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THE EFFECTS OF LOW-DOSE RADIATION ON STRUCTURAL ISOMERIZATION OF GUNASHLI OIL'S HYDROCARBONS IN PRESENCE OF BENTONITE

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Abstract: Herein, has been presented the results of petroleum crude oil isomerization and also investigated the dynamics of dose-dependent changes in the number of isostructural hydrocarbons. It has been shown, that the main reasons for the change of its form under radiation are the configuration distortion of the n-hydrocarbon structure of crude oil, the conformation transformation and reorientation of some sections of petroleum molecules and weakening of intermodular interaction. By using the method of reflection-absorption IR and EPR spectroscopy, the possible mechanism of radio-catalytic reaction for the conversion of n-alkanes to branched hydrocarbons at low dose irradiation has been discussed

Key words: low dose, isostructural hydrocarbon, crude oil, bentonite clay, nanostructure

1. Introduction

The main study of this paper is the effect of radiation on the transformation mechanism of crude oil from Gunashli oilfields (platform 8) of Azerbaijan. Another observation is the crude oil from platform 14 in Balakhani X Horizon of Gunashli field in Azerbaijan, which contains a significant amount of aromatics. The isomerization is produced with this type of oil under the gamma rays. It is one of the reasons for this research to be on focus.

Another relevant factor is to find the effective catalyst, which favors the isomerization of *n*-alkanes without too much cracking. The regulation of active sites and adsorption properties, as well as the topology of supporting surfaces, allows a potential predictive design of novel catalysts for conversion of n-alkanes into their branched isomers [2]. In this paper, bentonite clay from Alpoid deposit, Azerbaijan was proposed as a catalyst for radiation-induced isomerization. Natural clays, which are a low-cost and scarce natural resource, are nontoxic to the ecosystem.

2. Experimental part

Isomerization of n-alkanes into branched hydrocarbons of high-aromatic crude oil from platform 14 was achieved using the influence of gamma rays at room temperature in the presence of raw bentonite clay from the Alpoid deposit of Azerbaijan. The raw bentonite clay sample used in these experiments has a nanostructured composition with particle size in the range of 55≤ d [nm] ≤175 nm)[1]. The crude oil samples were irradiated with gamma radiation from the ^{60}Co isotope under static conditions, within vacuum-sealed quartz tubes at room temperature. The dose rate was 10.5 Rad/sec. Spectrophotometric measurements were performed in a VARIAN 640-IR spectrophotometer in the 4000-400 cm^{-1} region. Reaction conditions: Given the amount of catalyst- bentonite sample (in the range 0.01-0.03 g) was added to high –aromatic crude oil (2.0 g) in glass ampules and sealed, then subjected to various doses of radiation energy (from 0.72 to 6.12kGy). Radiation carried out for 1-17 hours at room temperature: with and without bentonite clay.

Electron Paramagnetic Resonance (EPR) method is used to study paramagnet centers (ions metals and radicals) involved in chemical processes. Experimental measurements were obtained from EPR techniques (“Bruker” EMX microX) at room temperature. Parameters for signal measurement: microwave frequency 9.87 GHz, modulation frequency 100 kHz, modulation amplitude 5 G, sweep width 100G, microwave power 2.2Mw.

The crude oil was obtained from a well of platform 14 of Gunashli field in Balakhani X Horizon in Azerbaijan and irradiated. Irradiation was carried out for 1-17 hours at a dose rate of 10.5 Rad/ sec. Crude oil isomerization was conducted with and without bentonite at a dose of 72-612kRad (0.72 - 6,12kGy) at room temperature.

3. Results and discussion

It was observed that, during the radiation of crude oil in the presence of clay, irradiated hydrocarbons contained much more isomers than without catalyst. The concentration of ($\sum C_{5-7}$) branched hydrocarbons was determined using FT-IR methods. The obtained experimental results are represented in Figure 1, 2.

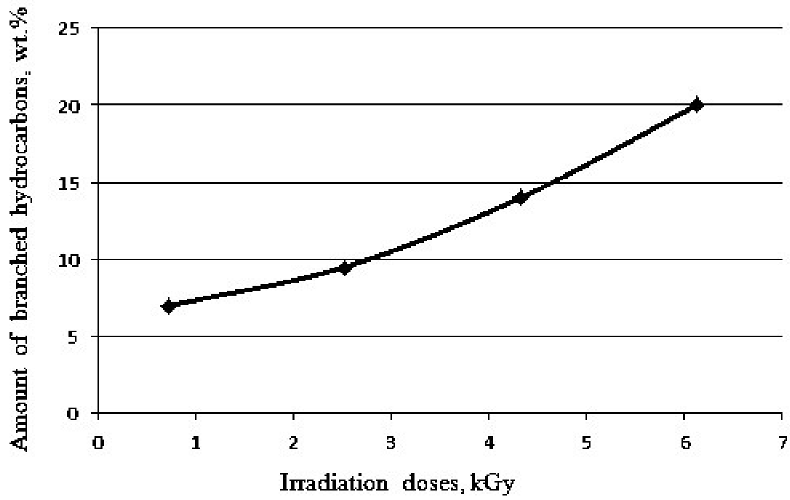

Fig.1. Dependence of amount of branched hydrocarbons and the irradiation doses (irradiation without sodium-bentonite clay)

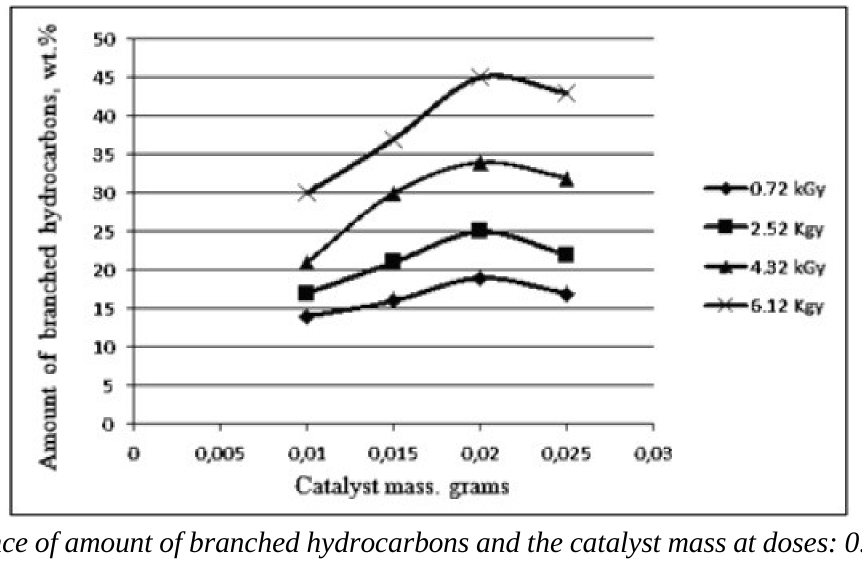

Fig.2. Dependence of amount of branched hydrocarbons and the catalyst mass at doses: 0.72kGy; 2.5kGy; 4.32kGy; 6.12kGy, mcat. = 0.01-0.025 grams

The results on the variation of the yield of the radiation-induced isomerization product with the γ-dose and amount of the clay have been presented. Figure 2 shows a considerable increase in isoalkane concentrations. At the same time, the arenes concentration remained nearly the same after Gunashli crude oil radiation processing in the presence of bentonite clay. A larger surface area of catalyst (d=55-175 nm) increases the areas of contact between reactant particles. This, in turn, increases the chances of successful collisions. Growth in the number of branched hydrocarbons occurred with a rise in radiation dose ranging from 0.72 to 6.12kGy and catalyst mass in the range of 0.01-0.02g. Results show that during petroleum radiation-induced isomerization the amount of branched hydrocarbons reaches the maximum value (45 wt. %) at 6.12kGy dose and 0.02g bentonite. However, after adding more than 0.02g catalysts at various doses (from 0.72 to 6.12kGy) the value of isomers began to decrease, which may be due to some of the agglomerations created with nanoparticles of clay.

The clay mineral bentonite is formed by hydrated aluminosilicates. Under gamma-rays, they lose constitutional water and form Lewis acid H^*AlO_3 [1]. The adsorption of the hydrocarbon molecule on Lewis sites occurred dissociatively on coordinately unsaturated Al sites- acid pairs. Therefore, Lewis acidity plays a definite role in the isomerization of crude oil under radiation processes. According to the concept developed by G. Ola [3], carbocations are formed directly from n-alkane molecules in the presence of an acid catalyst. The first protonation occurs via the σ bond and the formation of carbonium ion in which the existing 3 central and 2 electron bonds were put forward. Then carbonium ions decay by releasing hydrogen molecule and form carbenium ion. By FTIR spectroscopy, it was determined that among the isomers - $C(CH_3)_2$ dimethyl substituted products dominated in the liquid mixture. For carbenium ions, the rearrangements are characteristic, that is, 1, 2-shifts of alkyl groups. The nature of the unpaired electron density (spin density) in the carbenium ion is well explained by the fact that during isomerization of n-alkanes, dimethyl substituted products are formed only from hexane:

$$\text{n-}C_6H_{14}^+ \rightarrow CH(CH_3)_2(CH_2)CH_3^+ \rightarrow CH(CH_3)_2CH(CH_3)_2^+ \rightarrow C(CH_3)_3C_2H_5^+ \qquad (1)$$

The presence of $\sum C_7$ isomers indicates side-effects of disproportionation during isomerization of a mixture of n-pentane with n-hexanes. On the other hand, it has to be emphasized that isomerization on the clay occurred due to alkanes, but no olefins. As shown in the above-presented scheme (1), a comparison of the results confirmed that the reaction mechanism occurred in the presence of bentonite. It is the most probable transformation of hydrocarbons. Radiation-enhanced isomerization makes an important contribution to the formation of the unstable molecular states necessary for the propagation of the chain reactions at lowered temperatures [4, 5]. By nuclear reactions various fragments of the molecules, such as CH^+; CH_2^+; CH_4^+; CH_5^+; $C_2H_3^+$; $C_2H_4^+$; $C_2H_5^+$; CH_3^+; $C_3H_3^+$; $C_3H_2^+$; C_3H^+ $C_4H_3^+$; $C_4H_5^+$; $C_4H_7^+$ are produced. However, because of the extremely small concentration and the tendency to disappear quickly by subsequent reactions, they are difficult to detect.

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \qquad (2)$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \qquad (3)$$

$$CH_2^+ + CH_4 \rightarrow C_3H^+ + H \qquad (4)$$

etc.

Besides, for the study of paramagnetic centers and radicals involved in chemical processes, the EPR spectrum was introduced. The EPR spectrum of samples (crude oil from platform 14, irradiated crude oil with and without sodium bentonite clay), as shown in Fig.3, is obtained at the room temperature.

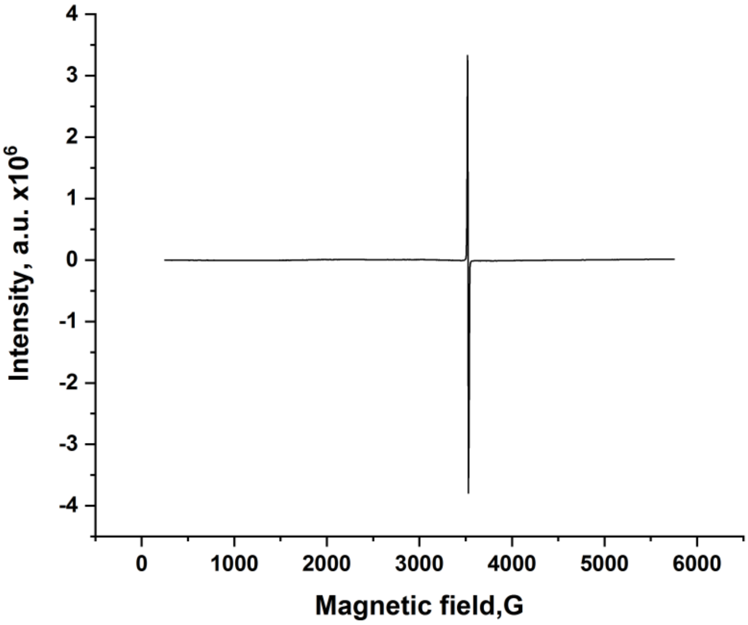

Fig 3a. EPR specter of irradiated crude oil samples

As we can see in figure 3a, no metal ions, except free radical spectra, were observed, which means that this petroleum sample is free from heavy atoms. Additionally, EPR spectrum reveals only one symmetric singlet line, discovered in studied petroleum samples.

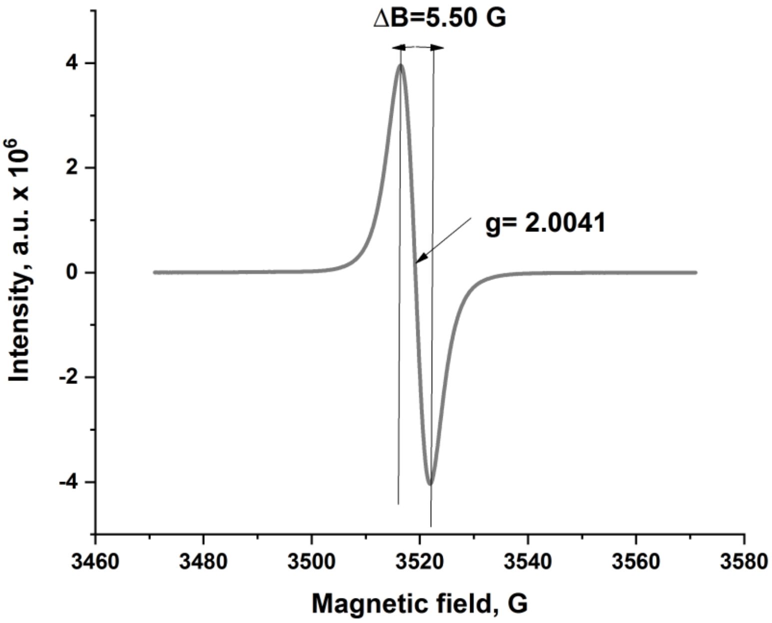

Fig.3b. EPR spectra of crude oil from the platform in an extended magnetic field

From the spectrum in fig.3b, it can be obtained that, g factor for free radical is 2.0041± 0.0002; and line width ΔB=5.50G±0.05. Also, it was discovered that after irradiation, the petroleum samples with and without bentonite catalysts, do not change line width, g factor, and the form of EPR spectra of the free radical. Therefore, the irradiation does not influence the chemical substance of the paramagnet centers assigned to free radicals.

The stability of EPR specters for with and without bentonite catalysts is due to π electrons of the aromatic rings and stable organic radicals of the side chains.

Thus, the results observed from platform 14 of Gunashli crude oil, leads to the conclusion that the presence of a considerable amount of aromatics in the field might have a strong negative effect on aromatization. On the contrary, this compound acts as a catalyst for the isomerization of n-alkanes in branched hydrocarbons. Using nanostructured clay with this type of crude oil creates a synergism effect. That is why the yield of isostructural-alkanes increases by 45% wt. in the presence of sodium - bentonite clay. In the work [5, 6], it is reported that the addition of aromatics to petroleum results in the combination of rather high dose rates and temperatures for the favorable conditions for isomerization.

Results:

- The advantages of this presented radio-catalytic isomerization technology are low capital and operational costs, processing at lowered temperatures with a low-cost nanostructured catalyst (d=55-175 nm), relatively low energy consumption.
- Studies of radiation effect mechanisms in nanostructured sodium- bentonite clay have an essential impact on progress in the practical application of radiation. "Low" dose irradiation gives rise to non-monotonous dependence of different properties of samples on the value of doses absorbed, thus making it possible to obtain hydrocarbons with predicted properties.
- Taking into account that EPR is a non-destructive method and there is no need for sample preparation, it demonstrates that EPR can be used for the on-line monitoring or even for the EPR logging to follow the influence of thermal or catalytic treatment of heavy crude oil.

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ВЛИЯНИЕ НИЗКОДОЗОВОГО ИЗЛУЧЕНИЯ НА СТРУКТУРНУЮ ИЗОМЕРИЗАЦИЮ УГЛЕВОДОРОДОВ ГЮНАШЛИНСКОЙ НЕФТИ В ПРИСУТСТВИИ БЕНТОНИТА.

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Резюме: В данной работе представлены результаты изомеризации сырой нефти, а также исследована динамика изменения содержания изоструктурных углеводородов в зависимости от дозы. Показано, что основными причинами изменения его формы, под воздействием излучения, являются искажение конфигурации н-углеводородной структуры сырой нефти, конформационное преобразование и переориентация некоторых участков молекул нефти, а также ослабление межмодульного взаимодействия. С использованием метода отражательно-абсорбционной ИК- и ЭПР-спектроскопии обсуждался возможный механизм радиокаталитической реакции превращения н-алканов в разветвленные углеводороды при облучении малыми дозами.

Ключевые слова: низкая доза, изоструктурный углеводород, сырая нефть, бентонитовая глина, наноструктура.

GÜNƏŞLİ NEFTİNDƏ KARBOHİDROGENLƏRİN BENTONİTİN İŞTİRAKI İLƏ STRUKTUR İZOMERLƏŞMƏSİNDƏ KİCİK DOZA EFFEKTİ

M.K. İsmayilova, R.J. Qasımov, M.A. Bayramov, S.Z. Məlikova

Xülasə: Məgalədə xam neftin izomerləşməsinin nəticələri təqdim edilmiş və izostruktur karbohidrogenlərin miqdarının dozadan asılı dəyişikliklərinin dinamikası araşdırılmışdır. Göstərilmişdir ki, radiasiyanın təsiri altında dəyişmənin əsas səbəbi xam neftin n-karbohidrogenlərinin struktur konfiqurasiyasının pozulması, neft molekullarının bəzi hissələrinin konformasiya çevrilməsi və yenidən istiqamətləndirilməsi ilə fraqmentlərdə qarşılıqlı əlaqənin zəifləməsidir. İR və EPR spektroskopiyadan istifadə edərək, kiçik dozalarda şüalanma zamanı n-alkanların şaxələnmiş izo-karbohidrogenlərə çevrilməsinin radiokatalitik reaksiya mexanizmi müzakirə edilmişdir.

Açar sözlər: kiçik doza, izostrukturlu karbohidrogen, xam neft, bentonit gili, nanostruktur