

# Determination of optimal parameters for obtaining synthetic oil acids and oxyacids mixture from the catalytic oxidation of naphthene-paraffinic hydrocarbons of diesel distillation

L.I. Aliyeva, L.M. Afandiyeva, L.H. Nuriyev, F.M. Valiyeva

Azerbaijan National Academy of Sciences  
 Yu.H. Mamedaliyev Institute of Petrochemical Processes

## Abstract

The article deals on oxidation of the mixture of naphthene-paraffinic hydrocarbons emitted from the fraction of Azerbaijan oils boiling at 217-349°C, with the air oxygen in the presence of Cr and Mn salts of natural oil acids and the mixture of their different proportions. Dependence of the yield of the obtained synthetic oil acids and oxyacids on the concentration of catalyst, temperature and time has been studied. The optimal parameters of the synthetic oil acids and oxyacids have been determined and the optimal regime selected.

**Key words:** diesel fraction, oxidation process in liquid phase, oxidation catalysts, synthetic petroleum acids, optimization process

## 1. Introduction

Natural petroleum acids (NPA) have a wide application area and a significant role among the compounds of valuable raw materials of petrochemical industry. Though NPA and its derivatives have been used in different directions, according to the less amount of these acids in oil composition they include a limited number of products of petrochemical industry. One of the ways for the solution of this limitation is the conversion of naphthenic hydrocarbons to the acid, that's to say, obtaining petroleum acids by synthetic method. One of more perspective methods for the synthesis of synthetic petroleum acids (SPA) is the catalytic oxidation of diesel fraction of oil in liquid phase in the presence of oxygen.

## 2. Experimental / Methodology

For this purpose, the fractions of Azerbaijan oil boiling up to 217-349°C have been taken as the research object. The fraction has been dearomatized and the mixture of naphthene-paraffinic hydrocarbons, obtained as a result of the process, has been oxidized with air oxygen in the presence of Cr, Mn salts of NPA [1-4]. Some physical-chemical properties of diesel fractions, before and after dearomatization are presented in Tab. 1.

**Table 1.** Physical-chemical properties of diesel fractions before and after dearomatization

Indicators	Diesel fraction	
	Before dearomatization	After dearomatization
Molecular weight, $M_w$	225	200
Density, $\rho_4^{20}$ , kg/m <sup>3</sup>	842	835.9
Refraction coefficient, $n_D^{20}$	1.4677	1.4638
Kinematic viscosity, 20°C-də, mm <sup>2</sup> /s	5.71	5.52
Freezing temperature, °C	minus 41.4	minus 51
Boiling temperature, °C	217-349	220-340
Acid number, mgKOH/g	1.73	-
Iodine number, at 100 g fuel, gJ <sub>2</sub>	2.25	-
Amount of sulfur, % wt	0.0936	0.03
Amount of aromatic hydrocarbons, % wt	~17-18	1
Amount of paraffine h/c, % wt	28.48	5-6
Amount of naphthene-isoparaffinic h/c, % wt	54.2	93-94

Then, dearomatized diesel fraction has been oxidized in the presence of Cr, Mn salts of NPA, air speed 300 l/kg-hour, in different temperature intervals, during 5-7 hours and there has been obtained the mixture of synthetic petroleum acids (SPA) and synthetic oxyacids (OSPA).

## 2. Results and discussion

The results of oxidation process in the different concentrations of Cr and Mn salts are presented in Tab. 2.

**Table 2.** The results of oxidation process of naphthene-paraffinic concentration with the catalytic presence of Mn and Cr-salts (t=135-140°C, the air speed 300 l/kg-hour, the reaction time - 5 hours)

	Concentration of catalyst, % wt	Oxidate		SPA		OSPA	
		Acid number, mgKOH/g	Yield, %	Acid number mgKOH/g	Yield, %	Acid number mgKOH/g	Yield, %
Cr salt	0.2	59.5	97.1	132.8	23	105.8	8.9
	0.3	53.8	97	131.4	18.4	112.2	8
	0.5	56.9	95.6	140.6	16.2	115.9	13.1
	0.7	53.5	95.4	140.2	15.4	118.7	10
	1	50.8	97	133.4	15	116.4	7.2
Mn salt	0.2	40.1	95.8	130.7	10	119	5.2
	0.3	36.9	96	131.1	12.5	112.4	3
	0.5	39.4	97.4	130	13.6	109	5.2
	0.7	40	95.8	135.2	15.1	112.6	4.3
	1	42.4	95.5	137.8	17.4	115.5	4.5

As is seen from Tab. 2, the loss is less during the process. Because oxidate yield is ~ 96-97%. While considering of the influence of Cr and Mn catalysts on the oxidation process, it seems that, the effect of Cr salt taken in the range of 0.2-1% concentration is higher than Mn salt. In case of Cr-salt, the yield of SPA on average – 17.6%, the yield of OSPA is – 9.44%; the yield of SPA for Mn salt-13.72%, yield of OSPA is- 4.4%.

On the basis of experimental data the statistical model of the process has been compiled. The model is based on the principle of “black box” [6] and the analytic contact between the input-output parameters has been determined. All reports have been carried out by the program “Matlab-7” used for statistical analysis and visualization of the data. The method for reporting requires the implementation of the following stages:

1. The inclusion of initial data;
2. The inclusion of output parameters;
3. The inclusion of the restrictions on input and output parameters.

For the description of mathematical process, obtained by this method it is required not only determination of optimal conditions for the implementation of the process, but also forming of optimal management and the regulation system.

Comparison of experimentally and theoretically calculated values taken by the oxidation in the presence of catalytic oxidation of Cr salt, has been presented in Tab.3.

**Table 3.** Comparison of experimentally and theoretically calculated values taken by the oxidation in the presence of catalytic oxidation of Cr salt

Concentration of catalyst, %wt	Cr salt					
	Oxidate		SPA		OSPA	
	Yield, %, exp., Y <sub>1</sub>	Yield, %, theor., Y <sub>1</sub>	Yield, %, exp., Y <sub>2</sub>	Yield, %, theor., Y <sub>2</sub>	Yield, %, exp., Y <sub>3</sub>	Yield, %, theor., Y <sub>3</sub>
0.2	97.1	97.35	23.0	22.04	8.9	8.17
0.3	97.0	96.56	18.4	19.72	8.0	9.68
0.5	95.6	95.56	16.2	16.35	1.1	11.29
0.7	95.4	95.36	15.4	14.65	10.0	11.01
1.0	97.0	96.56	15.0	15.28	7.2	7.036

$$\begin{aligned}
 Y_1 &= 99,56 - 13 * X_1 + 10 * X_1^2 \\
 Y_2 &= 27,94 - 33,7 * X_1 + 21,04 * X_1^2 \\
 Y_3 &= 3,71 + 27,026 * X_1 - 23,7 * X_1^2 \quad (1)
 \end{aligned}$$

here, X<sub>1</sub> - the amount of catalyst according to the raw materials, %; Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> – the yield of oxidate, SPA, OSPA.

The values of SPA and OSPA yields depending on the change of catalyst concentration are given in Fig. 1 and 2.

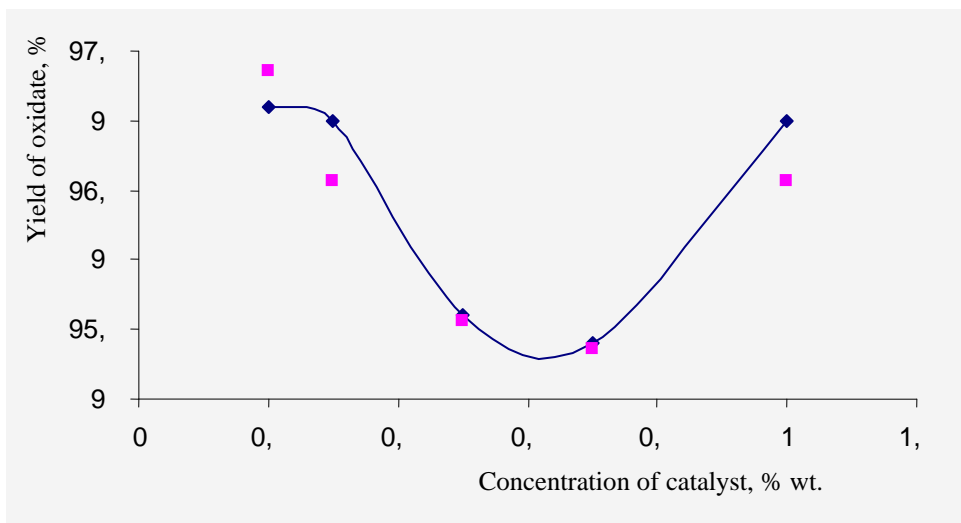


Fig. 1. Dependence of the oxidate yield of on the amount of catalyst (Cr salt) according to raw material

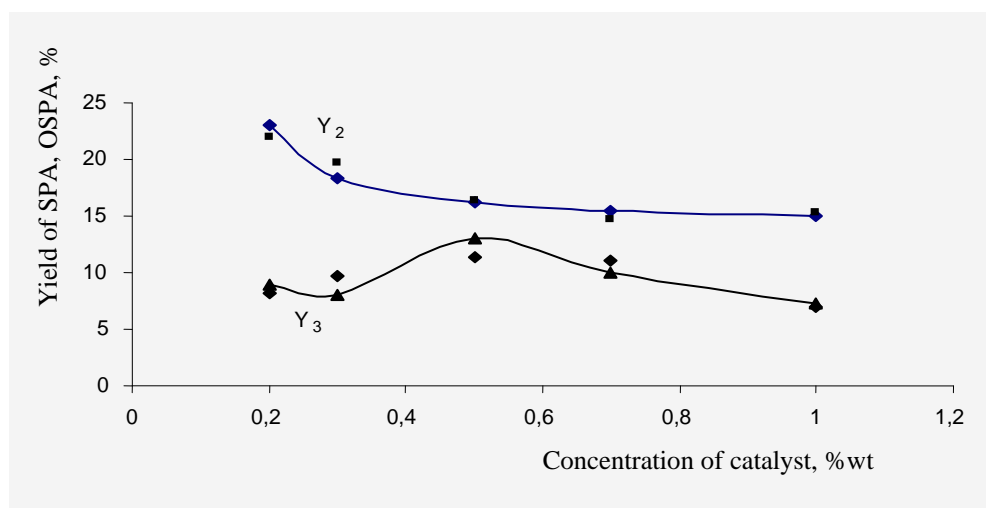


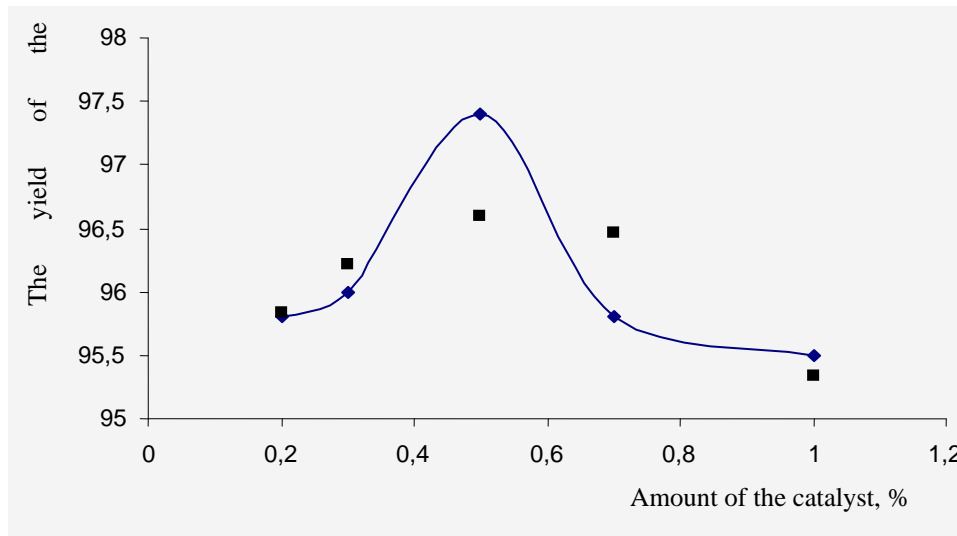
Fig. 2. Dependence of SPA, OSPA yield of on the amount of catalyst (Cr salt) according to raw material

Comparison of experimentally and theoretically calculated values taken by the oxidation process in the presence of catalytic oxidation of Mn salt has been presented in Tab. 4.

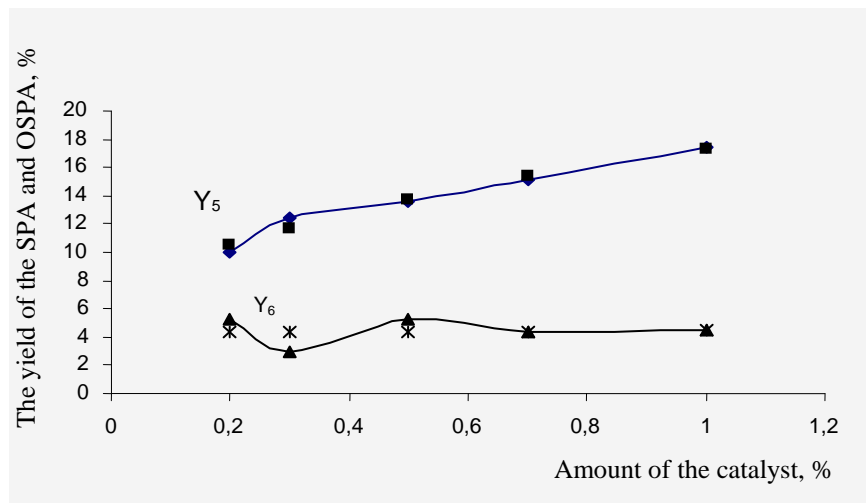
Table 4. Comparison of experimentally and theoretically calculated values taken by the oxidation process in the presence of catalytic oxidation of Mn salt

Amount of the catalyst, %	Mn salt					
	Oxidate		SPA		OSPA	
	Yield, %, exp., $Y_4$	Yield, %, theor., $Y_4$	Yield, %, exp., $Y_5$	Yield, %, theor., $Y_5$	Yield, %, exp., $Y_6$	Yield, %, theor., $Y_6$
0.2	95.8	95.83	10.0	10.54	5.2	4.41
0.3	96	96.21	12.5	11.67	3.0	4.40
0.5	97.4	96.60	13.6	13.69	5.2	4.41
0.7	95.8	96.47	15.1	15.37	4.3	4.3
1.0	95.5	95.33	17.4	17.28	4.5	4.5

$$\begin{aligned}
 Y_4 &= 94.68 + 7.03 * X_1 - 6.38 * X_1^2 \\
 Y_5 &= 8.033 + 13.4 * X_1 - 4.15 * X_1^2 \\
 Y_6 &= 4.455 - 0.2738 * X_1 + 0.3544 * X_1^2 \quad (2)
 \end{aligned}$$



**Fig. 3.** Dependence of oxidate yield on the amount of catalyst (Mn salt) according to raw material



**Fig. 4.** Dependence between the amount of catalyst (Mn salt) according to the raw materials and the yield of SPA, OSPA

The salts and complexes of variable-valent metals accelerate the autooxidation reaction of the hydrocarbons and decomposition of the hydroperoxides and it is already known in literature [5]. So that, variable valences of the salts of metals influence active as catalyst in initiation of a chain in the oxidation reaction. Each molecule of catalyst turns molecular oxidation products to the free radical by participating several times in the initiation of a chain.

In addition, in order to learn the influence of the oxidation process to the yield and quality indicators of SPA and OSPA, the catalytic oxidation reactions have been conducted in the presence of the various proportions of Cr and Mn salts. According to the raw materials, taken 0.2 % mass of the concentration of this catalysts a positive result has been obtained and they have been tested at the same concentration in the mixture form. The obtained results are presented in Tab. 5.

**Table 5.** The results of oxidation process of naphthene-paraffinic hydrocarbons in the presence of the mixture of different amounts of Mn and Cr-salts (t=135-140°C, the air speed 300 l/kg·hour, the reaction time - 5 hours)

№	Catalyst	A. N. of the oxidate, mgKOH/g	The yield of oxidate, %	SPA		OSPA	
				Yield, %	A.N. mgKOH/g	Yield, %	A.N., mgKOH/g
1	NPA Cr:NPA Mn 1:1	59.3	95.8	11	137.5	8.8	113.8
2	NPA Cr:NPA Mn 2:1	67	96	18.2	138.4	8.2	117.4
3	TNT Cr:TNT Mn 3:1	65	96.5	23.3	135.7	12.8	115.7

As is seen from the table, the best result has been taken by the 3rd example. Thus, the yield of the SPA is 23.3%, the yield of the OSPA is 8.9 %. This is the highest result compared with the other examples. Thus, during the process of oxidation in the presence of the mixture of catalysts, the third example can be considered as the best option. Comparison of Tab. 2 and Tab. 3 proves that, the results obtained (the yield of SPA+OSPA- 36.1%) in the presence of the mixture of NPA Cr:NPA Mn = 3:1 (according to the raw materials 0.2%), are higher than in comparison to Cr salt (the yield of SNT+ONT 31.9%).

Comparison of experimentally and theoretically calculated values taken by the oxidation process in the presence of catalytic oxidation of Cr and Mn salts has been presented in Tab. 6.

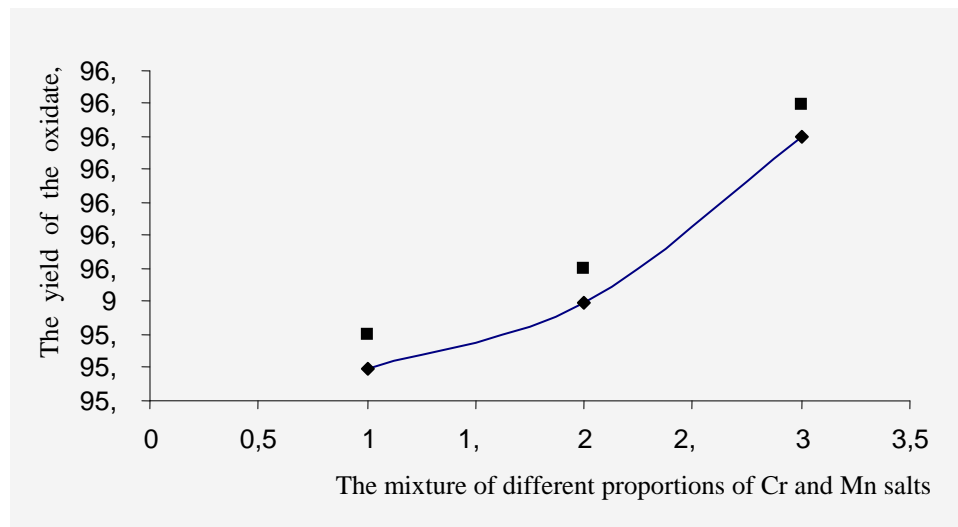
**Table 6.** Comparison of experimentally and theoretically calculated values taken by the oxidation process in the presence of catalytic oxidation of Cr and Mn salts

Catalyst	Oxidate		SPA		OSPA	
	Yield, %, exp., Y <sub>7</sub>	Yield, %, theor., Y <sub>7</sub>	Yield, %, exp., Y <sub>8</sub>	Yield, % th., Y <sub>8</sub>	Yield, %, exp., Y <sub>9</sub>	Yield, %, theor., Y <sub>9</sub>
TNT Cr:TNT Mn 1:1	95.8	96.5	11	11.5	8.8	8.97
TNT Cr:TNT Mn 2:1	96	97.2	18.2	18.6	8.2	8.15
TNT Cr:TNT Mn 3:1	96.5	96.9	23.3	23.7	12.8	13.1

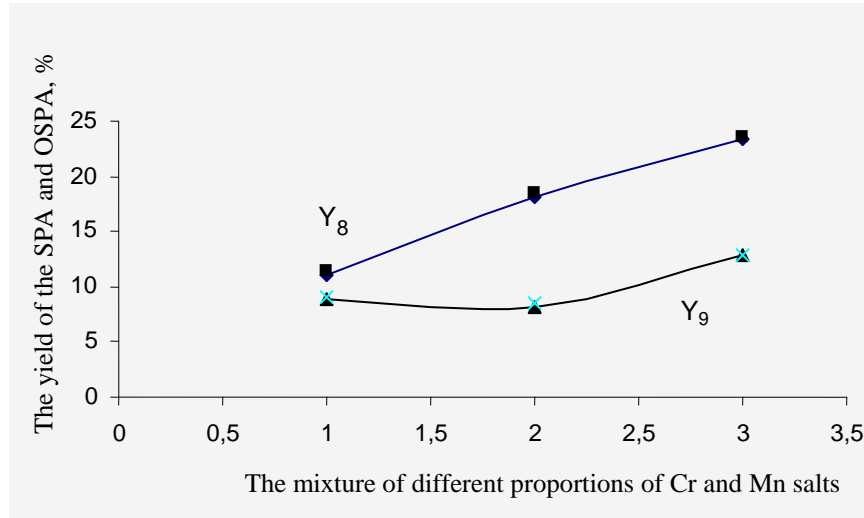
$$Y_7 = 95.9 - 0.25 * X_1 + 0.15 * X_1^2$$

$$Y_8 = 1.7 + 10.35 * X_1 - 1.05 * X_1^2$$

$$Y_9 = 14.6 - 8.4 * X_1 + 2.6 * X_1^2 \tag{3}$$



**Fig. 5.** Dependence between the mixture of different proportions of Cr and Mn salts and oxidate's yield



**Fig. 6.** Dependence of the yield of SOA v̄ ONA on the mixture of different proportions of Mn and Cr salts

Besides, according to the raw materials, when taken the mixture of Cr and Mn salts (3:1) 0.2 % mass as a catalyst in the oxidation process of naphthene-paraffinic hydrocarbons dependence of the yield and quality parameters of the obtained SPA on time have been investigated. For this purpose, oxidation process of the mixture of naphthene-paraffinic mixture has been carried out within 7 hours and by taking a sample every one hour, its yield and the acid number has been calculated. The results obtained are presented in Tab. 7.

**Table 7.** Dependence of the oxidation of naphthene-paraffin hydrocarbons in the precense of Cr and Mn salts (3:1) on time (the amount of catalyst according to the raw materials 0,2 %, temperature 135-140°C, the air consumption 300 l/kg-hour)

Reaction time, hour	A.N. of oxidate, mgKOH/g	The yield of acid, %		A.N. of acid, mgKOH/g		Water soluble acids	
		OSPA	SPA	OSPA	SPA	Yield,%	A.N, mg KOH/g
1	12.4	2	3.3	105	108.8	0.2	245.2
2	18.2	3	6.2	115.2	115.7	0.36	256
3	36.4	3.5	8.2	118.8	121	1.2	257.2
4	43.8	6	15.2	110.2	126.9	1.8	264.5
5	65	12.8	23.3	115.7	135.7	2.8	285
6	61.1	30.2	10.4	114	128	2.8	289.4
7	65	44	4.8	114.7	138.9	3	318.2

As seen from Tab. 7, more expedient results are when the oxidation process is carried out within 5 hours. Thus, when the process is conducted over 5 hours, most of SPA are becoming oxyacid and it reduces the selectiveness of the process. Therefore, the reaction time has been adopted 5 hours in conducting the oxidation process.

Comparison of experimental and theoretical calculated values of dependence of temperature on catalytic oxidation process is presented in Tab. 8.

**Table 8.** Comparison of experimental and theoretical calculated values of dependence of temperature on catalytic oxidation process

Reaction time, hour	OSPA		SPA		Water soluble acids	
	Yield, % exp., Y <sub>10</sub>	Yield, %, theor., Y <sub>10</sub>	Yield, % exp., Y <sub>11</sub>	Yield, %, theor., Y <sub>11</sub>	Yield, % exp., Y <sub>12</sub>	Yield, %, theor., Y <sub>12</sub>
1	2	2.34	3.3	3.37	0.2	0.21
2	3	2.95	6.2	6.22	0.36	0.37
3	3.5	3.6	8.2	8.35	1.2	1.32
4	6	6.29	15.2	15.76	1.8	1.89
5	12.8	12.62	23.3	23.45	2.8	2.78
6	30.2	29.99	10.4	10.42	2.8	2.82
7	44	44.1	4.8	4.67	3	3.14

$$Y_{10} = 9.87 - 8.2 * X_1 + 1.87 * X_1^2$$

$$Y_{11} = -10.2 + 11.93 * X_1 - 1.36 * X_1^2$$

$$Y_{12} = -0.84 + 0.836 * X_1 - 0.0381 * X_1^2 \quad (4)$$

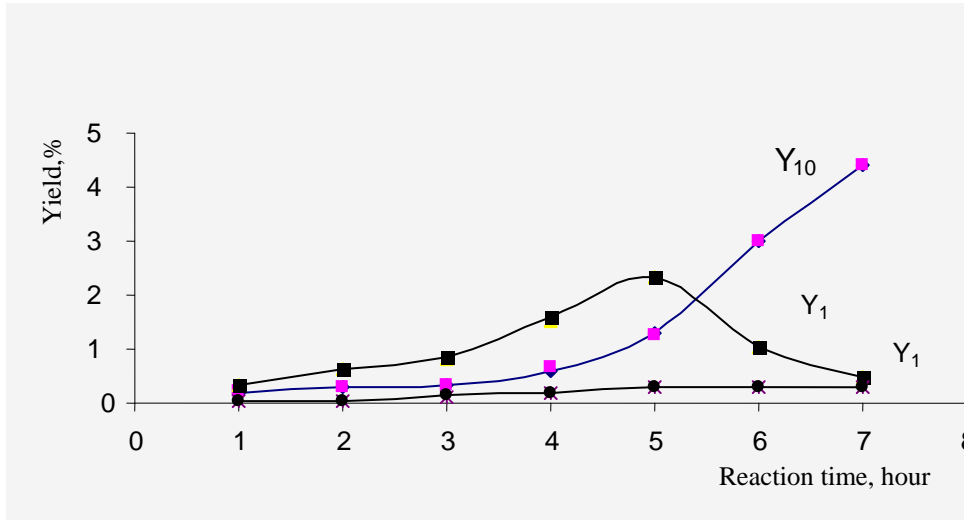


Fig. 7. Dependence of the yield of oxidate, SPA vø OSPA on reaction time (catalyst - TNT Cr:TNT Mn=3:1)

Dependence of the oxidation of Cr and Mn salts (3:1) of naphthene-paraffinic hydrocarbons on temperature have been studied and the results are presented in Tab.9.

Table 9. Dependence of the oxidation process of the mixture of naphthene-paraffinic hydrocarbons on temperature in the presence of TNT Cr:TNT Mn=3:1 (the concentration of catalyst according to the raw materials 0,2 % mass, air consumption 300 l/kg·hour)

Temperature°C	Acid number of, mgKOH/g	Yield of the acid, %		A.N. of the acid, mgKOH/g	
		SNT	ONT	SNT	ONT
130	48.8	20.2	3.2	115.8	121.5
135-140	65	23.3	12.8	135.7	115.7
150	62.7	21.2	8.8	148	133

As seen from Tab. 9, carrying out of oxidation process at 130°C and in the presence of the mixture of catalysts haven't good results, so that, SPA and OSPA are obtained with very little yield. A part of OSPA turns into other oxygen components, their yield reduces. So, higher yield of SPA and OSPA has been achieved at 135-140°C.

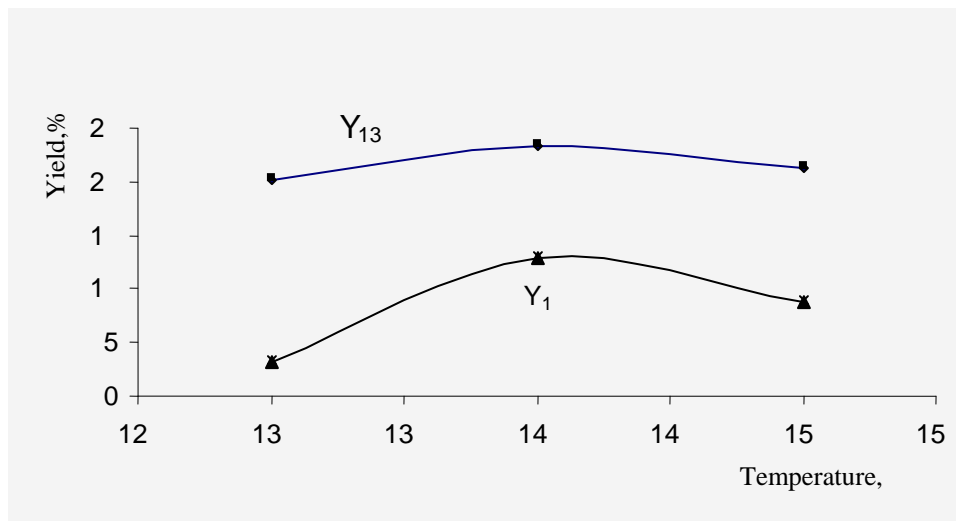
Comparison of experimental and theoretical calculated values of dependence of temperature on catalytic oxidation process is presented in Tab 10.

Table 10. Comparison of experimental and theoretical calculated values of dependence of temperature on catalytic oxidation process

Temperature, °C	SPA		OSPA	
	Yield, % exp., Y <sub>13</sub>	Yield, % theor., Y <sub>13</sub>	Yield, % exp., Y <sub>14</sub>	Yield, % theor., Y <sub>14</sub>
130	20.2	20.3	3.2	3.3
135-140	23.3	23.5	12.8	13
150	21.2	21.4	8,8	9

$$Y_{13} = -493.3 + 7.33 * X_1 - 0.026 * X_1^2$$

$$Y_{14} = -1359.2 + 19.32 * X_1 - 0.068 * X_1^2 \quad (4)$$



**Fig. 8.** Dependence of the yield of the mixture of obtained SPA and OSPA on temperature

#### 4. Conclusion

As a result of the studies there have been determined that, by oxidation of naphthene-paraffinic concentration emitted from the fractions of Azerbaijan oils boiling at 217-349°C under the known reaction conditions, it is possible the synthesis of SPA and OSPA with high yield and simultaneously taking of the mixture of NPACr and NPAMn (3:1) 0.2% mas., reaction time 5 hour and temperature 135-140°C as optimal condition, it results well by quality.

#### REFERENCES

1. V.M. Abbasov, E.B. Zeynalov, L.M. Afandiyeva et all. Selective oxidation of naphthene-isoparaffin hydrocarbons of diesel fraction in the presence of Cr and Mn salts of natural oil acids, Processes of petrochemistry and oil-refining, vol.14, №3(55), 2013, p.161-168
2. V.M. Abbasov, E.B. Zeynalov, L.M. Afandiyeva, L.H. Nuriyev. Synthesis synthetic naphthenic acids by aerobic oxidation of naphthenic hydrocarbons of diesel fraction in the presence of the mix of Cr and Mn salts, The II Russian-Azerbaijan symposium with international participation "Catalysis in solving the problems of petrochemical and oil refining", St. Petersburg, 17-19 september, 2013, p. 21-22
3. V.M. Abbasov, S.A. Mammadkhanova, L.M. Afandiyeva et all. Synthetic petroleum acids and some syntjeses based on them, Processes of petrochemistry and oil-refining, vol.15, №1(57), 2014, p.3-15
4. E.B. Zeynalov, V.M. Abbasov, L.M. Afandiyeva et all. Catalytic Activity of Naphthenates of the Transition Metals in Reaction Aerobic Oxidation of an Oil Fraction, Mir nefteproductov, Journal of oil companies, № 2, 2012, p.23-26
5. V.M. Potexin, V.V. Potexin. Osnovi teorii ximicheskix processov texnologii orqanicheskix veshestv i neftepererabotki, St. Petersburg . Ximizdat, 2005. 912 p.
6. B. Bandi. Metodi optimizatsii. Vvodniy kurs: M.: Radio i svyaz, 1988. — 128 p.
7. Matlab-7. The MathWorks, Inc. All Right Reserved. USA. 2005.
8. Matlab. Rukovodstvo dlya nachinayushix. Rossiyskoe xemometricheskoe obshestvo <http://rscs.chph.ras.ru>.
9. Matlab-8 New Features By Release R2014a (Version 8.3)