1} aromatic and vinyl =C-O-C- groups. 1600-1494 cm^{-1} N=N azocompounds, 1606-cm^{-1} C=C valence vibrations of the aromatic ring. 2140-2080 cm^{-1} - deformation vibrations of NH group of C-N vibrations (all amino acids). 2732-

2339 cm^{-1} group of bands of amine salts, 2923 cm^{-1} vibrations of CH_2 bonds in alkenes, as well as 2975-2950 cm^{-1} vibrations of CH_3 bonds in alkenes grow with the increase of irradiation temperature, 3175-3070 cm^{-1}-valence vibrations of N-H bonds are formed.

As the temperature increases, the bands of deformation vibrations (3130-3030) cm^{-1} -NH_2 of the amino acid group increase with an absorbed dose of 0.64 kGy in automobile petrol AI-92. As the irradiation temperature increases, there is observed a growth in the intensity of the bands (485-610 cm^{-1}) - halogen derivatives of organic compounds. The intensity of the bands (1606 cm^{-1}) C=C, (1020-1075) cm^{-1} aromatic and vinyl =C-O-C- groups grows. (700-600 cm^{-1}) -alkynes and triple bonds C≡ N appear. (2975-2950 cm^{-1}) vibrations of CH_3 bonds increase in alkenes. (2732-2339 cm^{-1}) a group of bands of amine salts appear. The intensity of the bands of 3175-3070 cm^{-1}-valence vibrations of N-H bonds increases with the change of temperature. 3095-3075 cm^{-1}- valence vibrations of C-H bonds in alkenes increase sharply with the increase of irradiation temperature.

Kinetic curves of gas accumulation during gamma-radiolysis of petrol AI-92 at high temperatures are presented below (Fig.3).

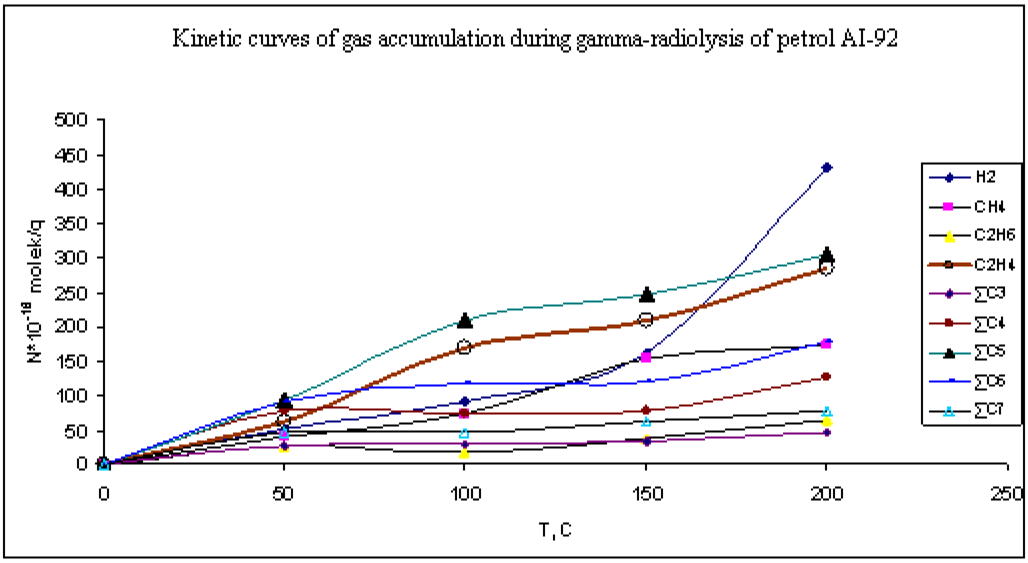


Fig.3. The formation of gases in the gamma-radiolysis of petrol AI-92 at various temperatures

Table 1. Radiation-chemical yields of gases of petrol AI-92 (mol/100eV) at the absorbed dose of 0.64 kGy and various temperatures (50-250°C).

Radiation-chemical yields of petrol AI-92 at an absorbed dose of 0.64 kGy and various temperatures (50-200°C).									
Temperature	Gases								
	H_2	*CH_4*	*C_2H_6*	*C_2H_4*	*ΣC_3*	*ΣC_4*	*ΣC_5*	*ΣC_6*	*ΣC_7*
50°C	1.27	0.99	0.64	1.56	0.67	1.90	2.33	2.24	1.14
100 °C	2.26	1.81	0.82	4.23	0.72	1.91	5.20	2.91	1.15
150°C	4.05	3.80	0.94	5.17	0.84	1.91	6.12	3.01	1.56
200 °C	10.75	4.33	1.59	7.09	1.14	3.13	7.56	4.43	1.94

4. Discussion and conclusions

Every year the use of organic materials - polymers, lubricants, fuels, coolants is expanding in such operating conditions when they are exposed to ionizing radiation, in the conditions of operation of atomic and thermonuclear reactors, electron and ion accelerators, installations with radionuclides, in outer space conditions. The fuels are organic compounds, so the radiation leads to chemical destruction and the formation of new chemical structures. As a result of the influence of γ-radiation, high-energy fast electrons that can change the chemical properties of molecules are formed in the irradiated medium, chemical bonds are broken, radicals and polymers are formed. As the temperature of the irradiated fuels increases, the rate of free radical reactions, mainly hydrogen and polymerization products, increases with the formation of an increasing amount of gaseous products. In addition, the generation of hydrogen at high temperatures can be facilitated by the radiation-induced accumulation of alkenes, in which the dissociation energy of C-H bonds adjacent to the unsaturated bond decreases. In gaseous hydrocarbons, several types of ion-molecular reactions occur: transfer of proton, hydrogen atoms and hydride ion; reactions associated with the rupture and formation of new C-C bonds; reaction of H_2 transfer. These are exothermic reactions that do not require activation energy and occur during each collision of ions with molecules [7]. Investigating the effect of temperature on the radiolytic transformations of fuel hydrocarbons, two types of reactions are distinguished: low-temperature non-chain reactions and high-temperature chain reactions.

The main reaction is dehydrogenation at low-temperature irradiation and low degrees of hydrocarbon conversion. The conversion depends, first of all, on the total absorbed energy and, to a lesser extent, on the dose rate.

High-temperature radiolysis is a chain process of the decomposition of free radicals or accelerated thermal cracking, when there are no other reactions typical for low-temperature radiolysis, besides the thermally stimulated chain decomposition of the radicals. As the temperature of the irradiated fuels increases, the rate of free radical reactions increases with the formation of an increasing amount of gaseous products, mainly hydrogen and polymerization products and radical disproportionation. At high temperatures (above 250°C), the radiolysis of hydrocarbons causes a process that develops in a chain free-radical scheme, like thermal cracking, the development of which is initiated by irradiation. The conducted studies show that in high-temperature radiolysis at an absorbed dose of 0.64 kGy in fuels, the effect of temperature on the course of ion-molecular radiolytic reactions can be manifested mainly due to the temperature dependence of the reaction rate and the thermal instability of certain ions and free radicals. An increase in the yields of the conversion products was observed with the increase of temperature. In petrol, the yield of C_2-C_5 fractions increased with the increase of temperature. At $\leq$ 100°C, the yields of C_2-C_5 have a small temperature inclination, but it rises sharply at higher irradiation temperatures. The rise in temperature also stimulates the formation of alkenes and aromatic hydrocarbons in liquid products. As a result of irradiation, gaseous products increase the amount of unsaturated hydrocarbons. The processes formed in connection with radiolysis can continue to develop for a long time after the termination of irradiation, and it leads to a change in the composition of the fuel. As a result, at the ambient temperature, the operating properties of petroleum fuels are deteriorating. Petrol containing a large number of unsaturated hydrocarbons in fuels slightly increases coking ability and deteriorates color during storage. Presence of unsaturated hydrocarbons in fuel, as well as such easily oxidizing compounds as mercaptans, determines the chemical stability of fuels during long-term storage. When storing such fuels, the content of actual gums in them increases, the content of mercaptans decreases, and sediments are formed. In recent years, there has been an increased interest in the oxidation and stabilization of jet fuels. This is due to the tightening of the requirements for the operation characteristics of fuels with the increase in the thermal stress of aircraft engines. It is necessary to select a composition of petroleum fuels that, even at elevated temperatures, will be better able to withstand the effect of radioactive irradiation by changing the hydrocarbon composition of petroleum products due to minor changes in composition and the introduction of additives.

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ВЫСОКОТЕМПЕРАТУРНЫЙ РАДИОЛИЗ АВТОМОБИЛЬНОГО БЕНЗИНА АИ-92

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Резюме: В качестве объекта исследования использовались образцы бензина АИ-92 из нефтей Азербайджана. Лабораторные исследования проводились на гамма-источнике Co^{60} при мощности дозы P=0.18 Гр/с и поглощенной дозе D=0,64 кГр при различных температурах (50-250ºC). Изучалось влияние совместного воздействия радиации и температуры на автомобильный бензин АИ-92 в статических условиях по обычной методике до и после облучения. Методы, применяемые для определения радиационной стабильности основаны на облучении продукта и последующем определении происшедших в нем изменений. Радиационные окисления процессов рассматривали в области высоких температур, когда происходят цепные процессы. Представлены результаты хроматографического, ИК-спектроскопического исследований. Установлены концентрации, радиационно-химические выходы полученных газов образцов бензина АИ-92 после облучения при различных температурах и оценена их радиационная стойкость.

Ключевые слова: топливо, радиолиз, ИК-спектр, газы, бензин

AI-92 AVTOMOBİL BENZİNİNİN YÜKSƏK TEMPERATURLU RADİOLİZİ

L.Y. Cabbarova, S.Z. Malikova, S.M. Əliyev

Xülasə: Tədqiqat obyekti olaraq Azərbaycan neftindən AI-92 benzin nümunələri götürülmüşdür**.** Laboratoriya tədqiqatları müxtəlif temperaturlarda (50-250°C) Co^{60} gamma-mənbələrində P = 0,18 Gy/s gücündə və D=0,64 kGy udulma doasında həyata keçirilmişdir. Radiasiya və temperaturun AI-92 benzininə birgə təsiri statik şəraitdə radiasiyadan əvvəl və sonra öyrənilmişdir. Radiasiya sabitliyini müəyyənləşdirmək üçün istifadə edilən üsullar məhsulun şüalanmasına və orada baş verən dəyişikliklərin müəyyən edilməsinə əsaslanır. Zəncir prosesləri meydana gəldiyi zaman yüksək temperatur bölgəsində proseslərin radiasiya oksidləşmələri nəzərdən keçirilmişdir. Xromatoqrafik, İQ-spektroskopik tədqiqatların nəticələri təqdim edilmişdir. Müxtəlif temperaturlarda radiasiyadan sonra AI-92 benzinin əldə etdiyi qazların konsentrasiyaları, radiasiya-kimyəvi çıxımları müəyyən edilmiş və onların radiasiya müqaviməti hesablanmışdır.

Açar sözlər: yanacacaq, radioliz, İQ-spektr, qazlar, benzin.