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**Influence of CuO, $Al_2O_3$, $Fe_2O_3$ nanoparticles and γ – quanta on crude oil transformation: the role of concentration and structure effects**

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# INFLUENCE OF CuO, $Al_2O_3$, $Fe_2O_3$ NANOPARTICLES AND γ – QUANTA ON CRUDE OIL TRANSFORMATION: THE ROLE OF CONCENTRATION AND STRUCTURE EFFECTS

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***Abstract*:** The present work deals with the transformation of crude oil by metal oxide nanoparticles. In this paper, a quantitative structure-property relationship has been developed. The effect of catalytic structure modification of petroleum over CuO, $Al_2O_3$, $Fe_2O_3$ nanoparticles has been studied by FT-IR spectroscopy method. SEM images also showed and demonstrated the structure of oxides nanoparticles. It was studied that structure change in crude oil's hydrocarbons occurs with $Al_2O_3$ and $Fe_2O_3$ nanoparticles, but over the CuO, it remains unchangeable. The concentration effect of nanoparticles for surface modification of hydrocarbons was investigated. The current study deals with comparative analysis of the interactions of various acyclic and cyclic hydrocarbons in both saturated and unsaturated forms with the different nanostructures. The received results are explained using of a super-molecule approach. It was also investigated crude oil upgrading using gamma- irradiation, without nanoparticles and founded that aromatic hydrocarbons in petroleum are stable towards radiation exposure.

***Key words***: crude oil, surface modification, hydrocarbons, transformation, gamma-irradiation, nanostructures

## 1. Introduction

Many published scales reflect the irreversible effects of organic metamorphism. A.Hood, C.C.M.Gutjahr and R.L.Heacock refer to the process of thermal metamorphism of organic matter as "organic metamorphism'. It also has been called "transformation" (Dobryansky, 1963), metamorphism (Landes, 1966-67), "thermal alteration" (Henderson et al, 1968, Staplin, 1969) and subsequently many others described the process as a series of thermocatalytic reactions leading to products of lower free energy by degradation, leading to smaller molecules of increasing volatility, mobility and hydrogen content and condensation. For application to petroleum exploration problems, however, there has been a need for a single numerical scale that is applicable over the entire thermal range of interest in the generation and destruction petroleum [1-3]. Several investigations were carried out on crude oil upgrading with nanoparticles. At present, there are few researchers done concerning the influence of nanoparticles Fe, TiO and activated C on crude oil, including radioactive irradiation. The effects of nanomaterials of Fe, titanium oxide (TO) and super activated carbon (CA) as catalysts in the process of upgrading heavy oil from the Azadegan Oilfield in Southwest Iran using microwave (MW) radiation has been investigated. The presence of nanoparticles in heavy oil leads to a greater reduction in viscosity at initial and even longer intervals. These nanoparticles, by absorbing MWs over longer periods, cause cracking of heavier compounds the effect of which exceeds that of the loss of lighter compounds from the heavy oil. It was studied according to Fourier transform infrared (FTIR) spectra, the presence of nanoparticles reduces the concentration of OH, S-H, alkyl groups, carbonyl, carboxylic acid or derivative groups and aromatic compounds in heavy oil. The changes are more evident with CA and Fe nanoparticles. In terms of deasphalting heavy oil, the Fe nanoparticle has the greatest effectiveness with asphaltene content reduced from 12.75 wt% to 9.13 wt% [4]. It was studied the hydrocarbon transformation by Yu.V.Larichev and O.N.Martyanov. They presented the results of the in situ SAXS study of the asphaltene aggregate transformations due to dilution of several heavy crude oils by heptane within the time range from 5 min to 3 days. The main growth of the asphaltene aggregates was usually observed within the first minutes. The analysis of the SAXS data obtained *in situ* for the oils having significantly different relative content of resins showed their great influence on the dynamics of aggregates formation on a nanometer scale. In particular, it has been shown that the resins can prevent the asphaltene aggregation via a certain mechanism which usually leads to the high anisotropy of the aggregates. Therefore the relative content of resin and asphaltenes as well, as aromatics and aliphatic, lead to the asphaltene aggregates with different shapes and different density of deposits. It has been found that asphaltene could form secondary aggregates with different shapes (worm –like and micelle-like shapes) and the Shape of asphaltene aggregate and their evolution during the time are dependent on the resin content in the heavy crude oils [5].

It has been investigated that after treatment materials based on hydrocarbons, by Al nanoparticles the rheological parameters of the obtained composite are improved [6-7]. It has been explained the correlation with the structure and properties of the nanostructured composition. It was studied nanosystems' structural characteristics using IR spectroscopy method and investigated the effects of $Al_2O_3$ nanoparticles on the rheological parameters of hydrocarbons [8]. In many currently explored applications of organic-inorganic hybrid materials, the achievement of superior properties is often hampered by the weak chemical (i.e. van der Waals, hydrogen bonding) interactions existing between the inorganic building blocks, leading, inter alia, to leaching of the inorganic components, agglomeration, phase separation, low mechanical stability. This is particularly critical for heterogeneous catalysis applications, where a robust linkage between the components would afford better performances in terms of recovery and re-use of the catalyst. A further factor affecting the actual effectiveness of heterogeneous catalysts is the accessibility of the active component, being facilitated by either a porous microstructure or by a loosely cross-linked structure enabling swelling of the hybrid catalyst in the reaction medium, where the substrate is dispersed. In the latter case, an important role is played by the polarity of the medium in which the catalysis is carried out [9].

In recent years there has been a great deal of research on the subject of nanostructured materials. Many nanostructured materials have been and are being prepared with increasing control over molecular configurations, conformations, and supramolecular assembly. These nanomaterials place an increasing challenge for characterization techniques to confirm the proposed structure and morphology [10]. From these methods, Fourier Infrared (FT-IR) Spectroscopy is very interesting and gives important information about structural change. Taking the above into consideration, by methods of FT-IR Spectroscopy was studied the features of structural changes, which observed in the nanoheterogeneous systems based on crude oil and metal oxide nanoparticles, depending on changes in concentration of nanoparticles and their structures.

## 2. Experimental part

FT-IR analysis was applied to investigate the reaction between nanoparticles and hydrocarbons matrix. Spectrophotometric measurements were performed for petroleum irradiation products too. IR spectra were taken with FT-IR Spectrometer Varian 640-IR in the frequency range 4000–400cm$^{-1}$ at room temperature. The absorption spectra of the samples were obtained as a form of a thin layer on the KBr boards. Two KBr prisms were used to constitute the interferometer cavity.

Crude oil used in this study was obtained from the oil field, located in Azerbaijan. CuO, $Al_2O_3$, $Fe_2O_3$ nanoparticles (d=60nm) impacted on crude oil (figure1). These nanoparticles with percentages 0. 01 %, 0.05%, 0.1% and 1,0 wt.% were added on the surface petroleum. It has been investigated the changes in petroleum's chemical composition and structures. It was also studied the influence of gamma – radiation on crude petroleum. Investigations were carried out under the influence of gamma rays at room temperature. 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/sec. Radiation carried out at doses 0.86÷8.64 kGy for 1÷10 hours.

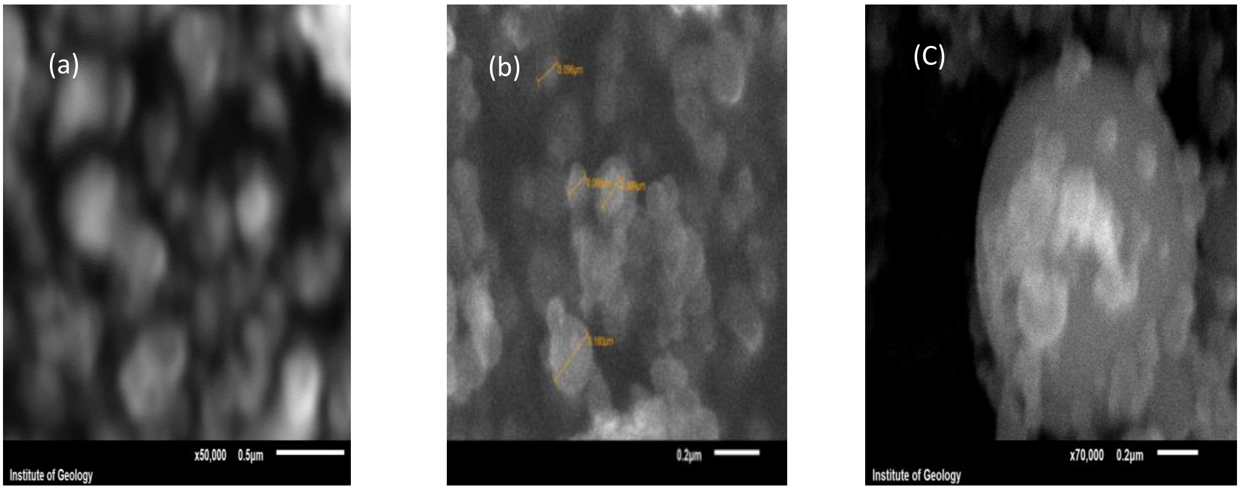


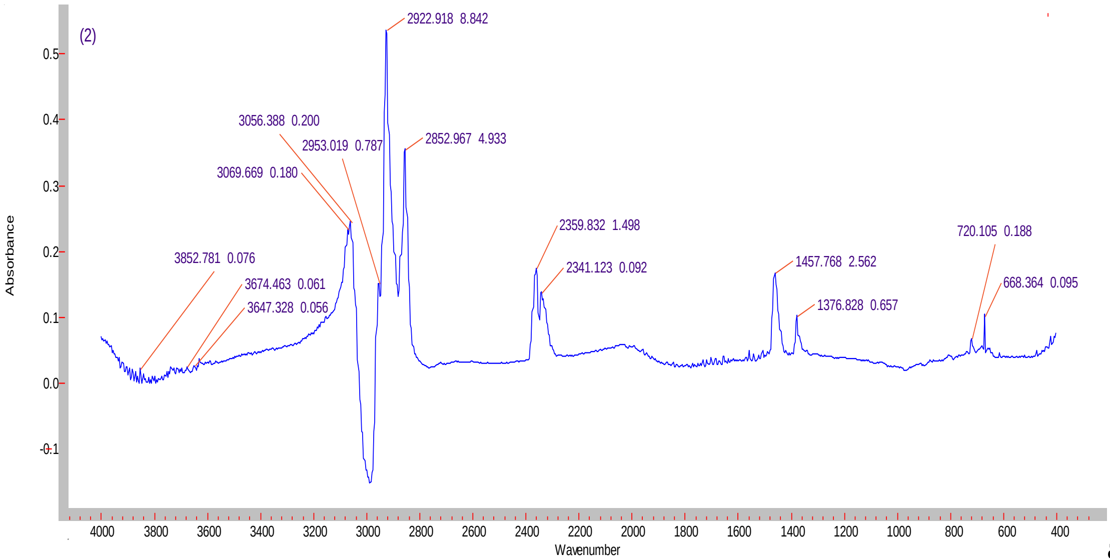

*Fig. 1. SEM images of nanoparticles : (a) - CuO ; (b) - $Al_2O_3$; (c)- $Fe_2O_3$ .*

## 3. Results and discussion

The IR absorption spectra analysis of these samples with nanoparticles shows that over the CuO nanoparticles no change occurs and with $Fe_2O_3$ nanoparticles crude oil destructed. Only over the $Al_2O_3$ nanoparticles occurs surface modification of crude oil (figure 2), taking into account some concentrations of nanoparticles.

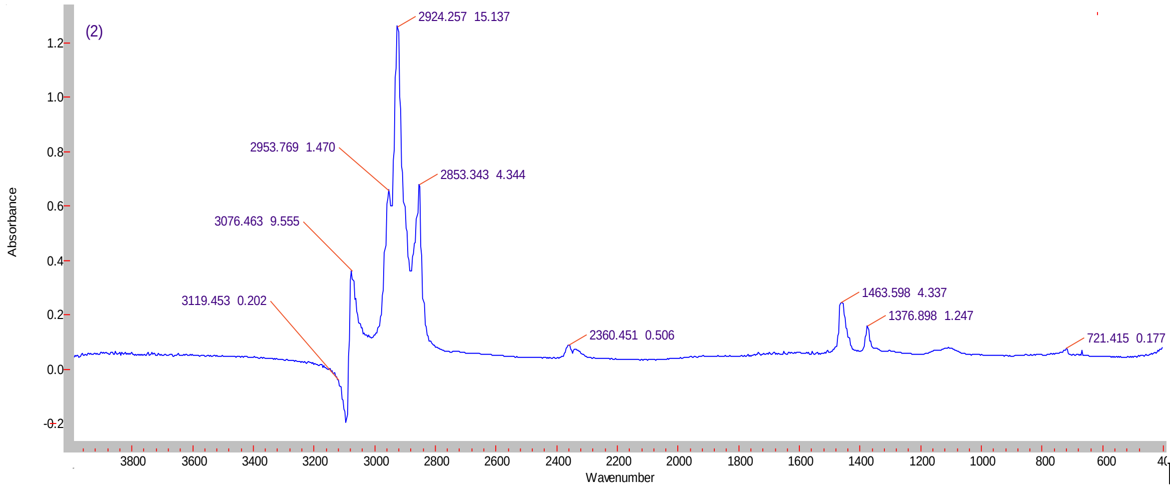
On the infrared spectra of the crude oil, it is possible to identify the following frequencies of absorption bands with several maximums:

• 3070 cm$^{-1}$ - stretch vibrations of -C = C in aromatics ring
• 2950 cm$^{-1}$-asymmetric stretch vibrations of methyl ($CH_3$) groups
• 2923 and 2853 cm$^{-1}$ –symmetric and asymmetric stretch vibrations of $CH_2$ groups
• 1457 and 1376 cm$^{-1}$-asymmetric (as) and symmetric (s) deformation vibrations of methyl ($CH_3$) groups
• 720 and 660 cm$^{-1}$- pendulum vibrations of $(CH_2)_n$



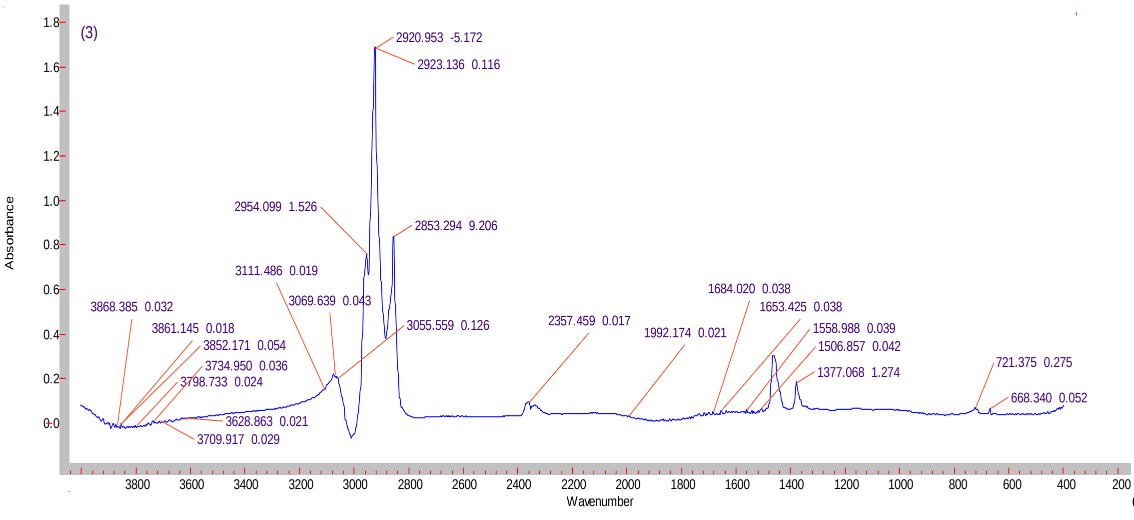
(2)
Absorbance
Wavenumber
2922.918 8.842
3056.388 0.200
2953.019 0.787
2852.967 4.933
3069.669 0.180
2359.832 1.498
2341.123 0.092
3852.781 0.076
3674.463 0.061
3647.328 0.056
1457.768 2.562
1376.828 0.657
720.105 0.188
668.364 0.095


a



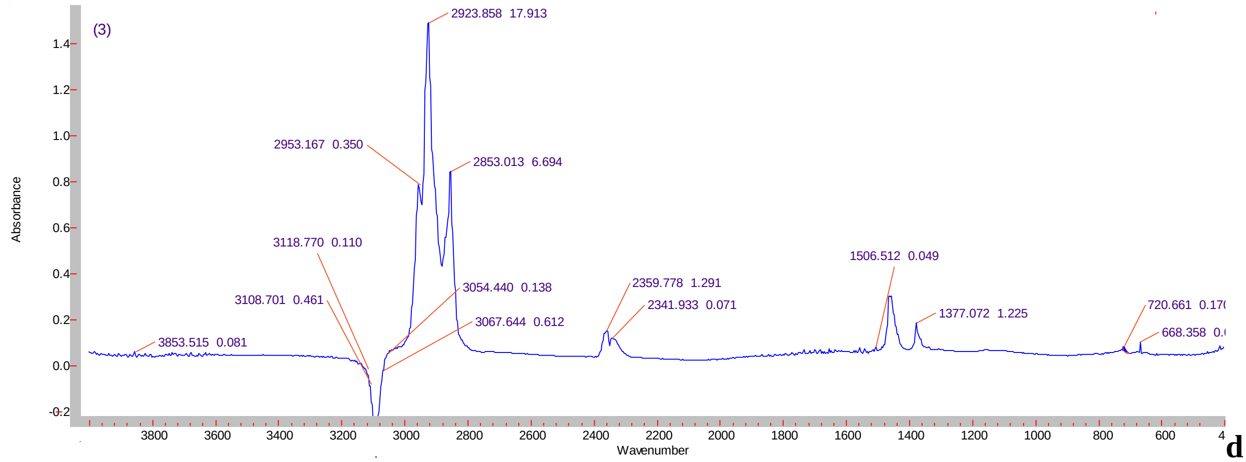
(2)
Absorbance
Wavenumber
2924.257 15.137
2953.769 1.470
2853.343 4.344
3076.463 9.555
3119.453 0.202
2360.451 0.506
1463.598 4.337
1376.898 1.247
721.415 0.177


b

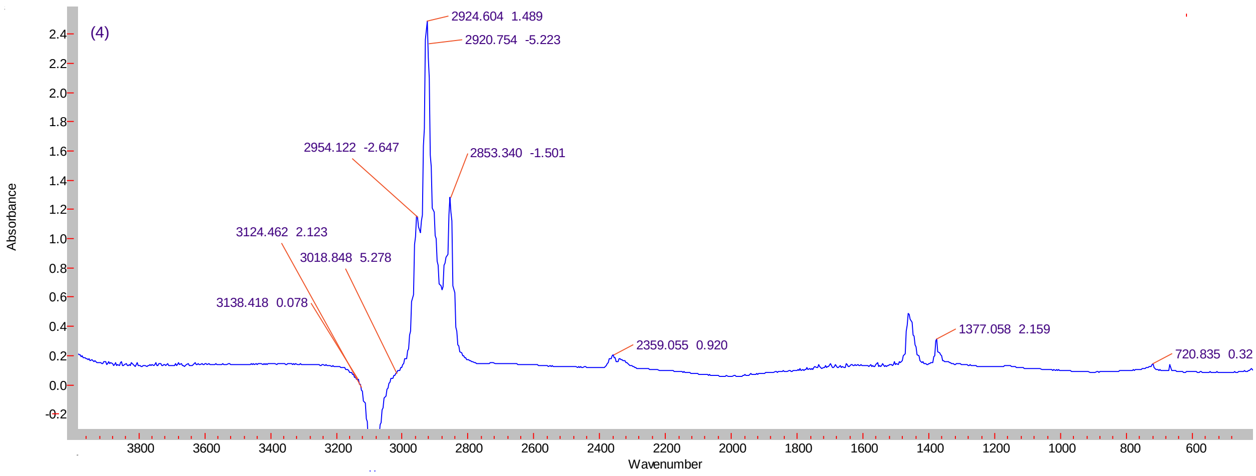


(3)
Absorbance
Wavenumber
2920.953 -5.172
2923.136 0.116
2954.099 1.526
2853.294 9.206
3111.486 0.019
3069.639 0.043
3055.559 0.126
3868.385 0.032
3861.145 0.018
3852.171 0.054
3734.950 0.036
3798.733 0.024
3628.863 0.021
3709.917 0.029
2357.459 0.017
1992.174 0.021
1684.020 0.038
1653.425 0.038
1558.988 0.039
1506.857 0.042
1377.068 1.274
721.375 0.275
668.340 0.052


c




d




e

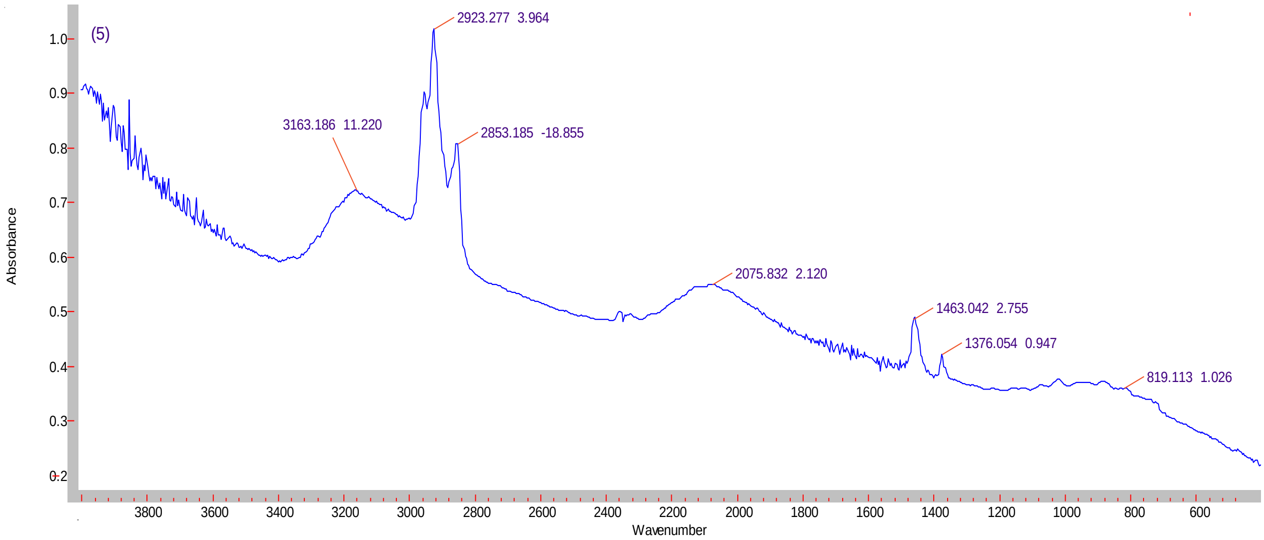
*Fig. 2. FT-IR spectra of crude oill (a); crude oil +0,01 wt.% $Al_2O_3$ (b); crude oil+0,05 wt.% $Al_2O_3$ (c); crude oil + 0,1%wt. $Al_2O_3$ (d); crude oil +1% wt.$Al_2O_3$ (e)*

In the IR spectra of modified crude oil, obtained by mixing of petroleum with $Al_2O_3$ nanoparticles (where the concentration of $Al_2O_3$ nanoparticles content 0,01wt.%) several changes have been observed. Comparative analysis of the infrared absorption spectra between crude oil and nanostructured petroleum allows to say the following:

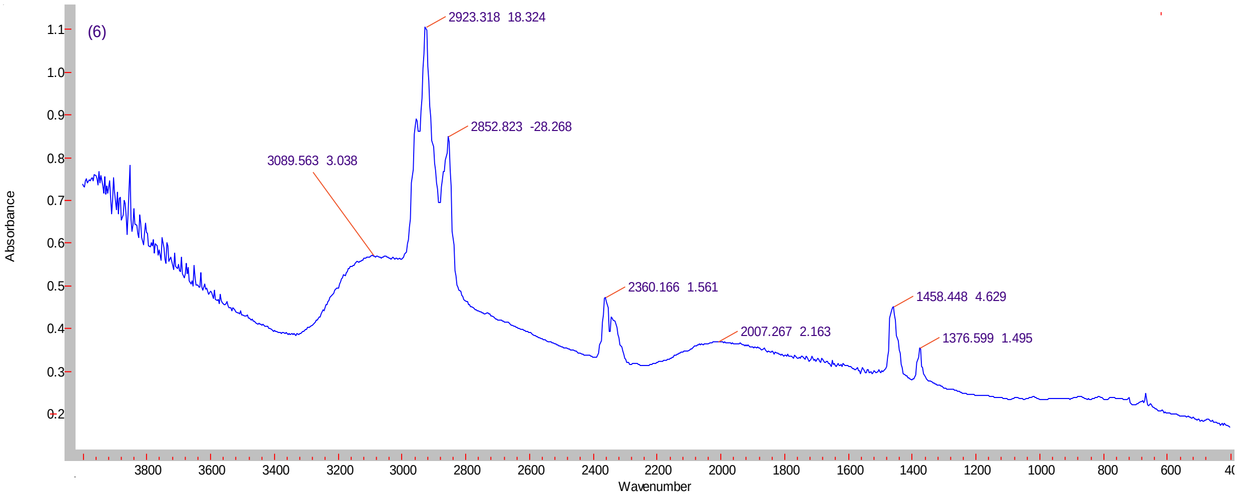
1. There is no change in the frequency value of maximums in the range 4000-400 $cm^{-1}$ which corresponds to the absorption frequencies of methyl ($CH_3$) and methylene ($CH_2$) groups, which is the functional structure of substances (petroleum and nanocomposites). New absorption bands maximums are not observed.
2. Simultaneously with increasing absorption coefficient of nanostructured crude oil, changing takes place in the intensity ratio of methyl/methylene groups. The ratio $CH_2$: $CH_3$ was 5,2:1 in petroleum, but this value after nano-impact decreases by 2,1:1. It means that the amount of $CH_3$ groups in nanostructured petroleum, increases by 2-2,5 times, after interaction $Al_2O_3$ nanoparticles with oil's hydrocarbons.

The change of intensity ratio of methyl and methylene groups in nanosystems confirms that $Al_2O_3$ nanoparticles interacted with hydrocarbons of petroleum, consequently nanostructuring takes place in the presented sample (figure 2). It was found that with the impact of small amounts of nanoparticles (in the range of 0,01-0,05 wt.%) on crude oil re-grouping process took place in a certain part of hydrocarbons. With the increase of the concentration of $Al_2O_3$ nanoparticles the change of absorption bands' intensities corresponding to $CH_2$ and $CH_3$ groups are not observed. New characteristic bands were not found in the IR spectrum of the nanostructured hydrocarbons. However, the stretch vibrations of the -C = C- absorption at 3070 $cm^{-1}$ band, which characterizes aromatics, with the increase of concentration of $Al_2O_3$ nanoparticles from 0,1 till 1,0 %, the vibration of the bands disappeared in comparison with the spectrum of initial crude oils. The surface properties of modified hydrocarbons were confirmed by FTIR spectroscopy and showed that noncovalent interaction occurred between nanostructures and hydrocarbons. Bader's theory of atoms in molecules has been invoked to characterize the noncovalent interactions of saturated and unsaturated cyclic hydrocarbons [11]. An interesting observation is that the binding affinity of saturated is higher than the aromatics, the saturated molecules bind more strongly than the unsaturated cyclic hydrocarbons toward nanoparticles. The $\pi - \pi$ stacking interactions of aromatic molecules with nanostructures are central in explaining this case. It should be noted however the noncovalent interactions, such as cation$-\pi$, $\pi - \pi$, and CH·$\pi$ with metal are taking into account. Based on the results of spectral analysis, we can conclude that with the addition of more than 0,05 % $Al_2O_3$ nanoparticles, the modification of hydrocarbons stopped and the decomposition process began, that leading to "ring-opening reaction", therefore the -C=C- absorption at 3070 $cm^{-1}$ band disappeared. The correlation between concentration of nano $Al_2O_3$ nanoparticles and change of absorption bands of methyl ($\nu_s$ = 2923 $cm^{-1}$) and methylene ($\nu_s$= 2853 $cm^{-1}$) groups in nanosystems confirms that the ratio of $CH_2$: $CH_3$ reaches maximum value, when the concentration of $Al_2O_3$ nanoparticles is 0,01 wt.%, and by increasing concentration this value decreases. This value becomes invariable when the concentration of $Al_2O_3$ nanoparticles is 0,01-0,05 wt.% in nano compounds.

The IR absorption spectra analyses of irradiated petroleum samples show that aromatic hydrocarbons in crude oil are stable toward γ- radiation in 0.86÷8.64 kGy doses range (Figure 3). As can be seen from figure 3 the stretch vibrations of the -C = C- absorption at 3089 and 3163 $cm^{-1}$ band, which characterizes aromatics, didn't break down under ionizing radiation. For demonstration the spectra of oil sample at 8,64 kGy is shown in Fig. 3.




**a**




**b**

*Fig. 3. IR spectra of the original petrol (a) from oilfield of Gunashli at room temperature; (b) IR spectra after the influence of the gamma-radiation on petrol at 8.64 kGy doses at room temperature*

## 4. Conclusions

- It has been established that CuO nanoparticles remain neutral concerning transformation in petroleum's hydrocarbons structure, but decomposition takes places in presence of $Fe_2O_3$ nanoparticles.
- It was determined that nanostructuring takes place in petroleum, with 0,01 - 0.05 wt.% $Al_2O_3$ nanoparticles. When $Al_2O_3$ nanoparticles concentration is over 0, 1 wt.%, crudes' hydrocarbons behave as a reducing agent.
- IR spectrums revealed that $Al_2O_3$ nanoparticles performed as a hybrid catalyst in the modification of crude oil. Both nanoparticles: $Al_2O_3$ and $Fe_2O_3$ performed as an oxidizing agent.
- It was determined the dual properties of $Al_2O_3$ nanoparticles; their presence leads to surface modification of petroleum, on the other hand, cause cracking of hydrocarbons.
- Unsaturated cyclic hydrocarbons in crude oil are stable toward radiation. But saturated hydrocarbons are stable toward nanoparticles.

## *References*


1. Hood A., Gutjahr C.C.M., Heacock R.L. Organic metamorphism and the generation of petroleum. The American Association of Petroleum Geologist Bulletin.1975, V59(6), p.986-996.
2. Ismayilova M.K. Review of scientific literature on the role of radiation and clay in the petroleum generation. Journal of Radiation Research,2017,volume 4, №2.p.66-72
3. Mustafayev I.I., Ismayilova M.K. Review: the role of radiation, Fe (III) oxides and montmorillonite in organic metamorphism. Journal of Radiation Research, 2018, volume 5, №1.p.40-46
4. Jaber Taheri-Shakib, Ali Shekarifard, Hassan Nader. Heavy crude oil upgrading using nanoparticles by applying the electromagnetic technique. Fuel, 2018, Vol.232(15),pp 704-711.

5. Yu.V.Larichev, O.N.Martyanov. The dynamics of asphaltene aggregates in heavy crude oils on a nanometer scale studied via small-angle X-ray scattering in situ. Journal of Petroleum Science and Engineering.2018. Vol. 165. pp. 575-58.
6. Shamilov V.M., Gadzhieva N.M., Babayev E.R., Ismayilova M.K. İnvestigation of the effect of nanoparticles on nanosystems' rheological parameters. Austrian Journal of Technical and Natural Sciences, 2014, № 11-12, pp. 24 -27.
7. Pat. I 20015 003103 AR / Shamilov V.M., Ismayilova M.K., C 09D 171/02 B82B 1/00,03.06.2015.
8. Mahmudov H.M, Ismayilova M.K.,Gadzhieva N.N.,Melikova S.Z. Study of the impact of $Al_2O_3$ nanoparticles on an aqueous solution of carboxymethyl cellulose (CMC). J. European Science Review, 2015 ,№ 9-10, pp.30-32
9. CORDIS. NMBP-01-2016 - Novel hybrid materials for heterogeneous catalysis
10. Yadali Jamaloei, B, Kharrat, R: The performance evaluation of viscous-modified surfactant water flooding in heavy oil reservoirs at varying salinity of injected polymer-contained surfactant solution. Iran. J. Chem. Chem. Eng 2012, 31(1), pp. 99–111.
11. Deivasigamani Umadevi and G. Narahari Sastry. Saturated vs. unsaturated hydrocarbon interactions with carbon nanostructures.Front Chem.2014,2,75.

## ВЛИЯНИЕ γ - КВАНТА И НАНОЧАСТИЦ CuO, $Al_2O_3$, $Fe_2O_3$ НА ТРАНСФОРМАЦИИ СЫРОЙ НЕФТИ: РОЛЬ КОНЦЕНТРАЦИОННОЙ И СТРУКТУРНЫХ ЭФФЕКТОВ

**М.К. Исмаилова, Ф.Н. Нурмамедова, С.М. Алиев**

***Резюме:*** В настоящей работе исследованы трансформации сырой нефти наночастицами оксида металла. В статье была изучена зависимость между структурой и свойствами. Влияние наночастиц CuO, $Al_2O_3$, $Fe_2O_3$ на модификации структуры нефти исследовали методом спектроскопии FT-IR. SEM изображения, также показали структуру наночастиц оксидов. Выявлено, что изменение структуры углеводородов сырой нефти происходит с наночастицами $Al_2O_3$, $Fe_2O_3$, а с наночастицами CuO без изменения. Настоящее исследование посвящено сравнительному анализу взаимодействий различных ациклических и циклических углеводородов как в насыщенной, так и в ненасыщенной формах с различными наноструктурами. Полученные результаты объясняются при помощи супрамолекулярного подхода. Исследовалось также влияние наночастиц на алифатические и ароматические углеводороды сырой нефти при воздействии гамма-облучения и было установлено, что ароматические углеводороды в нефти устойчивы к радиационному облучению.

***Ключевые слова:*** **с**ырая нефть, поверхностная модификация**,** углеводороды, трансформация, γ-радиация, наноструктуры

## γ – ŞÜALANMA və CuO, $Al_2O_3$, $Fe_2O_3$ NANOHİSSƏCİKLƏRİN XAM NEFTİN TRANSFORMASİYASINA TƏSİRİ: KONSENTRASİYA VƏ STRUKTUR EFFEKTİNİN ROLU

**M.K. İsmayılova, F.N. Nurməmmədova, S.M. Əliyev**

***Xülasə:*** Təqdim edilmiş işdə xam neftin metal oksid nanohissəciklərlə γ-şüalanmanın təsiri altında çevrilmə prosessi öyrənilmişdir. Bu məqalədə nanohissəciklərin struktur və xassələri arasındakı asılıq müəyyən edilmişdir. CuO, $Al_2O_3$, $Fe_2O_3$ nanohissəciklərin iştirakı ilə baş verən üstmolekulyar strukturlaşmanın təsiri FT-IR spektroskopiya üsulu ilə tədqiq edilmişdir. Metal oksid nanohissəciklərinin strukturu SEM-də müəyyən edilmişdir. Xam neftin karbohidrogen strukturunda dəyişiklik $Al_2O_3$, $Fe_2O_3$ nanohissəciklərin təsirilə meydana gəldiyi halda, CuO nanohissəcikləri neftin transformasiyasında iştirak etmir. Karbohidrogenlərin səthi modifikasiyasına nanohissəciklərin konsentrasiyasının rolu tədqiq edilmişdir. Tədqiqatlarda alifatik və aromatik karbohidrogenlərə müxtəlif nanostrukturların təsirləri müqayisəli şəkildə təhlil edilmişdir. Alınan nəticələr süper molekulyar yanaşma ilə açıqlanır. Eyni zamanda xam neftin gamma-radiasiyanın təsiri altında transformasiyası tədqiq edilmiş və neftdə aromatik karbohidrogenlərin radiasiyaya məruz qalmadığı müəyyən edilmişdir.

***Açar sözlər:*** xam neft, səthi modifikasiya, üstmolekulyar strukturlaşma, karbohidrogenlər, transformasiya, $\gamma$ –radiasiya, nanoctrukturlar