



INVESTIGATION OF LIQUID-PHASE OXIDATION OF NAPHTHENE-PARAFFINIC HYDROCARBONS OF BALAKHANY OIL

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ABSTRACT

Liquid-phase aerobic oxidation of naphthene-paraffinic hydrocarbons at 217-330° C of diesel fraction of Balakhany oils in the presence of the mixtures of Mn, Cr salts of natural petroleum acids (MeNPA) has been investigated. The catalytic oxidation process is realized for 7 hours at temperature 135-140°C in a barbotage reactor. Samples were taken every hour and oxidized product was separated by composition in accordance with known methods. Mechanism of oxidation process of naphthene-paraffinic hydrocarbons has been studied by IR- spectroscopy. It has been found that, after 5 hours oxidation of naphthene-paraffinic hydrocarbons the yield of obtaining synthetic petroleum acids rich 16,5%, the yield of oxysynthetic petroleum acids-18%. The changes of the optical density of a carbonyl and a hydroxyl groups depending on the time were studied. It was found that the oxidation reaction should be conducted within 6 hours, as $D_{1713}(C=O)$ and $D_{941}(OH)$ after 6 hours decrease and it's probably connected with beginning decomposition process of the acids and oxyacids.

KEYWORDS: diesel fraction, petroleum hydrocarbons, liquid-phase oxidation, catalysts of oxidation, synthetic and oxysynthetic petroleum acids

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1. INTRODUCTION

Oxidative conversion of petroleum hydrocarbons in oxygenated products is one of the effective ways of rational processing of natural hydrocarbons.

It may be noted, in particular, the studies of the catalytic oxidation of petroleum paraffinic fraction [1], oil fraction from the oil with low and high sulfur and aromatics content [2], naphthene and naphthene-paraffinic hydrocarbons of oil [3-6].

The oxidizing transformation of petroleum hydrocarbons to afford respective oxygen containing compounds is estimated as effective approach to the rational processing of oil hydrocarbons raw stock [7]. A special place have synthetic and oxysynthetic petroleum acids (SPA и OSPA) among the products of oxidative expansion of petroleum hydrocarbons .

Synthetic petroleum acids (SPA, including oxyacids, OSPA) obtained by this type of hydrocarbons oxidation are welcomed to be full-fledged substitutes for naturally occurring petroleum acids. SPA are widely used in the preparation of corrosion inhibitors, desiccants, homogeneous catalysts, surface - active detergents, softeners, emulsifiers, bactericides, additives for fuels and many other substantially beneficial products [8]. Thus, the growing demand to oil acid and at the same time the limited natural resources, as well as the fact that they exist in the form of complex mixtures, makes the production of synthetic petroleum acids relevant and important. It is known that oxidation of naphthene-paraffinic hydrocarbons of petroleum fractions is the most promising way of synthesis synthetic petroleum acids [4-7]. The works on creation of new selective catalysts possessing high activity for oxidation of oil fractions are continuing. Thus, the synthesis of the SPA with a high-yield is of a great practical importance, and accordingly we involve a naphthene-paraffinic hydrocarbons of Azerbaijan oil blend as a major research object to conduct the research work to obtain the targeted products.

Qualitative methods, such as acid and etheric number are used to study the oxidation of naphthene-paraffinic hydrocarbons. However, it is impossible to investigate oxidation laws of fractions on different stages using these methods. Selected samples were investigated by IR- spectroscopy, which is the most informative in the study of the oxidation process for a more detailed study of the processes occurring during the oxidation of naphthene-paraffinic hydrocarbons.

This work has been devoted to the aerobic oxidation of naphthene-paraffinic hydrocarbons in the presence of Mn and Cr salts of natural petroleum acids (NPA). The aim of work is to achieve higher parameters of synthesis of SPA and OSPA by special preparation of the catalysts and investigation of the mechanism of oxidation process.

2. MATERIALS AND METHODS

The diesel fraction of Balakhany oil was used in the feedstock oxidation, which was previously dearomatized [4]. The diesel fraction (DF) mentioned below boiled in 217-330°C is purified from aromatic hydrocarbons and sulfur compounds content by extraction method and obtained positive results. The n-methyl pyrrolidon (NMP) has been used as an extractant. Defined that the amount of aromatic hydrocarbon in the content of fraction decreases from 16% nearly to 1 % by taking NMP:df=4:1. Some physical-chemical indices of the diesel fraction of Balakhany oil before and after the extraction have been determined and presented in Table 1.

Table 1. Physical-chemical indices of the diesel fraction before and after the extraction

Indices	Diesel fraction	
	Before extraction	After extraction
Molecular weight, M_w	216.8	210
Density, ρ_4^{20} , kg/m ³	848.1	834.8
Refraction coefficient, n_D^{20}	1.4704	1.4640
Kinematic viscosity, at 20°C, mm ² /s	3.61	3.39
Freezing temperature, °C	< minus 60	<minus 65
Boiling temperature, °C	217-330	225-320
Acid number (A.n.), mgKOH/g	2.3	-
Iodine number, at 100 g fuel, qJ ₂	1.04	0.39
Amount of sulfur, % wt.	0.5560	0.0088
Amount of the aromatic hydr., % wt	~16	1



IR-spectra samples were recorded on a FT-IR spectrometer ALPHA (company BRUKER, Germany) in the range of wave frequencies of 600-4000 cm^{-1} . Assignment of the bands obtained spectra was carried out as described in [9].

The IR- spectrum of the diesel fraction of Balakhany oil after dearomatization shows absorption band at 728 cm^{-1} , responsible for the pendulum vibration of the C-H bond in $-\text{CH}_2$ groups, as well as - deformation vibration at 1375 cm^{-1} and valence vibrations at 2856, 2925 cm^{-1} , which is characteristic of C-H bond in the methyl group. Absorption band of deformation at 1458 cm^{-1} and the valence vibrations at 2920 cm^{-1} , correspond to a C-H bond in the methylene group. The spectrum contains absorption bands at 962, 1029 cm^{-1} , related to the deformation vibrations of C-H bonds in naphthenes $-\text{CH}_2$ groups.

The catalytic oxidation process is realized for 7 hours at temperature 135-140 $^{\circ}\text{C}$ in a barbotage reactor. Samples were taken every hour and oxidized product was separated by composition in accordance with known methods. The construction of a reactor and principle of its work are presented in work [10]. The acid number (A.n.) of the oxidation products were determined according to the standard conventional methods [11]. Mn and Cr salts of natural petroleum acids (MnNPA, CrNPA) were employed as catalyst. The Mn and Cr salts of NPA have been synthesized from sodium salt of NPA by exchange reaction [12].

3. RESULTS AND DISCUSSION

The results of time dependence of oxidation process of naphthene-paraffinic hydrocarbons in the presence of MnNPA, CrNPA are presented in table 2.

Table 2. The results of time dependence of oxidation process of naphthene-paraffinic hydrocarbons (catalysts- CrNPA:MnNPA=3:1=0.2% weight)

Time, hour	example	Acid number of oxidate, mgKOH/g	Yield, %		Acid number, mgKOH/g	
			OSPA	SPA	OSPA	SPA
2	1	33	1.4	2.5	98.5	100.8
3	2	52	5.3	8	102.6	115.8
4	3	60	8.7	10	118.6	120.9
5	4	68	18	16.5	130	158
6	5	70	24.8	10.8	131.6	159.2
7	6	71	30	5.8	132	159.8

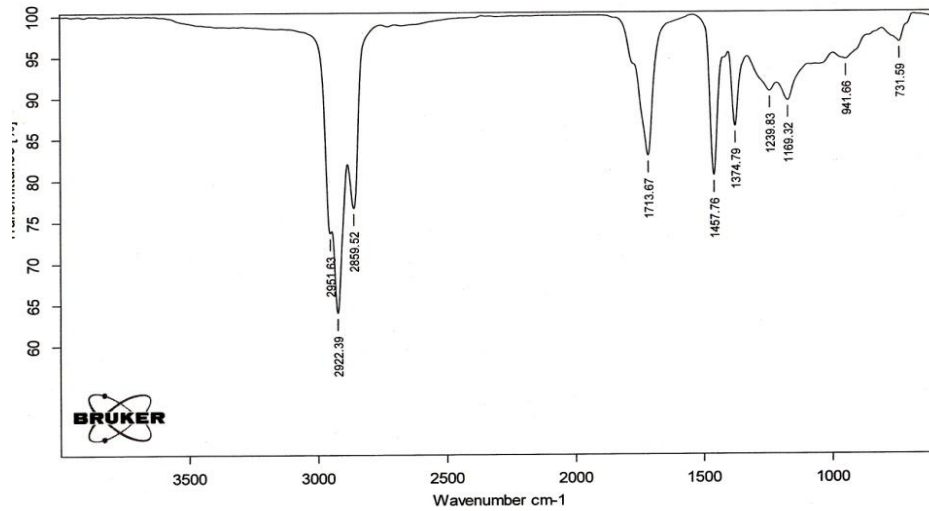
The table shows that when the process of oxidation is carried out within 5 hours, the results are more accurate. Thus, the yield of obtained SPA after 5 hours is 16.5%, yield of OPA is 18% (32.5% yield of a mixture of SPA + OPA). Acid number of obtained acid rises to the maximum extent. Despite the fact that the yield of acids mixture is high in 6th hour (~ 35%), yield of SPA is decreases, yield of OPA is increases. On the other hand, acid number of the obtained acids changes in a small amount. The yield of a mixture of SPA and OPA (~ 35%) and acid number almost remains unchanged in the 7th hour. Thus, the process is not advisable to continue for 7 hours, because it would be directed towards to produce by-products.

Depending on the time the changes of optical density of carbonyl and hydroxyl groups were studied for investigation of kinetics of oxidation of naphthene-paraffinic hydrocarbons. The optical densities of absorption bands [13] describing the vibrational motion of the diesel fraction of Balakhany oil after dearomatization and after oxidation in the 900-1800 cm^{-1} : at 730 and 1457 cm^{-1} – CH_2 group, at 941 cm^{-1} -OH group, at 1713 cm^{-1} - C = O group (acid) was calculated by the equation:

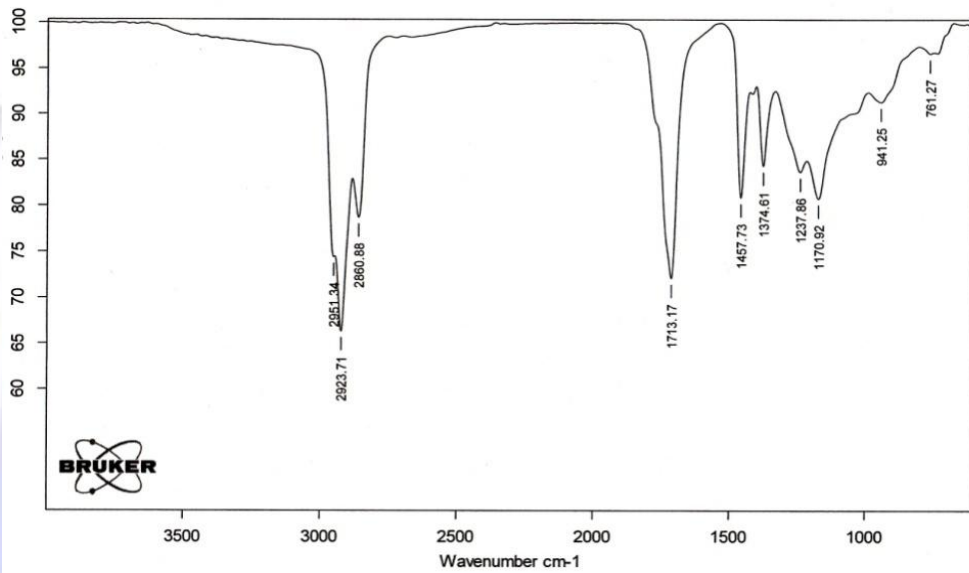
$$D = \lg \frac{I_0}{I},$$

where D - optical density, I_0 – the intensity of incident light, I - intensity of the transmitted light.

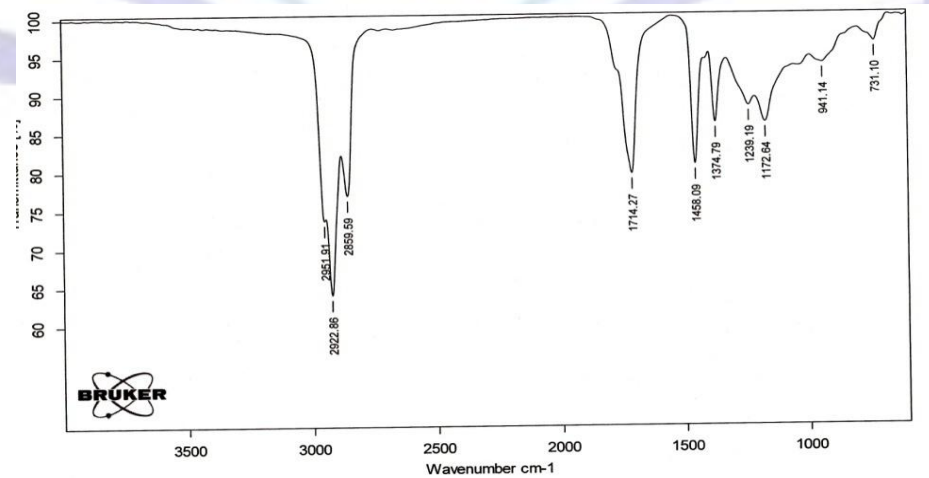
Samples were taken every hour and recorded their infrared spectra for the study the oxidation process (fig.1). In the sample №1 IR- spectrum the peaks are observed at 941 and 1713 cm^{-1} , respectively, are responsible for vibrations in hydroxyl and carbonyl groups of acid. Acid formation was studied by the accumulation of hydroxyl and carbonyl groups by increasing reaction time.



a)



b)



c)

Fig.1. IR spectra of samples: a) IR spectra of oxidate after 2 hours of oxidation; b) IR spectra of oxidate after 5 hours of oxidation; c) IR spectra of oxidate after 7 hours of oxidation



Changes in the optical density of the reaction time appropriate functional groups in the samples are presented in Table 3.

Table 3. Optical density of some functional groups and acid number of SPA, OSPA

Example	$D_{730}(\text{CH}_2)$	$D_{1457}(\text{CH}_2)$	$D_{1713}(\text{C}=\text{O})$	$D_{941}(\text{OH})$	A.N of SPA, mgKOH/g	A.N of OSPA, mgKOH/g
Raw material	0.026	0.104	-	-	-	-
1	0.015	0.094	0.081	0.024	100.8	98.5
2	0.015	0.092	0.102	0.030	115.8	102.6
3	0.015	0.093	0.131	0.037	120.9	118.6
4	0.015	0.093	0.142	0.039	158	130
5	0.015	0.092	0.154	0.043	159.2	131.6
6	0.015	0.093	0.099	0.028	159.8	132

The peak at 1713 cm^{-1} is observed during the oxidation of naphthene-paraffinic hydrocarbons, and responsible for the valence vibrations of the carbonyl group, which increases by time. It was found that the oxidation reaction should be conducted within 6 hours, because $D_{1713}(\text{C}=\text{O})$ and $D_{941}(\text{OH})$ decrease after 6 hours and it's probably connected with beginning decomposition process of SPA and OSPA. This absorption band can serve as an objective criterion for characterizing the depth of oxidation of naphthene-paraffinic hydrocarbons. The absorption band of the carbonyl group in the IR-spectrum is complex, and its intensity at the maximum of 1713 cm^{-1} is qualitative characteristic for the overlapping bands and, consequently, reflects the total content of carbonyl compounds. However, based to the acid number and yield of the acids which have been obtained from oxidation process can be noted that the amount of SPA after 5 hours, and the amount of the OSPA after 6 hours reached to maximum. Thus, to direct reaction for obtaining the SPA reaction would be continue 5 hours, to direct for obtaining OSPA-6 hours. Based on optical density and acid number can be noted that it is not reasonable to extend reaction for 6 hours.

Dependence of the value of carbonyl group (related to acid) optical density from time is presented in figure 2.

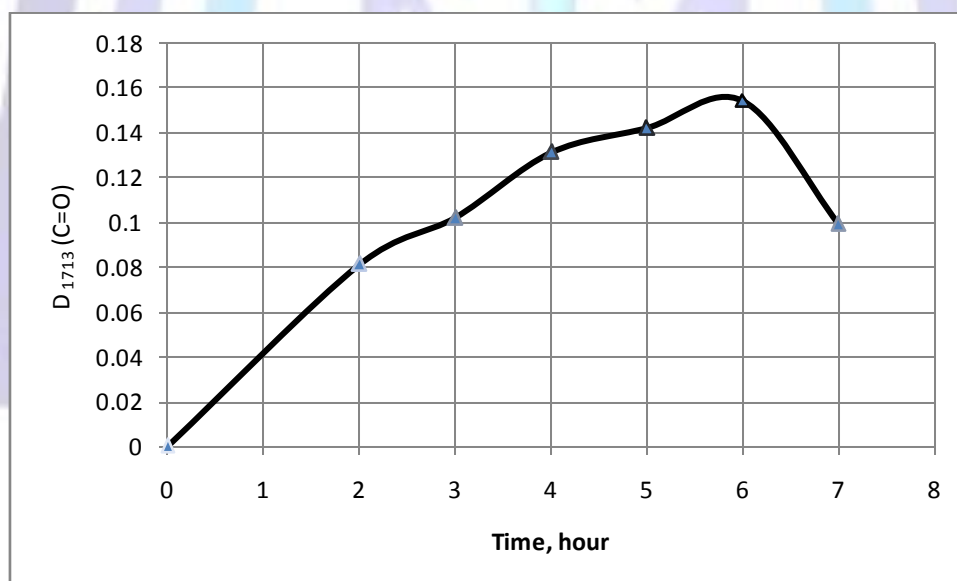
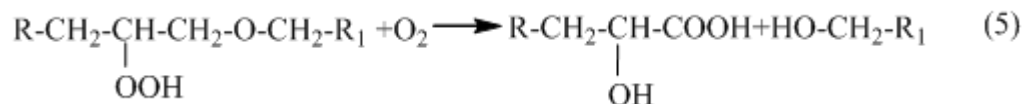


Fig. 2. The time dependence of the optical density of carbonyl group

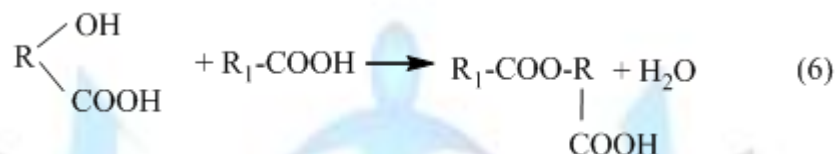
The figure shows that in the oxidation of naphthene-paraffinic hydrocarbons accumulation of oxygen-containing products is increasing over the time. The optical density at 1713 cm^{-1} and 941 cm^{-1} increases with the first hour, but after the 6th hour begins to decrease. The appearance of the absorption bands of weak intensity at $1731, 941\text{ cm}^{-1}$ in the spectra of naphthene-paraffinic hydrocarbons gives the reason to conclude that after oxidation due to rupture of $\alpha\text{-C-H}$ bonds radical are formed. Interaction between this radical with molecular oxygen leads to the formation of peroxide radicals, which recombination produces a molecular products of the reaction [14]:



In the next step radical R^\cdot continues oxidation process of naphthene-paraffinic hydrocarbons by atmospheric oxygen. Thus, as a result of collapse of hydroperoxide obtained SPA. We should note that the aldehydes, alcohols and ketones are major intermediates in the SPA preparation. With the passage of time by the peroxidation of oxygenate products, the formation of oxyacids is possible:



Unfused ether acids can be formed by etherification of carboxylic acids with hydroxide of hydroxyacids:



Double esters may form while condensation of two molecules of α -hydroxy acids. These oxidation reactions of organic substrates is a base.

So, after 5 hours of oxidation process flow direction was (4) and SPA output is maximal, after 6 hours -flow direction was (5), and since the seventh hour flow change direction to (6). The obtained results based on the reaction equations and IR-spektra of the samples was coincide.

4. CONCLUSION

The naphthene-paraffinic hydrocarbons of Balakhany oil has been oxidized in the catalytic presence of Mn and Cr salts of natural petroleum acids (NPA). It has been found that, after 5 hours oxidation of naphthene-paraffinic hydrocarbons the yield of obtaining synthetic petroleum acids rich 16,5%, the yield of oxysynthetic petroleum acids - 18%. IR- spectroscopy allows us to study the oxidation of naphthene-paraffinic hydrocarbons, and mostly its initial stages, in which is dominated radicals. The changes of the optical density of a carbonyl and a hydroxyl groups depending on the time were studied. It was found that within 5 hours of oxidation process flow direction was (4) and yield of the SPA is maximal, after 6 hours -flow direction was (5), and since the seventh hour flow change direction to (6).

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