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STUDY OF POST-RADIATION PROCESSES IN MODEL HEXANE/HEXENE BINARY SYSTEMS

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Abstract: Studies have been conducted on the example of radiolysis of a model hydrocarbon mixture - hexane/hexene system. The kinetics of the occurring processes was studied at the temperature T=20^{0}C, dose rate P=0.0764 Gy/s, absorbed dose D=27-78 kGy. It was studied changes in density, viscosity, iodine number and molecular structure at concentrations of 5, 10, 20 and 40% of olefin in binary composition. Experimental study of radiolysis of hydrocarbon mixtures allows to draw conclusions about the nature of radiation-chemical processes, speed and direction of post-radiation effects.

Keywords: hexane/hexene, radiolysis, concentration, binary liquid systems

1. Introduction

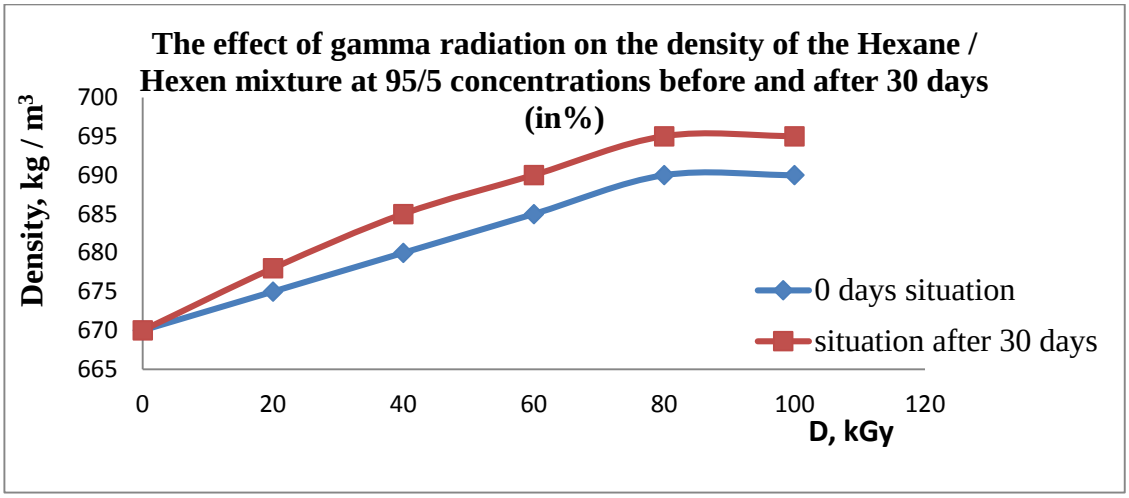
The concentration of olefins in motor fuels varies in the range of 10-25%, depending on the properties and composition of the initial raw material, as well as on the production technology [1]. When complex systems with this composition are exposed to radiation, the polymerization of olefins occurs under certain conditions, which affects the quality of fuels. Depending on the degree of solubility of the generated polymer, such polymerization continues after the cessation of radiation, and a post-polymerization process takes place. It is known from the theory of the radiation polymerization process that the speed and direction of this process depend on the concentration of olefin in the irradiated system, the ambient temperature, the radiation dose, and the dose rate. This issue has not been studied for petroleum hydrocarbon mixtures, especially fuels. The effect of radiation on petroleum fuels was presented in previous works [2-7]. In this article, the results of the study of post-polymerization processes in the model hexane/hexene system are presented.

2. Research methodology

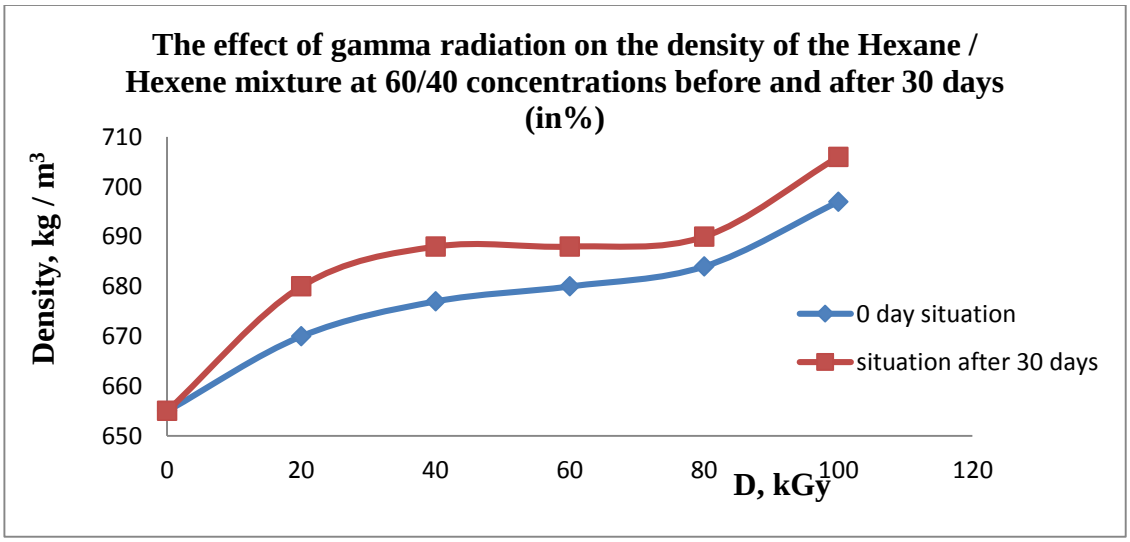
The dependence of the speed of the post-polymerization process in the hexane/hexene system on the olefin concentration and dose will guide the further development of research. In the studies, the effects before and one month after radiation as a result the radiolysis of the model hydrocarbon mixture - hexane/hexene system were examined. Iodine number was determined on a BRUKER MPA spectrometer, density was defined by pycnometers in accordance with GOST 3900–85, and viscosity was measured by VPZh-2 type viscometers in accordance with GOST 33-66 and GOST 10028-81.

3. Experimental results and their discussion

Figure 1 (a, b) shows the effect of the hexane-hexene mixture on the density of the system at different concentrations and absorbed doses immediately and one month after gamma irradiation (post radiation effect).



a



b

Fig. 1 (a,b). The density of the Hexane/Hexene mixture at different concentrations before and 30 days after gamma radiation

The graphs describing the effect of the radiation dose on the density of system show that low doses are more effective in changing the density. Dose dependence of the density associated with changes in viscosity shows that as the amount of olefin in the system increases, the density changes more, which is related to the increase in the liquid density during polymerization. As the amount of olefin and the radiation dose increase, the viscosity increases rapidly, which can be explained by the polymerization process. The dose-dependent nature of the intermolecular interactions that determine viscosity is explained by the varying degrees of radiation dose-dependence. The dose dependence of viscosity is shown in Figure 2.

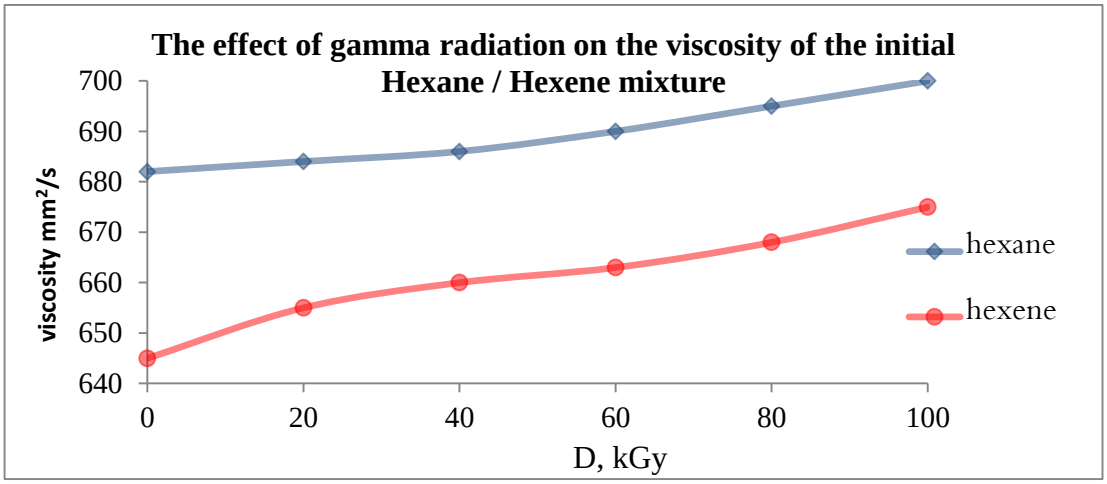


Fig. 2. The effect of gamma radiation on the viscosity of the initial Hexane/Hexene mixture

As can be seen, the viscosity of the system increases monotonically with increasing radiation, there is weak dose dependence, and at values higher than 64 hours there is a relatively rapid increase in viscosity. As the dose of ionizing radiation increases, the density of the hexane-hexene mixture also increases. To be sure that the change in the physical characteristics of the model hydrocarbon mixture is due to the radiation-stimulated polymerization process, it is necessary to study the changing process of double bonds in the system experimentally. In this regard, the measurement of the iodine number and the study of the molecular structure are of particular importance. Iodine number is an indicator of the presence of unsaturated hydrocarbons, which determines the chemical instability of fuels. The change in the iodine number of samples of hexane-hexene mixtures in different concentrations before and a month after irradiation is shown (Figure 3-4).

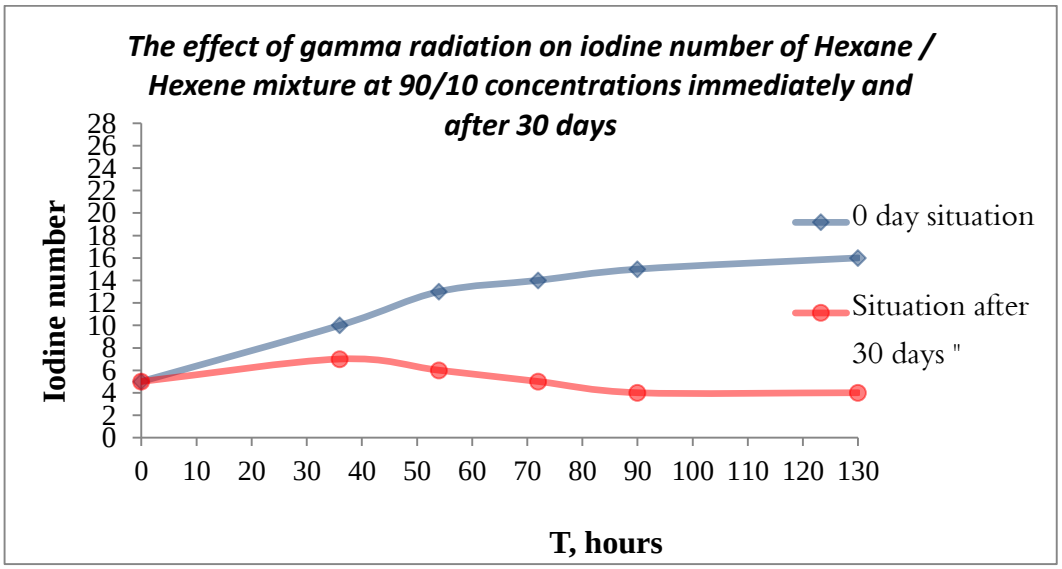


Fig. 3. Effect of Hexane/Hexene mixture in different concentrations on Iodine number immediately and 30 days after gamma irradiation

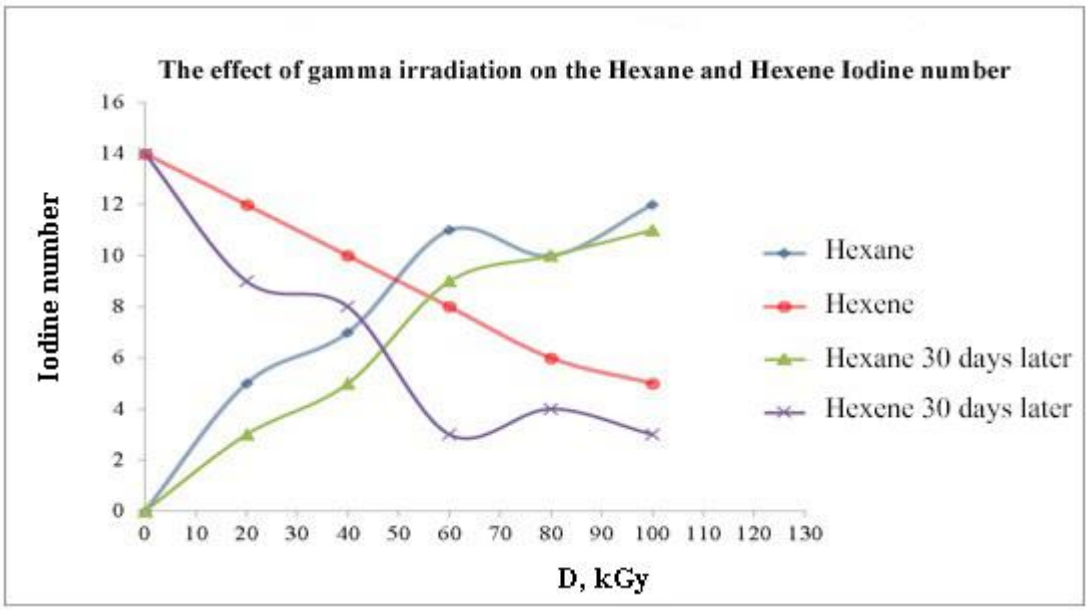


Fig. 4. The effect of gamma irradiation on the Hexane and Hexene Iodine number

When studying the effects of ionizing radiation on olefin-containing organic materials, we can mention two periods - immediately and after radiation. Changes that occur during radiolysis may be reversible. The reversal effects depend on the dose ratio. Irreversible changes in the properties of materials depend on the absorbed dose and temperature and continue after irradiation, causing the chemical transformation of molecules. One of the most important decomposition reactions of excited molecules formed during radiolysis of alkanes and alkenes is the breaking of C-H bonds, which leads to the formation of hydrogen. Polymerization of hydrocarbons under the influence of radioactive radiation leads to an increase in molecular weight and their simultaneous decomposition. Decomposition always occurs because gas is released during the radiolysis of all organic substances. The mechanism of dehydrogenation of alkenes during irradiation differs from that of alkanes because the p-bond is a very selective energy receiver. In the structure, viscosity, and density changes, the effect of radiation is manifested in organic liquids. Radiation of unsaturated hydrocarbons causes polymerization reactions. During the radiolysis of saturated hydrocarbons, the yield of some products does not depend on the dose, with increasing dose, they may increase or decrease. These yields are due to the occurrence of secondary reactions of unsaturated hydrocarbons accumulated during radiation [7].

In our experiment, the density, viscosity and iodine number of hexane/hexene mixtures change at P = 0.076 Gy/s and different absorbed doses (D = 25-78 kGy). As can be seen, a change in the hexane-hexene concentration from 5% to 40% changes the iodine number from 3 to 16, and this change is very close to a linear dependence. The effect of dose on the iodine number of binary mixture was studied for cases of changes in the concentration of olefin in the range of 5-40% and the results are given in Figure 3, 4. As can be seen, in almost all cases the dose dependence is characterized by complex curves. This is due to the competition between the formation and polymerization of olefins in the binary system. Radiation-stimulated reactions usually begin in the component with the highest concentration in the system.

4. Conclusion

The rate of polymerization during radiolysis of the olefin-paraffin mixture depends on the concentration of olefin in the system and the absorbed dose. In systems with a dose higher than 48 kGy, polymerization becomes a dominant process in systems containing more than 20% olefin.

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ИССЛЕДОВАНИЕ ПОСТРАДИАЦИОННЫХ ПРОЦЕССОВ В МОДЕЛЬНЫХ ГЕКСАН-ГЕКСЕН БИНАРНЫХ СИСТЕМАХ

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Резюме: Проведены исследования на примере радиолиза модельной углеводородной смеси - системы гексан/гексен. Кинетику протекающих процессов изучали при температуре T=20^{o}C, мощности дозы P=0,0764 Гр/с, поглощенной дозе D=27-78 кГр, исследовались изменения плотности, вязкости, изменения молекулярной структуры, йодных чисел в бинарном составе при концентрациях олефинов 5, 10, 20 и 40%. Изучение радиолиза смесей углеводородов позволяет сделать выводы о характере, относительной скорости и образующихся продуктах основных радиационно-химических процессов.

Ключевые слова: гексан/гексен, радиолиз, концентрация, бинарные жидкие системы

MODEL HEKSAN-HEKSEN BINAR SİSTEMLƏRDƏ POST-RADİASİYA PROSESLƏRİNİN TƏDQİQİ

L.Y. Cabbarova, İ.İ. Mustafayev, R.Y. Əkbərov, A.S. Mirzəyeva

Xülasə: Tədqiqatlar model karbohidrogen qarışığının – heksan/heksen sisteminin radiolizi timsalında aparılmışdır. Baş verən proseslərin kinetikası temperaturun T=20^0C, doza gücünün P=0.0764 Gy/s, udulan dozanın D=27-78 kGr qiymətlərində öyrənilmişdir. Binar tərkibdə olefinin 5, 10, 20 və 40 % qatılıqlarında sıxlığın,özlülüyün, yod ədədinin və molekulyar quruluşun dəyişməsi tədqiq olunmuşdur. Karbohidrogen qarışıqlarının radioliizinin eksperimental tədqiqi radiasiya-kimyəvi proseslərin təbiəti, post-radiasiya effektlərinin sürəti və istiqaməti barədə nəticə çıxarmağa imkan verir.

Açar sözlər: heksan/heksen, radioliz, konsentrasiya, binar maye sistemləri