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THE CHANGES OF HYDROCARBON GENERATION UNDER THE INFLUENCE OF GAMMA RADIATION WITH BENTONITE

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Abstract: The present article deals with investigation of gamma - irradiated petrole samples by means of FT-IR spectroscopy. The transformation of irradiated hydrocarbons takes play in the presence of bentonite. It was discovered that after irradiation of crude oil from Gunesli fields with bentonite it takes play isomerization of hydrocarbons.

Key words: IR-spectrum, γ-radiation, crude oil, hydrocarbons, bentonite, transformation

1. Introduction

Naturally occurring hydrocarbons come from the decomposed remains of ancient plants and animals. Through a sequence of geologic events that occurred over millions of years, organic material was deposited on the Earth's surface and then transported to depressions or basins, where it accumulated and gradually became buried at great depths under layers and layers of sediments. There, in what geologists refer to as source rocks, it was subjected to much higher pressures and temperatures. Over time, and through a series of intermediate chemical reactions, some of this material eventually turned into petroleum.

In general, the deeper a rock formation is located in the Earth's crust, the higher its temperature will be. Thus, the type of petroleum that formed through these processes depended largely on the depth of the source rocks.

- In relatively shallow source rocks, where temperatures ranged from about 60 to 80°C [140 - 176°F], the organic matter was converted into heavy oil.
- At lower depths and higher temperatures, from about 80°C to 175°C [176°F to 347°F], the heavier, long-chain organic molecules began to break up into shorter molecules and form medium and light oil.
- Where temperatures exceeded 175°C [347°F], the molecules became even shorter and lighter, with more and more matter transformed to rich gas until, by the time it had reached 600°F [315°C], all of it had been transformed to dry gas (methane).

Crude oil originates from the decomposition and transformation of aquatic, mainly marine, living organisms or land plants that became buried under successive layers of mud and silt some 15-500 million years ago. They are essentially very complex mixtures of many thousands of different hydrocarbons. Depending on the source, the oil predominantly contains various proportions of straight and branched-chain paraffin, cycloparaffins, and naphthenic, aromatic, and polynuclear aromatic hydrocarbons. These hydrocarbons can be gaseous, liquid, or solid under normal conditions of temperature and pressure, depending on the number and arrangement of carbon atoms in the molecules.

Crude oils vary widely in their physical and chemical properties from one geographical region to another and from field to field. Crude oils are usually classified into three groups according to the nature of the hydrocarbons they contain: paraffinic, naphthenic, asphaltic and their mixtures. The differences are due to the different proportions of the various molecular types and sizes. One crude oil can contain mostly paraffin, another mostly naphthenes. Whether paraffinic or naphthenic, one can contain a large quantity of lighter hydrocarbons and be mobile or contain dissolved gases; another can consist mainly of heavier hydrocarbons and be highly viscous, with little or no dissolved gas.

Azeri-Chiraq-Guneshli (ACG) field along with Shah Deniz, Neft Dashlari (Oil Rocks), Balakhani-Sabunchu-Ramani, Bibiheybat fields is one of the largest oil and gas producing fields of the South Caspian basin. Natural reservoirs and their content of oil and gas deposits occur almost in all horizons of the Middle Pliocene aged Productive Series (PS). The complexity of the geological structure of hydrocarbon's deposits related, first of all, on tectonic setting uncertainty and lithologic-reservoir nonuniformity of natural objects, conditioned by peculiarities of sedimentation of detrital materials (brought to this region by Paleo-Volga). Along with the study of the reservoir property of rocks, the reservoir's distribution on the area of horizons with different saturation (upper horizons are gas-condensate burring and lower horizons are saturated with oil/gas/condensate), the reasons of irregular oil-and-gas saturation of the field were studied [2]. The formation of hydrocarbon's structural trap of the ACG field occurred on the early stage of Late Pliocene with apotheosis in the Post Pliocene period. The filling of traps (by hydrocarbons probably of Oligocene – Miocene age) proceeded during short intervals of tectonic activity which caused the peculiarity revealed by oil and gas saturation of the section of deposits. The tectonic activity and lithological factors affect the field's development in the period of structure formation in the earlier and following stages of the Middle Pliocene. In spite of a detailed study of the field, in which in total more than 300 wells have been drilled, we keep facing surprises of nature. There are very complex phase states of hydrocarbon mixture observed in some deposits of the field. For example, the presence of gas condensate deposit with gas solved in water in Qala suit of PS in the Guneshli part of the field. A quite powerful oil rim was detected on gas saturated Upper Kirmaky Sandy Suite (QUQ) and Lover Kirmaky Suite (QA) on the north-west limb of the structure (Shallow Water Guneshli). Some intervals (VII and IX horizons) highly saturated within one area of the field are not saturated enough on another part of the field. Thus, the generalized research of the ACG field validates the necessity of a more detailed and systematic approach to the selection of exploitation objects, estimation of the reservoir properties and hydrocarbon potentials of the field [3].

Gunashli is an offshore oil field in the Caspian Sea, located 120 kilometers (75 mi) east of Baku, Azerbaijan, 12 kilometers (7.5 mi) southeast of Oil Rocks and its deepwater section is a part of the larger Azeri–Chirag–Guneshli (ACG) project. The Azeri translation of *Gunashli* means *"sunny"*. Gunashli is believed to have more than 100 million tonnes of oil reserves [3].

2. Experiment

The samples were irradiated with gamma radiation from the ^{60}Co isotope under static conditions, within vacuumed and then sealed quartz tubes at room temperature. The dose rate was 10,5 rad/san. Spectrophotometric measurements were performed in a VARIAN 640-IR spectrophotometer in the range of λ=4000-400 cm^{-1}. Samples were taken in the form of films with thickness d=1mm.

Reaction conditions: A given amount of catalyst-bentonite sample (depending on the reaction need) was loaded in the middle of the reactor tube, which was previously filled with crude oil. Radiation carried out for 10 hours at room temperature.

3. Results and Discussion

We studied three samples by IR-spectroscopy:

1. Original petrol from well 263 located on the platform 14 of the Gunashli field in Balakhani X Horizon with the depth of 2710 m
2. Crude oil from platform 14 after irradiation, at room temperature for 10 hours
3. Crude oil from platform 14 after irradiation in presence of bentonite, at room temperature for 10 hours

The results of IR spectroscopic studies of original petrol samples from well 263 located on the platform 14 of the Gunashli field in Balakhani X Horizon with the depth of 2710 m are given below.

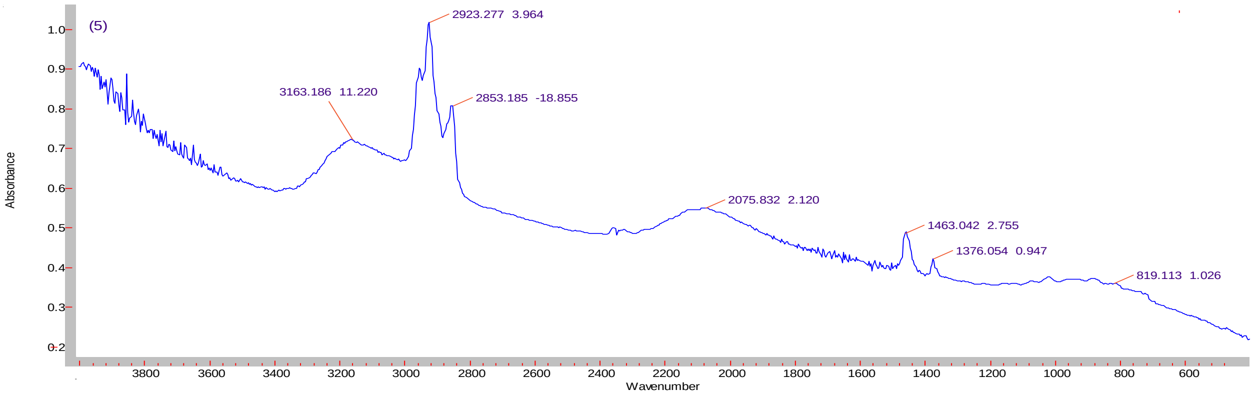


Fig.1. IR spectra of the original petrol from platform 14 at room temperature

The absorption at the range from 3000 to 2800 cm^{-1} shows the presence of alkanes. Twin peaks at about 2920 and 2850 cm^{-1} are found because of symmetrical and asymmetrical stretching of aliphatic C-H. All spectral curves have both peaks within this absorption range. The first peak at 2920 cm^{-1} features asymmetrical stretching of C-H bonds; the second peak shows symmetrical stretching. Locations of both absorption peaks show the presence of the methyl group of aliphatic hydrocarbons in the studied petrol sample. The absorption at the range from 3163 cm^{-1} shows the presence of aromatic rings [4].

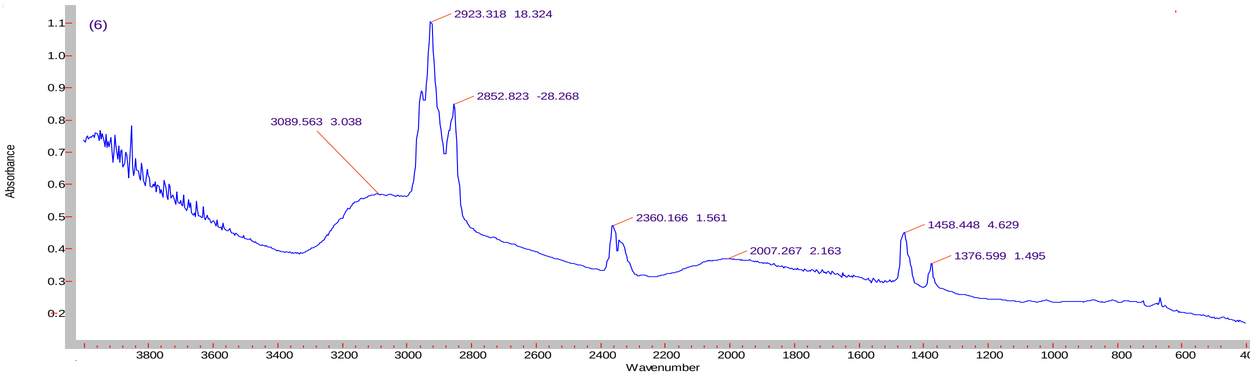


Fig. 2. IR spectra of the original petrol from platform 14 after irradiation, at room temperature for 10 hours

The absorption of aliphatic hydrocarbons is similar in first (figure 1) and second (figure 2) recorded spectra, because the dominant functional groups in samples are similar. After the irradiation of petrol at room temperature for 17 hours appeared the bands of 3089 cm^{-1} vibrations of C-H in aromatic ring (figure 2).

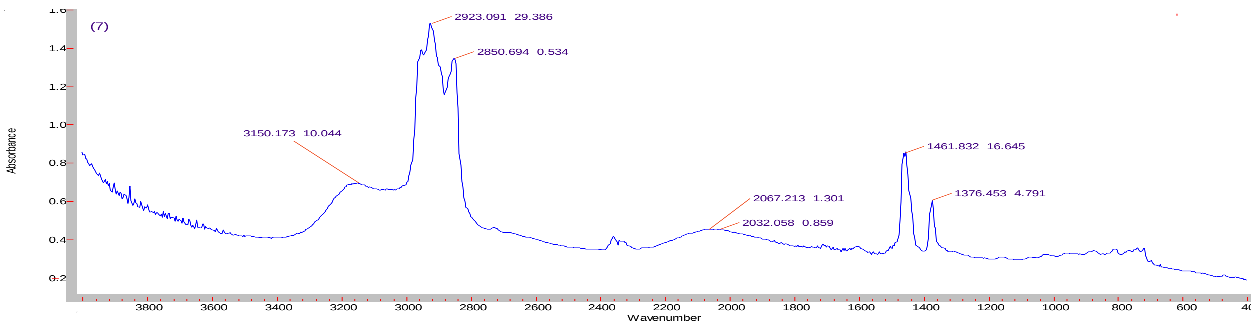
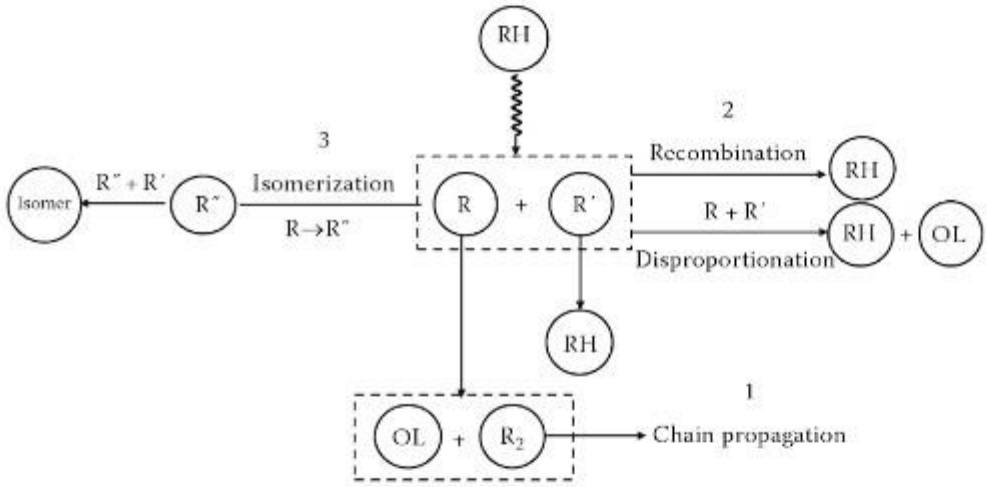


Fig. 3. IR spectra of the original petrol from platform 14 after irradiation in presence of bentonite, at room temperature for 10 hours

As shown in Fig.3, the amount of CH_3 groups increases sharply. The ratio of the intensity of symmetrical stretching of aliphatic C-H to asymmetrical stretching of aliphatic C-H increases. It can be explained with existing of aromatic compounds in all FT-IR spectra (fig.1-3.).T After irradiation of petrol with bentonite at room temperature for 10 hours appeared the bands of 3150 cm^{-1} vibrations of C-H in aromatic ring (figure 3).

The aromatic molecules have a higher capacity of excess energy absorption compared with the paraffin molecules. On the other hand, the high absorption capacity of the aromatic compounds reduces energy transfer at each interaction with a hydrocarbon molecule and creates shorter interaction chains. With a higher probability, it leads to isomerization rather than cracking. In general, isomerization may proceed by an ion mechanism similar to the heterogeneous catalytic isomerization of n-alkanes with the participation of the carbocations:



In the presence of bentonite crude oil under gamma – radiation changes the structure and obtained branched-chain paraffin (RH) via olefins (OL).

4. Conclusion

These investigations demonstrate that ionizing irradiation in the presence of bentonite plays a key role in changes in hydrocarbon generation processes.

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ИЗМЕНЕНИЯ ГЕНЕРАЦИИ УГЛЕВОДОРОДОВ ПРИ ВОЗДЕЙСТВИИ ГАММА-ИЗЛУЧЕНИЯ В ПРИСУТСТВИИ БЕНТОНИТА

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Резюме: Методом Фурье – ИК спектроскопии исследована сырая нефть под действием γ-облучения. Установлено, что трансформация облученных углеводородов происходит в присутствии бентонита. Выяснилось, что при воздействии ионизирующего излучения на сырую нефть с месторождений Гюнешли, происходит изомеризация углеводородов.

Ключевые слова: Фурье-ИК спектры, γ-излучения, сырая нефть, углеводороды, бентонит, трансформация

QAMMA ŞÜALANMA VƏ BENTONİTİN TƏSIRI İLƏ KARBOHIDROGENLƏRIN YARANMASINDA BAŞ VERƏN DƏYIŞIKLIKLƏR

M.K. İsmayılova

Xülasə: Bu məqalədə, gamma-şüalandırılmış neft nümunələri FT-IR spektroskopiya metodu ilə tədqiq edilmişdir. Şüalandırılmış karbohidrogenlərin transformasiyası bentonitin iştirakı ilə baş verir. Günəşli yatağından götürülmüş xam neftin bentonitin iştirakı ilə ionlaşdırıcı şüalanma zamanı karbohidrogenlərin izomerləşməsi müşahidə edilir.

Açar sözlər: Furye-İQ əksetmə spektrləri, γ-şüalanma, xam neft, karbohidrogenlər, bentonit, transformasiya