ISSN: online 2709-2666
print 2663-7006

AZERBAIJAN JOURNAL OF CHEMICAL NEWS

Vol. 5, No.2, 2023

Abstracting and indexing

Journal is indexed in Crossref, İndex Copernicus, Scilit and E-library

Azerbaijan Journal of Chemical News

Redaksiya Heyəti	
M.M.Ağahüseynova	Professor, Rusiya Təbiət Elmləri Akademiyasının müxbir üzvi (baş redaktor) minira_baku@yahoo.com
M.Y.Abdullayeva	Dosent, Azərbaycan Dövlət Neft və Sənaye Universiteti (redaktor müavini) mayaabdullayeva@hotmail.com
Üzvlər	
M.B.Babanlı	Professor, AMEA-nın müxbir üzvi, Kataliz və Qeyri-üzvi Kimya İnstitutu babanlymb@gmail.
Q.İ.Kəlbəliyev	Professor, AMEA-nın müxbir üzvi, Kataliz və Qeyri-üzvi Kimya İnstitutu kudret.kelbaliev@mail.ru
B.Ə.Məmmədov	Professor, AMEA-nın Polimer Materialları İnstitutu bazisaley@mail.ru
S. R. Hacıyeva	Professor, Bakı Dövlət Universiteti s.hajiyeva-bsu@mail.ru
T.A.Məmmədova	T.e.d, Akademik Yusif Məmmədəliyev adına Neft Kimya Prosesləri İnstitutu mammadova.tarana@rambler.ru
Amin Mousavi Khaneghah	Dr. University of Campinas, Sao Paulo, Brazil mousavi@unicamp.br
A.Q. Dedov	Professor,Rusiya Elmlər Akademiyasının akademiki, Qubkin adına Rusiya Dövlət Neft və Qaz Universiteti dedov.a@qubkin.ru
V.P. Meşalkin	Professor,Rusiya Elmlər Akademiyasının akademiki, D.İ.Mendeleyev adına Rusiya Dövlət Kimya Texnologiyalar Universiteti vpmeshlkin@gmail.com
V.F.Tretyakov	Professor, Moscow State Academy of Fine Chemical Technology tretyakov@bmsu.ru
Stefan Erast	Professor, Kaiserslautern Texniki Universiteti, Almaniya thiel@chemie.uni.ki.de
N.Z.Muradov	Professor, Florida Günəş Enerji Mərkəzi, Mərkəzi Florida Universiteti, ABŞ muradov@tser.ucf.edu
S.Ə.Məmmədxanova	Professor, Azərbaycan Dövlət Neft və Sənaye Universiteti sevinc.mammadxanova@asoiu.edu.az
M.Ş.Atayev	Dosent, Azərbaycan Dövlət Neft və Sənaye Universiteti matlab.atayev@gmail.ru
Ə.A.Həsənov	Professor, Azərbaycan Dövlət Neft və Sənaye Universiteti elekber.hasanov@asoiu.edu.az
F.Ə.Əmirov	Professor, Azərbaycan Dövlət Neft və Sənaye Universiteti fariz_emirov@mail.ru
Y.N.Qəhrəmanlı	Professor, Azərbaycan Dövlət Neft və Sənaye Universiteti yunisgahramanly@mail.ru
V.L.Bağiyev	Professor, Azərbaycan Dövlət Neft və Sənaye Universiteti vagif.bagiev@yahoo.com
T.M.Naibova	Dosent, Azərbaycan Dövlət Neft və Sənaye Universiteti n.tamilla51@gmail.com
R.V.Qurbanova	Dosent, Azərbaycan Dövlət Neft və Sənaye Universiteti (texniki redaktor) rena06.72@yandex.ru
Əlaqə	
Ünvan: 20 Azadlıq pr., Bakı, AZ1010, Azərbaycan, Tel: +994124986533, E-mail: minira_baku@yahoo.com, mayaabdullayeva@hotmail.com.	

Azerbaijan Journal of Chemical News

EDITORIAL BOARD	
M.M.Aghahuseynova	Professor, Corresponding Member of the Russian Academy of Natural Sciences (editor-in-chief) minira_baku@yahoo.com
M.Y.Abdullayeva	Associate Professor. (deputy chief editor) mayaabdullayeva@hotmail.com
Members	
M.B.Babanli	Professor, Corresponding Member of ANAS. Institute of Catalysis and Inorganic Chemistry babanlymb@gmail.
Q.J.Kalbaliyev	Professor, Corresponding Member of ANAS. Institute of Catalysis and Inorganic Chemistry kudret.kelbaliev@mail.ru
B.A.Mammadov	Professor, Corresponding Member of ANAS. Institute of Polymer Materials mammadova.tarana@rambler.ru
S.R.Hajiyeva	Professor, Baku State University s.hajiyeva-bsu@mail.ru
T.A.Mamedova	Dr. of Science, Yusif Mammadaliyev Institute of Petrochemical Processes mammadova.tarana@rambler.ru
Amin Mousavi Khaneghah	Dr. University of Campinas, Sao Paulo, Brazil mousavi@unicamp.br
A.Q.Dedov	Professor, Academician of the Russian Academy of Sciences, Gubkin Russian State University of Oil and Gas dedov.a@qubkin.ru
V.P. Mashalkin	Professor, Academician of the Russian Academy of Sciences. D. Mendeleev University of Chemical Technology of Russia vpmeshlkin@gmail.com
V.F.Tretyakov	Professor, Moscow State Academy of Fine Chemical Technology tretyakov@bmsu.ru
Stefan Ernst	Professor, Technical University of Kaiserslautern, Germany thiel@chemie.uni.ki.de
N.Z.Muradov	Professor, Florida Solar Energy Center University of Central Florida, USA muradov@tser.ucf.edu
S.M.Mammadkhanova	Professor, Azerbaijan State Oil and Industry University sevinc.mammadxanova@asoiu.edu.az
M.Sh.Atayev	Associate Professor, Azerbaijan State Oil and Industry University matlab.atayev@gmail.ru
A.H.Hasanov	Professor, Azerbaijan State Oil and Industry University elekber.hasanov@asoiu.edu.az
F.A.Amirov	Professor, Azerbaijan State Oil and Industry University fariz_emirov@mail.ru
Y.N.Gahramanli	Professor, Azerbaijan State Oil and Industry University yunisgahramanly@mail.ru
V.L.Bagiyev	Professor, Azerbaijan State Oil and Industry University vagif.bagiev@yahoo.com
T.M. Naibova	Associate Professor, Azerbaijan State Oil and Industry University n.tamilla51@gmail.com
R.V.Qurbanova	Associate Professor (managing editor), Azerbaijan State Oil and Industry University rena06.72@yandex.ru
Contacts	
Address: 20 Azadliq av., Baku, AZ1010, Azerbaijan, Phone: +994124986533, E-mail: minira_baku@yahoo.com, mayaabdullayeva@hotmail.com.	

CONTENT

AJCN, Vol. 5, No. 2., 2023, pp. 4-12
https://doi.org/10.32010/AJCN04022023-4

UDC: 660.63.726

SYNTHESIS OF CYCLOHEXYL ESTERS AND FIELDS OF THEIR APPLICATION

N.F. Sadiyeva[0000-0002-1633-6292], *G.G. Nasibova*[0000-0002-6738-3195],
L.M. Afandiyeva[0000-0002-1043-3446], *Y.P. Cherepnova*[0000-0001-6590-4797],
S.A. Iskenderova[0000-0001-5192-0665], *E.M. Guliyeva*[0000-0002-4797-8132]
Y.H.Mamedaliyev's Institute of Petrochemical Processes
uta1980@inbox.ru

This article is devoted to the method of obtaining cyclohexyl esters of fatty and petroleum acids in the presence of a heterogeneous TiO_2 *catalyst. In order to select the optimal conditions for the synthesis of cyclohexyl esters was studied the effect of the amount of catalyst, molar ratio of the feedstock and temperature. The esterification reactions were carried out and the target products were obtained in the selected optimal mode. In further studies, the indicators of the synthesized cyclohexyl esters were determined by analytical and spectral methods, material balances were drawn up for the processes of obtaining cyclohexyl esters based on fatty and petroleum acids. The resulting esters were tested as a new plasticizer antioxidant and depressant respectively to improve the properties of polymeric materials, thermooxidative and low-temperature properties of diesel fuels.*

Keywords: *cyclohexanol, fatty acids, synthetic petroleum acids, esterification, ester, catalyst, plasticizer, antioxidant, depressant.*

INTRODUCTION

There is a significant amount of research in the direction of the synthesis of esters of carboxylic acids with mono- and dihydric alcohols and the scope of their application as antioxidants, plasticizers [1-6]. Considering of a high cost and a shortage of the plasticizers, antioxidants and the growing need for new esters, we have developed a method for their production and are listed in this article.

In order to obtain plasticizers and antioxidants, a number of studies were carried out to determine the optimal temperature, amount of catalyst and the ratio of reacting components based on natural petroleum and aliphatic fatty acids (C_6-C_8) using a heterogeneous catalyst. Based on the studies carried out under optimal conditions (temperature -110-120°C, the amount of catalyst – 1,5 wt.%, acid, the molar ratio of components - acid:alcohol - 2:1,4), mixed diesters were synthesized with a yield of 88-90%. To confirm the structures of the synthesized diesters, the corresponding IR spectra were taken. In the spectra of the target products, absorption bands characteristic of the carbonyl and ester functional groups appear with greater intensity. The good compatibility of the synthesized plasticizers with the polymer matrix and the effect of these compounds on the reduction of sediment in diesel fuel are shown [7].

The authors synthesized mixed propylene glycol diesters based on NPA and fatty acids in the presence of a ZnO catalyst and carried out a preliminary assessment of the possibility of using the synthesized diesters as a plasticizer for polyvinyl chloride and an antioxidant for diesel fuel. The optimal conditions for esterification were found: the ratio of acids and alcohol is 2,0:1,3, the amount of catalyst is 1,2-1,6 wt.%, temperature - 110-120ºC, reaction time 3,5-4 hours. Depending taken on the fatty acid, the yields of mixed diesters ranged from 88-90%. The structural group composition of the obtained mixed diesters was determined by spectral methods (IR and NMR spectroscopy) [8].

Bis-m-dibromdibenzoat and bis-p-dibromdibenzoat esters of ethylene-glycol with the yield of 92,88% correspondingly have been synthesized based on the m-brombenzoic, p-brombenzoic acids and ethylene-glycol in the ratio of 2:1,2, at the temperature 110°C and with 6-7 hours duration in the presence of ionic-fluid catalyst of n-methylpyrrolidon-hydrosulfate. The physical-chemical parameters of synthesized esters have been defined and their structure identified spectrally. Due to the electrophilic (Cl, Br) heteroaromatic acids in the synthesized esters, the resin content (sedimentation capacity) of the components in the diesel fuel is reduced. The decrease of amount of resin in the synthesis of esters activates them as an antioxidant in the diesel fuel. These esters, used in 100 ml of diesel fuel at a concentration of 0,004%, reduced the sedimentation at temperature 120°C of by approximately five times. Synthesized compound esters have been tested on the increase of resistance of the diesel fuel against thermooxidation. Thus, it is justified that the ethylene-glycol esters may be used in the presence of n-methylpyrrolidon hydrosulfate catalyst for the increase thermooxidative stability of the diesel fuel [9].

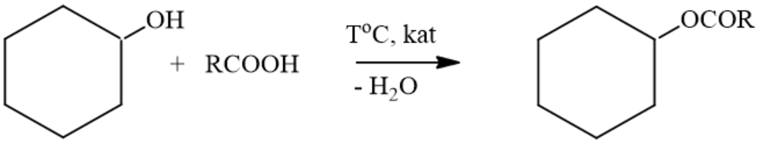
Despite the work carried out in the field of the synthesis of new plasticizers and antioxidants, research in the direction of the synthesis of cyclohexyl esters by heterogeneous catalysts is promising and relevant.

The purpose of the work is to search for optimal conditions for the synthesis of cyclohexyl esters of petroleum acids, as well as fatty acids, and study their areas of application: as plasticizers for polyvinyl chloride and antioxidants for diesel fuels in laboratory conditions.

EXPERIMENTAL PART

For obtain cyclohexyl esters, aliphatic fatty acids were used as raw materials: caproic acid (Alpha Aesar, A 13789, purity -98+%), enanthic acid (Alpha Aesar, A 17704, purity - 98+%), caprylic acid (Alpha Aesar, A 11149, purity - 98+%), pelargonic acid (Alpha Aesar, A 16188, purity - 98%), capric acid (Alpha Aesar, L 0349130, purity - 99%), cyclohexanol (CH) (Alpha Aesar, L 0349130, purity - 99%), TiO_2 (Alpha Aesar, A 16188, purity - 98%), toluene (Alpha Aesar, L 10967, purity - 99%), synthetic petroleum acids (SPA) were obtained by liquid-phase oxidation of the diesel fraction of a mixture of Azerbaijani oils in the presence of bromine-containing catalysts in a bubbling reactor at a temperature of 135-140°C (physico-chemical parameters: acid number (a. n.) - 225 mg KOH / g, molecular weight - 249 g / mol, n_d^{20} – 1,4651, ρ_4^{20}- 0,9805) [10], natural petroleum acids (NPA) were isolated from diesel fractions of 200-360ºC oils of Azerbaijan by leaching with an aqueous solution of sodium hydroxide of low concentration (1-5%) at an Oil Refinery named G. Aliyeva. For further purification, NPA was subjected to repeated double treatment with sodium hydroxide solution under laboratory conditions, separated from unsaponifiable components by washing with light gasoline or petroleum ether, followed by deoxidation of sodium salts of NPA with sulfuric acid [11]. The isolated and dried acids are a complex mixture of acids, mainly of bi- and tricycloaliphatic structures, the parameters of which are given below: boiling temperature - 110-220ºC/$2{,}66\cdot10^{-4}$ MPa; a.n. – 280 mg KOH/g; molecular weight calculated according to a.n., g/mol - 200; ρ_4^{20} – 0,9845 g/sm^3; n_d^{20} – 1,5034.

The synthesis of cyclohexyl esters in the presence of TiO_2 proceeds according to the following scheme:



where R - is the radical of SPA, NPA and aliphatic fatty acids (C_6-C_{10} series).

The influence of the molar ratio of acid and alcohol, the amount of TiO_2 and temperature on the course of the reaction were studied. The reactions carried out gave us the opportunity to find the optimal mode (temperature - 110-120ºC, amount of catalyst – 1,7-2,0 %, ratio PA : CH - 1:1,5 mol) for the synthesis of cyclohexyl ester of SPA, NPA, as well as fatty acids (FA) (temperature - 110-120 ºC, the amount of catalyst – 1,5-1,8 %, the ratio of FA : CH - 1:1,5 mol).

The synthesis of target esters is shown below, respectively:

- for the synthesis of cyclohexyl ester of SPA, 110 g (0,5 mol) of SPA, 75 g (0,75 mol) of cyclohexanol, 1,9 g (0,03 mol) of TiO_2 and 131 g (1,4 mol) of toluene (taken in the amount of 70% of the total mixture of components) were taken. Upon completion of the reaction, the contents of the flask are cooled to room temperature, after which the mixture is separated from the catalyst by filtration. It should be noted that when using TiO_2, the processing of crude ester takes place without neutralization, washing, and drying. After the distillation of the solvent - toluene, the crude ester is subjected to vacuum distillation, resulting in connection of the ester. The resulting ester has the following physico-chemical properties: boiling temperature – 210-220 ºC / 2,66 10^{-4} MPa, a.n. – 0,72 mg KOH / g, ρ_4^{20} – 0,9500 g / sm^3, n_d^{20} – 1,4712, found saponification number – 180,5 mgKOH /g, kinematic viscosity, 40ºC – 9,5 mm^2/s, temperature freezing point – -44-46 °C. The material balance of the ester has been compiled and it is shown in table 1.

Table 1

Material balance of obtaining a cyclohexyl ester of SPA

Taken			Received		
Denomination	Amount		Denomination	Amount	
	g	%		G	%
SPA	110,0	34,60	Water	8,9	2,80
CH	75,0	23,60	CH	25,0	7,85
TiO_2	1,9	0,60	TiO_2	1,75	0,54
Toluene	131,0	41,20	Toluene	125,0	39,31
Total	317,9	100	Cyclohexyl ester of SPA	151,0	47,50
			Remainder	6,25	2,0
			Total	317,9	100

Similarly, cyclohexyl ester of NPA was synthesized and physico-chemical parameters were determined. The resulting ester has the following physico-chemical properties: boiling temperature – 230-240°C / 6,65·10^{-4} MPa, a.n. – 0,50 mg KOH/g, ρ_4^{20} – 0,9600 g/sm^3, n_d^{20} – 1,4700, found saponification number – 190 mgKOH/g, kinematic viscosity – 9,0 mm^2/s, temperature freezing point – -42-44 °C.

For the synthesis of cyclohexyl ester of caprylic acid, 36,0 g (0,25 mol) of caprylic acid, 37,5 g (0,3 mol) of cyclohexanol, 0,64 g (0,008 mol) of TiO_2 and 52 g (0,72 mol) of toluene (taken in the amount of 70% of the total mixture of components) were taken. Upon completion of the reaction, the contents of the flask are cooled to room temperature, after which the mixture is separated from the catalyst by filtration. After the distillation of the solvent - toluene, the crude ester is subjected to vacuum distillation, resulting in connection of the ester which has the following physico-chemical parameters. Cyclohexyl ester of caprylic acid has the following physico-chemical parameters: boiling temperature – 142-144°C / $5{,}32 \cdot 10^{-4}$ MPa, a.n. – 0,6 mg KOH/g, ρ_4^{20} – 0,9164 g/sm^3, n_d^{20} – 1,4528, found saponification number – 243,0 mg KOH/g, flash temperature – 127°C. The material balance of the ester has been compiled and is shown in table 2.

Table 2

Material balance of obtaining a cyclohexyl ester of caprylic acid

Taken			Received		
Denomination	Amount		Denomination	Amount	
	g	%		g	%
Caprylic acid	36,0	28,5	Water	4,5	3,6
CH	37,5	29,8	CH	13,5	10,69
TiO_2	0,64	0,5	TiO_2	0,55	0,44
Toluene	52,0	41,2	Toluene	48,0	38,03
Total	126,14	100	Cyclohexyl ester of caprylic acid	56,5	44,8
			Remainder	3,09	2,44
			Total	126,14	100

The IR spectrum and NMR of the cyclohexyl esters was taken on the "Alpha" FT-IR spectrometer and Bruker MSL-300 universal instrument, with an operating frequency of 300,12 MHz manufactured by the German company BRUKER.

RESULTS AND DISCUSSION

Figure1 shows the IR spectrum of cyclohexyl ester of SPA. The spectrum shows absorption bands of carbonyl groups in the regions of 1732 sm^{-1}, as well as ester groups - 1040, 1124, 1168, 1250 sm^{-1}, C-H bond of the cyclic ring - 967, 1017 sm^{-1}.

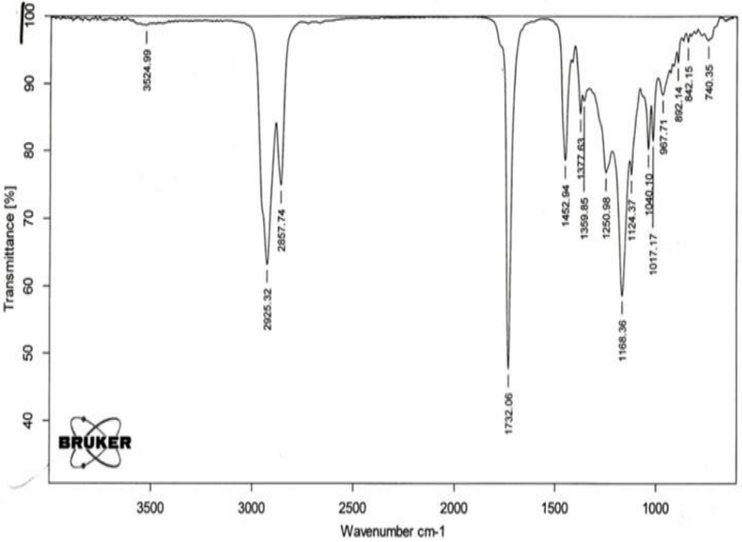


Fig. 1. IR spectrum of cyclohexyl ester of SPA

The structure of the synthesized cyclohexyl ester of SPA was also confirmed by nuclear magnetic resonance (NMR) spectroscopy.

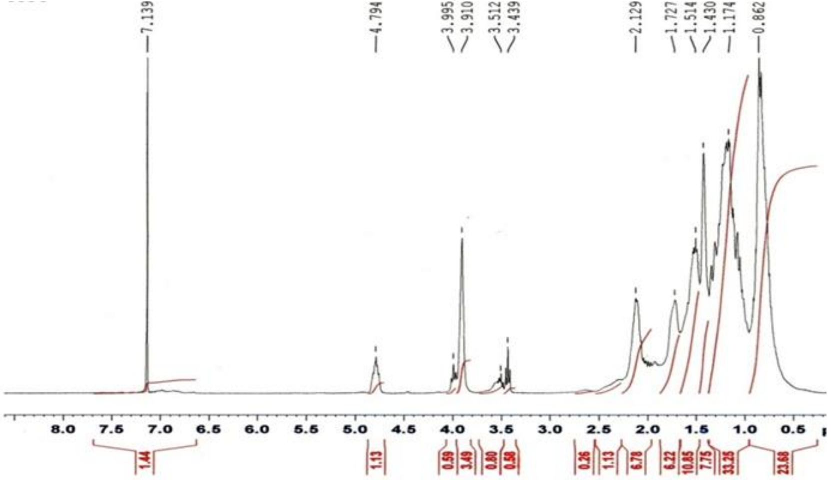


Fig. 2. Nuclear magnetic resonance spectrum of cyclohexyl ester of SPA

Figure 2 shows that the COOH fragment is not observed in the spectra. This means that the esterification reaction of CH and SPA goes to the end.

The IR spectrum of cyclohexyl ester of caproic acid was also recorded (fig.3).

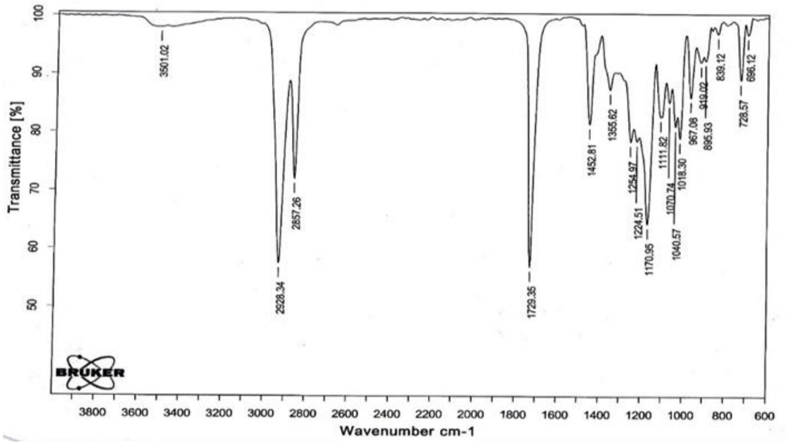


Fig. 3. IR spectrum of cyclohexyl ester of caprylic acid

In the IR-spectrum of the cyclohexyl ester of caprylic acid was observed the following absorption bands:

728, 1355, 1452, 2857, 2928 sm^{-1}	– deformation and stretching vibrations of C-H bonds of CH_3 and CH_2 groups;
1729 sm^{-1}	– C=O bond of the ester;
1170 sm^{-1}	– deformation vibrations of the C-O bond of the ester;
3501 sm^{-1}	– stretching vibrations of the H-O bond;
967,08, 1018,30 sm^{-1}	– C-H bond of benzen ring.

The presence, in the measured spectra, of bands in the region of 1729, 1170 sm^{1}, characterizing the carbonyl and ester groups, allows us to classify the resulting products as esters.

In a similar way, the reaction of esterification were carried out with other representatives of aliphatic fatty acids, the physico-chemical parameters of the synthesized esters were determined and presented in table 3.

Table 3

Some physico-chemical parameters of cyclohexyl esters of fatty acids

R	Yield, %	Boiling temperature, °C, 2,66·10^{-4} MPa	ρ_4^{20}, g/sm^3	n_D^{20}	A. n., Mg KOH/g	S. n., mg KOH/g	Flash tempe-rature, °C
C_5H_{11}	91,4	82-84/1,33	0,9246	1,4491	0,32	254,7	108,0
C_6H_{13}	90,3	96-98/1,33	0,9194	1,4512	0,9	253,0	118,0
C_7H_{15}	89,8	142-144/5,32	0,9164	1,4528	0,6	243,0	127,0
C_8H_{17}	89,0	122-124/2,66	0,9153	1,4552	0,4	222,0	142,0
C_9H_{19}	88,4	133-135/2,66	0,9004	1,4564	0,2	211,2	151,0

The synthesized cyclohexyl esters of the corresponding acids are light yellow oily liquids with a specific odor, insoluble in water, but readily soluble in organic solvents. Now, high-boiling esters of various classes are mainly used as plasticizers. Plasticizers based on petroleum raw materials, in particular naphthenic hydrocarbons, are of great practical and theoretical importance. Therefore, the purpose of this study was as follows: to study the plasticizing properties of the synthesized esters in the manufacture of a composition based on polyvinyl chloride (PVC). These compositions were kept in a thermostat for a certain time depending on the temperature, then the cooled compositions were held under load on filter paper until no oil stain was present. Thus, the optimal limits of compatibility of the synthesized esters with PVC were determined [12].

The research results showed that the synthesized cyclohexyl esters of petroleum acids can be recommended as primary, and cyclohexyl esters of fatty acids - secondary plasticizers.

It is known that thermal-oxidative and low-temperature properties are one of the main features based on which modern diesel fuels for high-speed engines are classified. To improve the thermal-oxidative and low-temperature properties of diesel fuels, we introduced the synthesized esters into diesel fuel as antioxidant and depressant additives (EN ISO 12205) and obtained positive results (table 4) [9, 13].

Table 4

Results of synthesized cyclohexyl esters as antioxidants and depressants

Denomination	Hydrotreated diesel fuel	Cyclohexyl ester of SPA	Cyclohexyl ester of NPA	Cyclohexyl ester of caprylic acid
Determination of thermo-oxidative stability, at 120°C, amount of sediment (0,004%) in mg/100 ml of fuel	1,7	0,3	1,7	0,2
Temperature, °C (0,05%) turbidity - solidification	-28 -38	-31 -38	-35 -40	-34 -41

The positive results obtained enable to increase the range of esters of carboxylic acids and recommend them to new plasticizers, antioxidants and pour point depressants.

CONCLUSION

Cyclohexyl esters based on petroleum and fatty acids were synthesized using TiO_2 as a catalyst. The influence of the molar ratio of acid and alcohol, the amount of -TiO_2 and temperature on the course of the reaction was studied and the optimal mode (temperature - 110-120ºC, amount of catalyst – 1,7-2,0 %, ratio PA : CH - 1:1,5 mol) for the synthesis of cyclohexyl ester of SPA, NPA, as well as fatty acids (temperature - 110-120ºC, amount of catalyst – 1,5-1,8 %, FA : CH ratio - 1: 1,5 mol) was found, respectively. The indicators of the synthesized esters are determined and their application is studied.

REFERENCES

1. Sadiyeva N.F., Iskenderova S.A., Cherepnova Y.P., Aliyeva S.Q., Mammadova X.R., Iskenderova V.R. "Synthesis and research of mixed diether of propylene glycol based on synthetic petroleum acids and caprylic acid". Ganja State University scientific conference on "Actual problems of modern natural and economic sciences". Ganja. 06-07.05.2022, pp. 297-299
2. Iskenderova S.A., Afandieva L.M., Nasibova G.G., Babanly N.N., Kulieva E.M., Asadova Sh.N. Obtaining mixed diesters of petroleum acids and their use as plasticizers and antioxidants. Oil refining and Petrochemistry. 2020, №6, pp. 19-21
3. Sadieva N.F., Jafarov R.P., Nasibova G.G., Zeynalov E.B., Afandieva L.M., Iskenderova S.A. Study of the process of obtaining diethylene glycol diester of synthetic petroleum acids on a mathematical model.World of petroleum products. 2018, №4, pp. 29-34
4. Liu T., Jiang P., Liu H., Li M., Dong Y., Wang R., Wang Y. Performance testing of a green plasticizer based on lactic acid for PVC. Polymer Testing. 2017, Vol.61, pp.205-213, https://doi.org/10.1016/j.polymertesting.2017.05.012
5. Efendiyeva L.M., Kerimov P.M., Alesgerova O.M., Guliyeva E.M., Musayeva A.P. The synthesis and study of ω-chlorine valerianate and ω-chlorine enant of ethylene-glycol esters based on monoethyleneglycol ester of synthetic fatty acids from C_7-C_9 fraction in the presence of sulphuric acid. Azerbaijan Oil İndustry. 2021, №12, pp. 45-48. https://doi.org/10.37474/0365-8554/2021-12-45-48
6. Aliyeva F.X., İsrafilov K.O., Guseynov L.N. "Synthesis of Malonic Acid Esters". Petroleum chemistry, synthesis of polyfunctional monomers, oligomers and polymers conference dedicated to the 90th anniversary of academician Sahib Museyib Aliyev, Baku. 23.06.2023, pp. 33
7. Sadiyeva N.F., Cherepnova Y.P., İskenderova S.A., Afandiyeva L.M., Guliyeva E.M. Synthesis and application of effective plasticizers, antioxidants. Azerbaijan Journal of Chemical News.2023,Vol.5,№1,pp.30-37. http://doi.org/10.32010/AJCN04022023-30

8. Sadiyeva N.F., Iskenderova S.A., Cherepnova Y.P., Nasibova G.Q., Afandiyeva L.M., Aliyeva S.G. Synthesis and study of mixed propylene glycol diesters of synthetic petroleum- and fatty acids. Azerbaijan Journal of Chemical News. 2022, Vol.4, №2, pp. 4-11. http://doi.org/10.32010/AJCN04022022-4
9. Kerimov P.M., Alasgarova O.M., Aghayev B.K., Aliyeva S.G., Nasibova G.G., Saadova L.M. The synthesis of bis-m-dibrombenzoat-, bis-p-dibrombenzoat esters of ethylene-glycol with ionic-fluid catalysts and their study in diesel fuel. Azerbaijan Oil İndustry. 2023, №1, pp. 29-34
10. Nasibova G.G., Aliyeva A.Z., Zeynalov E.B., Nuriyev L.G., Agayev B.K. Preparation of synthetic petroleum acids in the presence of brominated carbon nanocatalyst. Azerbaijan Oil İndustry. 2016, №2, pp. 50-52
11. Abbasov V.M., Zeynalov E.B., Veliyev M.G., Mustafayev S.A., Mamedova N.A., Afandiyeva L.M., Shakhmamedova A.G. Natural petroleum acids and derivatives based on them: origin, structure, and properties, synthetic and applied aspects. B.Science.2014, pp. 232
12. Nasibova G.G., Iskenderova S.A., Zeynalov E.B., Asadova Sh.N., Nuriev L.G., Agaev B.K. Effective plasticizers for polyvinyl chloride. Plastic masses. 2018, №3-4, pp. 17-19
13. Sadiyeva N.F., Iskenderova S.A., Cherepnova Y.P., Afandiyeva L.M., Quliyeva E.M., Mamedov A.M. Research and application of mixed propylene glycol diesters based on natural petroleum- and fatty acids. Polish journal of science. 2022, № 47, pp. 13-18

СИНТЕЗ ЦИКЛОГЕКСИЛОВЫХ ЭФИРОВ И ОБЛАСТИ ИХ ПРИМЕНЕНИЯ

Н.Ф. Садиева[0000-0002-1633-6292], *Г.Г. Насибова* [0000-0002-1460-3061],
Л.М. Эфендиева[0000-0002-1043-3446], *Ю.П. Черепнова*[0000-0001-6590-4797],
С.А. Искендерова[0000-0001-5192-0665], *Э.М. Кулиева*[0000-0002-47978132]
Институт Нефтехимических Процессов им. акад. Ю.Г. Мамедалиева
uta1980@inbox.ru

Данная статья посвящена методу получения циклогексиловых эфиров жирных-, а также нефтяных кислот в присутствии гетерогенного катализатора TiO_2*. С целью выбора оптимальных условий синтеза циклогексиловых эфиров изучено влияние количества катализатора, мольное соотношение исходного сырья и температуры. В выбранном оптимальном режиме проводились реакции этерификации и были получены целевые продукты. В дальнейших исследованиях были определены показатели синтезированных циклогексиловых эфиров аналитическими и спектральными методами, составлены материальные балансы процессов получения циклогексиловых эфиров на основе жирных-, а также нефтяных кислот. Для улучшения свойств полимерных материалов, термоокислительных и низкотемпературных свойств дизельных топлив, полученные эфиры были испытаны в качестве нового пластификатора, антиоксиданта и депрессанта соответственно.*

Ключевые слова: *циклогексанол, жирные кислоты, синтетические нефтяные кислоты, этерификация, эфир, катализатор, пластификатор, антиоксидант, депрессант.*

TSİKLOHEKSİL EFİRLƏRİNİN SİNTEZİ VƏ ONLARIN TƏTBİQ SAHƏLƏRİ

N.F. Sədiyeva$^{0000-0002-1633-6292}$ *,G.Q. Nəsibova*$^{0000-0002-1460-3061}$*,*
L.M. Əfəndiyeva$^{0000-0002-1043-3446}$*,Y.P. Çerepnova*$^{0000-0001-6590-4797}$*,*
S.A. İsgəndərova$^{0000-0001-5192-0665}$*, E.M. Quliyeva*$^{0000-0002-4797-8132}$
Akad. Y.H.Məmmədəliyev adına Neft-Kimya Prosesləri İnstitutu
uta1980@inbox.ru

Məqalə TiO_2 *heterogen katalizatorunun iştirakı ilə yağ- və neft turşularının tsikloheksil efirlərinin alınması üsuluna həsr edilmişdir. Tsikloheksil efirlərinin sintezinin optimal şəraitinin seçilməsi məqsədi ilə katalizatorun miqdarının, xammalların molyar nisbətinin və temperaturun təsiri öyrənilmişdir. Seçilmiş optimal rejimdə efirləşmə reaksiyaları aparılmış və məqsədli məhsullar alınmışdır. Sonrakı tədqiqatlarda sintez edilmiş tsikloheksil efirlərinin göstəriciləri analitik və spektral üsullarla müəyyən edilmiş, yağ- və neft turşuları əsasında tsikloheksil efirlərinin alınması proseslərinin material balansları tərtib edilmişdir. Polimer materiallarının xassələrinin, eləcə də dizel yanacağının termooksidləşmə və aşağıtemperatur xassələrinin yaxşılaşması üçün əldə edilən efirlər müvafiq olaraq yeni plastifikator, antioksidant və depressant kimi sınaqdan keçirilmişdir.*

Açar sözlər: *tsikloheksanol, yağ turşuları, sintetik neft turşuları, efirləşmə, efir, katalizator, plastifikator, antioksidant, depressant.*

AJCN, Vol. 5, No. 2, 2023, pp. 13-19
https://doi.org/10.32010/AJCN04022023-13

UDC -542.943.628

OXIDATION OF UNSATURATED HYDROCARBONS IN THE PRESENCE OF METALCOMPLEX CATALYSTS

*M. M. Aghahuseynova*0000-0003-2471-2136, *L. Z. Vazirova*0000-0003-0008-8973
Azerbaijan State Oil and Industry University,
minira_baku@yahoo.com

The work investigated the synthesis of complex compounds of TM with molecular oxygen, the establishment of the nature of the forces acting during complex formation, as well as the studying the possibility of reversible binding of molecular oxygen, identifying possible areas of practical application of the resulting complexes. The synthesized oxygen adducts are oxygen carriers and carry out oxidation reactions under mild conditions with high yield.This was established on the base of oxidation reaction of n-butene to methylethylketon. For the first time an oxidation reaction was carried out not directly between an alkene and oxygen as it case of Waker prosess, but in a liquid-phase oxidationbetween two metallocomplex systems. One of them is oxygenated complex of the first transition metal and another alken complex of the second tran nsition metal. It was revealed that during the prosees of complecsformation both oxygen and alkene transfer into an activated state ,reaction carried out between them., in mild conditions, which made it possible to develop of an effective and environmentally friendly metod of alkens oxidation

***Keywords**: molecular oxygen, butene oxidation, absorption, oxygeneted complexes, hexamethylphosphoramide.*

INTRODUCTION

The appearance of molecular oxygen in the earth's atmosphere as a by-product of photosynthesis was an event in biological evolution and had two important consequences: firstly, mechanisms arose in the cell for its use as an electron acceptor during respiration and oxidation of substrates, and secondly, living organisms were faced with the need to develop effective methods to prevent its toxic effects. Complex compounds of transition metals (TMs) with organic ligands that reversibly bind molecular oxygen have extremely important properties. This type of complex compounds has great prospects from the point of view of the possibility of their use as oxidizing agents in the oxidative reactions of organic substances. Molecular oxygen in its main form is a triplet state (it has two unpaired electrons with parallel spins, which are localized in different orbitals). Most organic molecules are singlets, their electrons have antiparallel spins. Due to differences in the direction of electron spins, the interaction of organic molecules with the O_2 molecule proceeds rather slowly. This is where the idea of activating molecular oxygen arose in order to increase its reactivity. The idea of activated molecular oxygen came from nature, and many scientists are now working in this area [1–6]. In the development of modern ideas about the participation of forms of activated oxygen (AO) and free radicals in biochemical processes, the Bach-Engler theory of peroxidation was of great importance [7-10]

A.N.Bach wrote: “The body has the ability to convert free oxygen from inactive state into an active state"), the theory of chain free radical oxidation, developed by N.N. Semenov, as well as research by the American scientist I. Fridovich, who showed the formation of oxygen radicals in enzymatic reactions and discovered the ability to destroy (dismutase) some free oxygen radicals with the help of enzymes. In living nature, the role of such oxygen complexes, including TM ions and enzymes play a role in their composition. Examples of these are iron-heme protein in mammals and copper-heme protein in molluscs. In these proteins, metals are in a low-valent state, although usually metal ions can obtain various states of oxidation upon contact with oxygen [11-15].

In the cavity of such complexes, the oxygen molecule is activated by its coordination with transition metal ions and can oxidize many organic substances both at low temperatures and at the temperature of living beings. The heat of this reaction is an integral part of the energy source of living organisms. However, when such complexes are isolated from living organisms, they become so unstable that metal ions are quickly oxidized by oxygen, as a result of which they lose their catalytic activity [16-18].

EXPERIMENTAL PART

Thus, the synthesis of metal complex systems, which are models of enzymes capable of carrying out substrate oxidation reactions under mild conditions and forming stable oxygen complexes with TM, is very relevant.

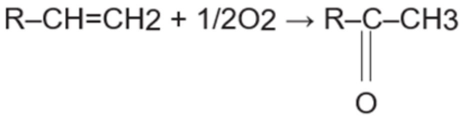
The purpose of this study is the synthesis of complex compounds of TM with molecular oxygen, establishing the nature of the forces acting during complex formation, as well as studying the possibility of reversible binding of molecular oxygen, identifying possible areas of practical application of the resulting complexes.

Complexes of PM with molecular oxygen were selected as objects of study for use as catalysts for the oxidation of unsaturated hydrocarbons. Currently, in many countries, ketones are obtained by oxidation of alkenes using the Wacker–Schmidt method in the presence of aqueous solutions of d-element chlorides. During the reaction, organochlorine products are formed as by-products, which complicate the technology for isolating ketones from the reaction mass.

Direct liquid-phase oxidation of alkenes to the corresponding ketones proceeding according to the scheme is the most promising method, proceeding with high selectivity, in one stage and under mild conditions. Effective catalysts for the propylene oxidation process are aqueous solutions phosphomolybdenum-vanadium heteropolyacids and phosphoric acid, thanks to which the yield of acetone reaches 90%.

Unfortunately, the oxidation of 1-butene and higher alkenes in these catalytic systems occurs with an unsatisfactory yield of the target product due to the low degree of absorption of the starting alkenes in aqueous solutions.

In this regard, we have carried out research to find simple catalytic systems that imitate the properties of natural metal complex systems, which would allow the selective oxidation of higher alkenes with a high yield of target products.



$$R{-}CH{=}CH_2 + 1/2O_2 \rightarrow R{-}\underset{\underset{O}{\|}}{C}{-}CH_3$$

Modern industry is experiencing a growing need for methyl ethyl ketone (MEK), which, being an excellent solvent, is widely used in the oil refining and petrochemical industries for dewaxing petroleum fractions, in the production of printing inks, audio and video cassettes, etc. [6].

The annual world production of MEK in 2000 was 1.2 million tons. Demand for it is constantly increasing and amounts to 7% per year. Neither Russia nor Azerbaijan currently produces MEK, and all demand for it is met through imports. The lack of in-house production of IEC is explained primarily by the lack of effective technologies for its production [7].

Currently, in industry, MEK is produced by the method of hydration (sulfuric acid or direct) of n-butylene with the formation of sec-butyl alcohol (SBA) in the first stage, followed by oxidation or dehydrogenation into the target product.

This method is widely practiced in Western Europe, Asia, and Latin America. In the USA, MEK is obtained as a by-product from the oxidation of n-butane and low hydrocarbons to acetic acid. More known 10 methods for producing MEK by oxidation of butylene, butane and sec-butanol. All these methods are multi-stage.

Known processes for producing MEK are carried out under relatively harsh conditions - high temperatures and pressures, which cause an increase in the yield of by-products. Strict environmental and economic requirements dictate the urgent need to create new technologies for the production of MEK, which could replace the existing multi-stage processes that lead to the formation of large amounts of waste.

In this regard, we have carried out research to find simple catalytic systems that imitate the properties of natural metal complexes, which would allow the selective oxidation of higher alkenes with a high yield of target products.

RESULTS AND DISCUSSION

Transition metal complexes (M = Fe(II), Co(II), Cu(I), Cu(II), V(III), Zn(II), Pd(II), Ti(II)) were prepared by dissolving anhydrous metal chlorides in hexamethylphosphoramide (hmpa). The choice of this solvent is not accidental. As homogeneous catalysts for the butene oxidation process. Phosphoric acid or aqueous solutions of heteropoly acids containing phosphorus. Therefore, we chose as catalysts complexes of transition metals Cu(I) and Pd(II) with the organophosphorus compound trisdimethyl aminophosphine oxide, which is designated “hmpa hexamethyl-phosphoramide” and is a derivative of phosphoric acid.

It has been established that the monovalent copper salt CuCl, dissolving in hmpa, forms the corresponding complex CuCl hmpa, capable of coordinating oxygen in the form of a stable oxygen complex $(CuCl\ hmpa)_2\ O_2$.

It is known that in monovalent copper salts in an aqueous environment, upon absorption of oxygen, Cu(I) is easily oxidized to the divalent state Cu(II). And in our case, there were concerns that monovalent copper in CuCl would oxidize to Cu(II) when oxygen binds, especially since the CuCl·hmpa complex is colorless, and when oxygen was passed through the solution of this complex, the color changed to dark green. However, verification studies showed that the $CuCl_2$ hmfa solution has a red-brown color:

$CuCl + hmpa \rightarrow CuCl\ hmpa$ colorless;

$2CuCl\ hmpa + O2 \rightarrow [CuCl\ hmpa]2\ O_2$ dark green;

$$CuCl_2 + hmpa \rightarrow CuCl_2\,hmpa \text{ red-brown.}$$

In this complex, the oxygen molecule is bound so tightly that elimination does not occur even during boiling. Oxygen can also be absorbed from air that is bubbled through the solution. The stability of the oxygen complex makes it possible to easily remove excess oxygen from the reaction medium, the contact of which with butene-1 can lead to undesirable effects, namely an explosion.

With irreversible absorption and coordination of an oxygen molecule by a metal complex, polarization and activation of the substrate occurs as a result of electron transfer.

UV absorption spectra of solutions of these substances were recorded in figure1.

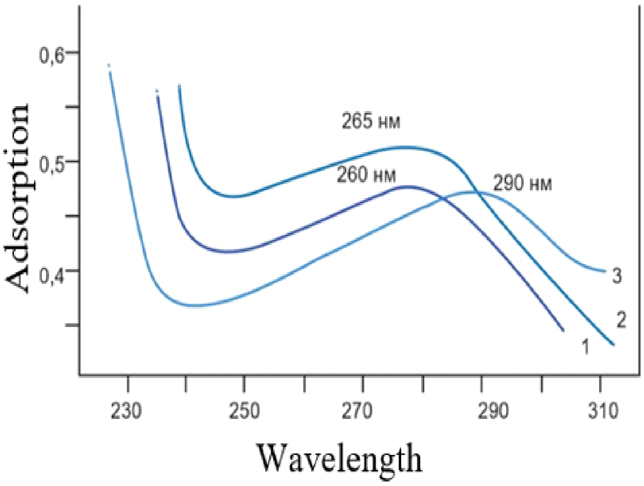


Fig.1. UV absorption spectra of solutions of substances.

The spectra of a solution of the Cu(I) complex - curve 1 and a solution of the complex with absorbed O_2 - curve 2 are completely different from the spectrum of a solution of the Cu (II) complex - curve 3.

Next, we investigated the degree of oxygen absorption by amide complexes of d-element chlorides obtained according to the scheme

$$2MCl_n + 2hmpa \rightarrow 2MCln\ hmpa + O_2 \rightarrow \rightarrow 2MnCl_n\ hmpa\ O_2\ (1)$$

M=Cu (II), Cr (II), Fe (II), Co (II), Cu(I), V(III)

Studies of the absorption properties of these complexes have shown that many of them satisfactorily absorb oxygen at room temperature, but in the case of Cu(I) the amount of absorbed oxygen reaches a maximum at 0.015 mol/l (180 ml), while the binding of oxygen at equilibrium constant showed that the affinity for oxygen of complexes varies depending on the nature of the complexing agent in the following order:

Cu(I) > Fe (II) > Co (II) > V(III)

Measuring the amount of oxygen absorbed by a solution of the CuCl hmpa complex revealed that the molar ratio of absorbed oxygen to Cu(I) was 1:2, and the compound having an absorption maximum at 265 nm and giving a green color is oxygen complex.

In order to discover complexes in which butene-1 would also be activated, a number of studies were carried out. It has been established that $PdCl_2$ dissolves well in hmpa to form the $PdCl_2\cdot(hmpa)_2$ complex, and when butene-1 is passed through this complex, a butene complex is formed at atmospheric pressure and room temperature.

Acetonitrile (AN), propionitrile (PN) and benzonitrile (BN) were used as modifying ligands. It has been shown that butene is highly soluble in aprotic solvents and in some complexes. But the highest absorption value for palladium complex with hmpa and acetonitrile. B-1 was subsequently passed through this complex, obtained at room temperature, at different values of time and temperature. The result is the complex $[Pd\,(AN)(B\text{-}1)]\,Cl_2$.

A study of the kinetic patterns of absorption of butene-1 by a palladium complex showed that the absorption of B-1 increases with increasing temperature to 60 °C and process time to 90 minutes. Experimental studies have shown the ease of isolating the target product and the safety of the process will make it possible to create an economically and environmentally beneficial and cheap process for obtaining MEK and open up great opportunities for its use on an industrial scale.

CONCLUSION

A study of the effect of complex formation on the reactivity of linear ligands showed that the redistribution of electron density during the transition of molecular oxygen from the free state coordinated leads to a change in its reactivity. The synthesized oxygen adducts are oxygen carriers and lead to an oxidation reaction under mild conditions with high yield. For the first time, a combined catalyst based on transition metal salts has been proposed for a highly efficient technology to produce methyl ethyl ketone by liquid-phase oxidation of butenes.

REFERENCES

1. Ramos-Suárez J.L., Martínez A., Carreras N. Optimization of the digestion process of Scenedesmus sp. and Opuntia maxima for biogas production. Energy Convers Manage. 2014, Vol.36, №5, pp.1263-1270
2. David M. Mousdale. Biofuels Biotechnology, Chemistry and Sustainable development, 2008, CRC Press and Taylor & Francis Group. 2008, 385 p.
3. Mat Aron N.S., Khoo K.S., Chew K.W., Show P.L., Chen W.H., Nguyen H.P. Sustainability of the four generations of biofuels-A review. Int. J. Energy Res. 2020, Vol.44, №12, pp. 266-282
4. Bertrand E., Vandenberghe L., Soccol C., Sigoillot J., Faulds C. First generation bioethanol, in: Green fuels technology. Springer, Cham, 2016, pp.175–212
5. Samios D., Pedrotti F., Nicolau A., Reiznautt Q.B., Martini D.D., Dalcin F.M. A transesterification Double Step Process - TDSP for biodiesel preparation from fatty acids triglycerides. Fuel Processing Technology.2009, Vol.90, pp.599-605
6. Aghahuseynova M.M., Abdullayeva G.N. Cataluticogenetion of olefines with petroleum metallophyrins. Chemistry and Chemical Technology.2020, Vol.53, №9, pp.12-15

7. Chow M.C., Jackson W.R., Chaffee A.L., Marshall M. Thermal treatment of algae for production of biofuel. Energy and Fuels. 2013, Vol.27, pp.1926-1950
8. Aghahuseynova M.M. Synteis and proporties of metalcomplexes catalysts based on oil metallophyrins. Eureka. Physic and Engineering. 2020, Vol.4, pp.19-28
9. Demirbas A., Demirbas M. Importance of algae oil as a source of biodiesel. Energy conversıon and management. 2011, Vol.52, №1, pp.163-170
10. Cesarini S., Pastor F., Nielsen P., Diaz P., Moving towards a competitive fully enzymatic biodiesel process. Sustainability. 2015, Vol.7, №6, pp.7884-7903
11. Olusegun D., Samuel, M., Olawale U. Critical Review of In-situ Transesterification Process for Biodiesel Production. The Pacific Journal of Science and Technology. 2012, Vol.13, №2, pp.98-109
12. Jiang R., Ingle K., Golberg A. Macroalgae (seaweed) for liquid transportation biofuel production: what is next. Algal Res. 2016, Vol.14, pp.48–57
13. Teresa M., Antonio A., Martins. S. Microalgae for biodiesel production and other applications: A review. Renewable and Sustainable Energy Reviews. 2010,Vol.14, pp. 217-232
14. Demirbas A. Biofuels sources, biofuel policy, biofuel economy and global biofuel projections. Energy Conversion and Management, 2008, Vol.49, pp. 2106-2116
15. Xia A., Herrmann C., Murphy J. D." Biofuels. Bioproducts and Biorefining. 2015, Vol.9, №4, pp.109-130
16. Notoya M. Production of biofuel by macroalgae with preservation of marine resources and environment, in: Seaweeds and Their Role in Globally Changing Environments. Springer, Dordrecht Netherlands. 2010, Vol.5, pp. 217–228
17. Oh S.Y., Yo D.I., Shin Y., Kim H.C., Kim H.K., Chung Y.S., Park W.H., Youk J.H. Crystalline structure analysis of cellulose treated sodium hydroxide and carbon dioxide by mean of X-ray diffraction and FTIR spectroscopy. Carbohydr. Res.2005, Vol.340, №15, pp. 2376-2391
18. Schenk P., Thomas-Hall S., Stephens E., Marx U., Mussgnug J., Posten C., Kruse O., Hankamer B. Second generation biofuels: high-efficiency microalgae for biodiesel production. Biodiesel Production Processes. 2008, Vol.1, pp.20–43

ОКИСЛЕНИЕ НЕНАСЫЩЕННЫХ УГЛЕВОДОРОДОВ В ПРИСУТСТВИИ МЕТАЛЛОКОМПЛЕКСНЫХ КАТАЛИЗАТОРОВ

М. М. Агагусейнова$^{0000-0003-2471-2136}$*, Л. З. Вазирова*$^{0000-0003-0008-8973}$
Азербайджанский Государственный университет нефти и промышленности
minira_baku@yahoo.com

В данной работе исследованы синтез комплексных соединений ПМ с молекулярным кислородом, установлена природа сил действующих при комплексообразовании, изучена возможность связывания молекулярного кислорода, а также возможные области практического применения полученных комплексов были определены. Синтезированные кислородные аддукты являются переносчиками кислорода и осуществляют реакции окисления в мягких условиях с высоким выходом.

Впервые была проведена реакция окисления непосредственно между алкеном и кислородом и жидкофазном окислении между двумя металлокомплексными системами. Они представляет собой кислородсодержащий комплекс переходного металла а *также— алкеновый комплекс переходного металла. Выявлено, что в процессе комплексообразования и кислород, и алкен переходят в активированное состояние, и между ними происходит реакция в мягких условиях, что позволило разработать эффективный и экологически чистый метод окисления алкенов.*

Ключевые слова: *молекулярный кислород, окисление бутена, абсорбция, гексаметилфосфорамид.*

DOYMAMIŞ KARBOHIDROGENLƏRIN METAL KOMPLEKS KATALİZATORLARIN İŞTİRAKI İLƏ OKSİDƏŞMƏSİ.

M. M. Ağahüseynova 0000-0003-2471-2136, *L. Z. Vəzirova* 0000-0003-0008-8973
Azərbaycan Dövlət Neft və Sənaye Universiteti
minira_baku@yahoo.com

Tədqiqat işində KM-nın molekulyar oksigenlə kompleks birləşmələrinin sintezi, kompleks əmələ gəlmə zamanı yaranan rabitələrin təbiətinin müəyyən edilib, həmçinin molekulyar oksigenin kompleks əmələ gətirmə imkanlarının öyrənilib. Eyni zamanda sintez olunan materialların praktiki tətbiqinin mümkün sahələri müəyyən edilmişdir. Müəyyən olunmuşdur ki, sintez edilmiş oksigen adduktlarının kompleksləri oksigen daşıyıcıları olub və mülayim şəraitdə yüksək məhsuldarlıqla oksidləşmə reaksiyalarını həyata keçirirlər.

İlk dəfə oksidləşmə reaksiyası birbaşa alkenlə oksigen arasında deyil, iki metallokompleks sistem arasında maye fazalı oksidləşmədə metodu ilə aparılmışdır. Müəyyən edilmişdir ki, komplekəmələgətirmə zamanı həm oksigen, həm də alken aktivləşmiş vəziyyətə keçir. Reagentlət arasında reaksiya mülayim şəraitdə aparılır ki, bu da alkenlərin ekoloji cəhətdən təmiz oksidləşməsinin effektiv üsulunu işləyib hazırlamağa imkan verir.

Açar sözlər: *molekulyar oksigen, buten oksidləşməsi, udma, heksametilfosforamid.*

AJCN, Vol .5, No. 2, 2023, pp. 20-29
https://doi.org/10.32010/AJCN04022023-20

UDC 622.276.5

THE RESULTS OF STUDIES CRUDE OIL DEMULSIFICATION IN THE CONDITIONS OF PRIMARY PREPARATION OF OIL OF SOME DIFFICULT FIELDS OF THE REPUBLIC OF KAZAKHSTAN

A.A.Gasanov[0000-0002-0149-1943] , *T.K.Dashdiyeva*[0000-0001-7962-4323]
Azerbaijan State Oil and Industry University
turanamammadova15@gmail.com

The article presents comparative results of laboratory tests of some of our own nano-demulsifiers and basic demulsifiers in the conditions of primary preparation of crude oil at some difficult oil fields of the Republic of Kazakhstan ("Karajanbasmunai", "Western Prorva", "S. Balgimbaeva"). The results of the generally accepted method "Bottle Test" established significant advantages of nanodemulsifiers of the brand "IKHLAS-1", "ES-03" relative to foreign demulsifiers of the type "Randem-2208" (Rauan-Nalco); "Disolvan-4795" (Germany Switzerland, "Clariant International Ltd"); "F-929" (Japan). Since 2019, "IKHLAS-1" successfully is introduced to the S. Balgimbayev field JSC "Embamunaigas" "National Company "KazMunayGaz" JSC (KMGZ) with a two-fold decrease in the specific consumption of the demulsifier, and in 2022 it successfully passed the pilot test at the oilfield "Karajanbasmunai". For the first time, a mechanism for the simultaneous destruction of water-oil and oil-water emulsions was proposed.

Keywords: *nanodemulsifiers, cold demulsification, primary preparation of oil, polynanostructure of demulsifiers, oilfield nanotechnology, mechanism of simultaneous destruction of water-oil and oil-water emulsions.*

INTRODUCTION

Demulsification is the breaking of a crude oil emulsion into oil and water phases. From a process point of view, the oil producer is interested in three aspects of demulsification [1]:

- Rate or the speed at which this separation takes place;
- The amount of water (not more than 0.5%), salts (not more than 100 mg / dm^3) and mechanical impurities (not more than 0.05%) remaining after separation in oil must comply with the requirements of GOST [2] for commercial oil. To do this, as usual, the thermochemical method is used (heating crude oil to a certain temperature using special demulsifiers for each field by conducting laboratory and industrial tests) breaking up oil emulsions [3, 4];
- Quality of separated water for disposal - it is a very important environmental, technological and economic question. [5]. The concentration of oil and oil products in wastewater for reinjection into the reservoir should not exceed 50 mg/dm^3 [6]. It should be noted that the concentration of petroleum hydrocarbons in wastewater under conditions of primary preparation of oil mostly significantly exceeds the norm. For this reason, the reality of two priority directions for solving the problem in the world experience is brought to the attention of the authors [7-15]: use of hydrocyclones with modern constructions; development and application of a new generation of demulsifiers capable of breaking both reverse and straight emulsions at the same time. BP is one of the

world's leading companies in the management of environmental problems in offshore oil field development projects. History of BP Azerbaijan's activities related to groundwater management (Primary Oil Project; ACG Phase -1; ACG Phase-2; ACG Phase-3; SD-1; SD-2; Western Chirag; Covers Central-Eastern Azeri field and other global projects [7-11, 14, 15). Ever since the Environmental Impact Assessment (EIA) for Early Petroleum Project (1996), the issue of groundwater management has always been in focus. Various options related to the problem were proposed, necessary studies were conducted and the obtained results were discussed with the relevant state institutions as well as with the public of the republic [7-11, 15]. After extensive research and discussion of a number of alternative options, the BP company decided on the option of disposal of formation waters to the Central Azeri field. The essence of the option: formation water will be collected in the area of Sangachal Terminal and after the initial preparation technology, it will be transported to the Compression and Water Injection Platform, which will be equipped with modern cleaning devices in the Central Azeri field, where will be implemented disposal to 72 water injection wells, for the purpose of maintaining formation pressure (MFP) [7-11, 14, 15]. At the same time, 6 gas injection wells have been designed on this platform. 420 million US dollars have been allocated for the realization of such a project [15]. Due to the rather expensive and efficient technologies, the BP company managed to reduce the concentration of residual hydrocarbons in formation water from 72 mg/dm^3 commitment by agreement to 29 mg/dm^3 [15]. At present, the re-injection of formation water by the BP company in order to maintain formation pressure in a centralized manner is considered acceptable by all state and control bodies from both ecological and technological points of view [7-11, 14, 15]. Since such projects with large capital investments are mainly designed for the option of developing a complex of large deposits, in other options these projects are inappropriate. Reagents called reverse demulsifiers are being developed in China to break down direct oil emulsions [16-20]. However, the reagents have not found application in the field of oil preparation. These reagents are generally, to a certain extent, water-soluble polymers, such as anionic substances. For these polymers as high-molecular surfactants, the surface-active and adsorption properties at the liquid-gas (air) and liquid-liquid (water-oil) interfaces have not been sufficiently studied. Except this for these reagents, there is no theory to justify the destruction of directs emulsions (type oil in-water). Therefore, the development and implementation of demulsifiers for the treatment of formation waters from oil in the conditions of primary preparation of oil acquires a special relevance. And the issues of cold demulsification of crude oil to the level of commercial oil using nanodemulsifiers are also one of the priority areas of modern oilfield nanotechnology [12]. The purpose of the work was to conduct research on the cold demulsification of crude oil in the conditions of primary oil treatment in some complex fields of the Republic of Kazakhstan.

EXPERIMENTAL PART

Crude oil field LLP "Karajanbasmunai" "KazMunayGas". Required information on the field:

- Necessary information on the field: since 1974 in operation; annual oil production (AOP) = ~2 million tons; ρ≈940 kq/m^3 (in terms of density it belongs to the “bituminous oil” type [21]); water cut, up to 30%; sulfur up to 2%; paraffins: 0.7-1.4%; resins up to 24%; asphaltenes, on average, 5.7%; viscosity on average 400 mPa·s) [22].

- The difficulty of the field is associated with relatively high demulsifier consumption, high preparation temperature and high pollution of wastewater with oil. Base technology conditions in the primary preparation of oil system (PPOS): treatment temperature, up to 93°C; base demulsifier, “Randem-2208” (Rauan-Nalco); specific consumption of the demulsifier, S_c=238 g/t. Information about IKHLAS approbation: numerous bottle tests of the authors and KazNIPI with IKHLAS samples; successful experimental - industrial tests (EIT) (2022) “IKHLAS-1” with polynanostructure. As a result of the EIT study “IKHLAS-1” compared to base demulsifier, advantages were established for all indicators of PPO technologies.

Crude oil from the “Western Prorva” field JSC “Embamunaigas” "National Company "KazMunayGaz" JSC (KMGZ). Necessary information on the field:

- Required information on the field: located in the Embensky district of the Atyrau region, 170 km south-southeast of the city of Atyrau. The deposit was discovered in 1964; the deposit is under development; since 1966 in operation; AOP = ~770 000 t [23]; CCD temperature 73-96°C; $\rho\approx$823-899 kq/m^3 (in terms of density, it belongs to the type “especially light oil” - “bituminous oil” [21]); water cut, up to 30%; sulfur up to 1.46%; paraffins: 2.05-4.22%; resins up to 15.5%; asphaltenes ~1.12%; formation water highly mineralized 298,000 – 307,000 ppm [24];
- The difficulty of the field is associated with a relatively high demulsifier consumption, low oil preparation temperature at which it was a problem to replace of the base Japanese demulsifier F-929, and high oil pollution of wastewater.
- Basic technology conditions in the primary preparation of oil (PPO): cold demulsification (18°C); basic demulsifier, “F-929” (Japan); specific consumption of the demulsifier, Ur=95 g/t.

Crude oil from the “Balgimbaev” field JSC “Embamunaigas” "National Company "KazMunayGaz" JSC (KMGZ). Necessary information on the field:

- **Necessary information on the field:** since 1962 in operation; annual oil production (AOP) = ~134 000 tons; $\rho\approx$890 kq/m^3 [25] (in terms of density it belongs to the “heavy oil” type [21]); water cut, up to 17%; sulfur up to 0.12%; paraffins: 1.51%; resins up to 11.6%; asphaltenes, on average, 0.12%; viscosity on average 30.8 mPa·s) [26];
- The difficulty of the field is associated with a relatively high consumption of the demulsifier (246 g/t), low oil treatment temperature (25°C), at which it is problematic to replace of the base Swiss (according to German technology) demulsifier Dissolvan 4795, and high pollution of wastewater with oil (>50 mg/ dm^3) [27, 28].
- Chemical preparation of oil from the S. Balgimbaev field is carried out only at the ShPPPO using the demulsifier Disolvan-4795 (daily consumption is 89.94 kg) [27, 28]. More detailed information on the S. Balgimbaev field and about the works carried out us at this field is presented by in previous publications [27, 28].

As a reagent for oil treatment in the conditions of primary oil treatment at the above fields, by polynanostructured demulsifier “IKHLAS-1” (the production plant is located in Atyrau) with the following properties was used: active phase concentration ~50%; density ~908 kg/m^3; viscosity 29 mPa·s; freezing point (T_{fp}) less than -45°C, i.e. T_{fp} < - 45°C; color, - is yellow.

To conduct experiments to determine the effectiveness of demulsifiers, the generally accepted method “Bottle Test” [29] was used. The concentration of water (in

%), chloride salts (in mg/dm^3) and mechanical impurities (in %) in oil and the concentration of oil in produced water were determined in accordance with existing standards [6, 30-32].

RESULTS AND DISCUSSION

The results of the experiments are shown in tables 1-3. The relevant comments and interpretations are given below for each table separately.

Table 1

Comparative results of laboratory tests of nanodemulsifier "IKHLAS-1" and basic demulsifier "Randem-2208" with oil emulsions of the "Karajanbasmunai" field

Demulsifier	X_s, g/t	T, °C	τ, min	water, %		Efficiency, times	C_{oil}, mg/dm^3	Efficiency, times
				initial	residue			
Water-oil emulsion belonging to Prorva field								
"Randem-2208"	240	93	180	36	0.27	-	112	-
"Randem-2208"	240	90	180	36	0.75	-	156	-
"Randem-2208"	240	85	180	36	4.2	-	193	-
"Randem-2208"	240	80	180	36	18	-	230	-
"IKHLAS-1"	240	93	180	36	0.06	4.5	36	3.1
"IKHLAS-1"	240	90	180	36	0.35	2.1	40	3.9
"IKHLAS-1"	240	85	180	36	0.46	9	45	4.3
"IKHLAS-1"	240	80	180	36	0.50	36	48	4.8

Table 1:

- Values of initial bound water (36%), specific consumption of demulsifiers (240 g/t), temperature of oil treatment (80-93°C), settling time of oil treated with demulsifiers in glasses in a water bath (180 minutes) are quite important for a full qualitative and quantitative assessment of the corresponding comparative demulsification processes;
- Efficiency of "IKHLAS-1" for all values of Wr is 2.1-36 times higher than that of "Randem-2208";
- All Wr values at T=80-93°C for "IKHLAS-1" are below the norm for commercial oil, and for "Randem-2208" at T=80-90°C values of Wr value are 1.5-36 times higher than the norm;
- Values of oil concentration in the composition of produced water (Coil) for "IKHLAS-1", in contrast to "Randem-2208", do not exceed the norm ($C_{oil} > 50$ mg/dm^3). In addition, the efficiency of "IKHLAS-1" for all C_{oil} values is 3.1-4.8 times higher than that of "Randem-2208";
- Efficiency of "IKHLAS-1" relative to "Randem-2208" with water in oil (W/O inverse emulsion) and oil in water (O/W direct emulsion) emulsions of "Karajanbasmunai" field is due to polynanostructure of demulsifier "IKHLAS-1" [12, 33, 34], as well as with the most patent designation "IKHLAS-1" [13];
- The authors developed for the first time a special mechanism for the destruction of oil emulsions [12, 34];
- Fourfold nanostructure {nanomycelear structure of asphaltenes in a dispersion [35-37]; nanosized particles (droplets) of the dispersed phase; nanomolecular - adsorption layers (NMAL) around the particles of the dispersed phase; nanoparticles of

organic and inorganic origin inside the NMAL [27, 33]} is the most important nanocolloidal-chemical property for crude oil (water-oil emulsions);

• Nanodemulsifier "IKHLAS-1" in 2022 successfully passed the pilot test on the "Karajanbasmunai" field

Table 2

Results of bottle tests with demulsifier “IOS KZ” “ES-03” and basic demulsifier F-929 at the first stage of oil treatment at the CPF "Embamunaygaz"-2 (Prorva)

Demulsifier	X_s, g/t	T, °C	τ, min	water, %		Efficiency, times	C_{oil}, mg/dm^3	Efficiency, times
				initial	residue			
Water-oil emulsion belonging to “Prorva” field								
“F-929”	95	8-14	20	11	4.9	-	460	-
“F-929”	95	8-14	30	11	4.4	-	409	-
“F-929”	95	8-14	60	11	3.7	-	322	-
“F-929”	95	8-14	90	11	2.4	-	197	-
“F-929”	95	8-14	180	11	0.9	-	134	-
“F-929”	95	8-14	600	11	0,53	-	95	-
“ES-03”	95	8-14	20	11	4.1	1.2	175	2.6
“ES-03”	95	8-14	30	11	3.8	1.2	162	2.5
“ES-03”	95	8-14	60	11	2.7	1.4	123	2.6
“ES-03”	95	8-14	90	11	1.8	1.3	79	2.5
“ES-03”	95	8-14	180	11	0.47	2.0	50	2.3
“ES-03”	95	8-14	600	11	0.26	2.0	43	2

Table 2:

• The values of the specific consumptions of demulsifiers (95 g/t), under conditions of cold (8-14°C) demulsification of crude oil, the settling time of the oil treated with demulsifiers in glasses in a water bath (up to 600 minutes) are quite sufficient for full-fledged high-quality and quantification of relevant efficiency comparative demulsification processes;

• Efficiency of “ES-03” for all values of Wr is 1.2-2 times higher than that of “F-929”;

• According to Wr values at τ=180; 600 minutes "ES-03", in contrast to the base demulsifier "F-929", meets the norm for commercial oil, and for "Randem-2208" at T=80-90°C, the value of Wr is 1.06-1.8 times higher than the norm;

• Values of oil concentration in the composition of produced water (Coil) at τ=180; 600 minutes for “ES-03”, in contrast to “F-929” does not exceed the norm (Coil < 50 mg/dm^3). In addition, the efficiency of "ES-03" for all Coil values is 2-2.6 times higher than the efficiency of "F-929";

• “ES-03” proved to be the first strong demulsifier relative to the base demulsifier “F-929”;

• Efficiency of “ES-03” relative to “F-929” with emulsion water in oil (W/O inverse emulsion) and oil in water emulsions (O/W direct emulsion) of " Prorva i" field is due to the polynano structure of “ES-03” [12, 33, 34];

Table 3:

• The values of the specific consumption of demulsifiers (up to a maximum of 246 g/t), under conditions of relatively cold (25°C) demulsification of crude oil, the settling time of the oil treated with demulsifiers in glasses in a water bath (up to 60 minutes) are quite sufficient for a full-fledged high-quality and quantitative assessment of the corresponding comparative processes of demulsification [27, 28];

- Efficiency of "IKHLAS-**1**" for all values of Wr is 12-48 times higher than that of "Dissolvan-4795";
- All Wr values at Xs=123-246 g/t for "IKHLAS-1" are below the norm for commercial oil, and for "Dissolvan-4795" at Xs=123-150 g/t, the values of Wr in 3.4-9.6 times exceed the norm
- All Wr values at Xs=123-246 g/t for "IKHLAS-1" are below the norm for commercial oil, and for "Dissolvan-4795" at Xs=123-150 g/t, the values of Wr in 3.4-9.6 times exceed the norm;
- Values of oil concentration in the composition of produced water (Coil) for “IKHLAS-1”, in contrast to “Dissolvan-4795”, do not exceed the norm (Coil < 50 mg/dm^3). In addition, the efficiency of "IKHLAS-1" at Xs=123-150 g/t for all Coil values is 3.3-14 times higher than the efficiency of "Dissolvan-4795";
- Efficiency of “IKHLAS-1” regarding “Dissolvan-4795” with oil emulsions “S.Balgimbayev” field, relative to “Dissolvan-4795” is due to the polynanostructure of the demulsifier “IKHLAS-1” [12, 27, 28, 33, 34] and also with patent purpose appointment “IKHLAS-1” [13];
- Nanodemulsifier “IKHLAS-1” after pilot testing with positive results [28], since 07.01.2019 with a two-fold reduction in the specific consumption of the demulsifier, successfully is introduced to the "S.Balgimbayev" field

Table 3

“Embamunaygaz” AC “Jaikmunaygaz”OGPM (oil and gas production management) S.Balgimbayev field laboratory test results with oil-water emulsion

Demulsifier	X_s, g/t	T, ^{o}C	τ, min	water, %		Efficiency, times	C_{oil}, mg/dm^3	Efficiency, times
				initial	residue			
Water-oil emulsion belonging to S.Balgimbayev field								
“Dissolvan-4795”	246	25	60	17	0,38	–	59	–
“Dissolvan-4795”	200	25	60	17	0,45	–	397	–
“Dissolvan-4795”	150	25	60	17	1,7	–	462	–
“Dissolvan-4795”	123	25	60	17	4,8	–	490	–
“IKHLAS-1”	246	25	60	17	0,03	12	18	3,3
“IKHLAS-1”	200	25	60	17	0,03	15	28	14
“IKHLAS-1”	150	25	60	17	0,03	56	40	11
“IKHLAS-1”	123	25	60	17	0,10	48	43	11

Mechanism for the simultaneous destruction of water-oil and oil-water emulsions. It should be noted that such a mechanism is considered for the first time. It is known that during the synthesis of oxyethylated ethers of n-alcohols, acids, and other compounds, a certain mixture of oligomer homologues is formed [38], with a certain regularity in the distribution of monomers in the mixture depending on the number of oxyethylene units (n) in surfactant molecules [39]. Industrial samples of such ethers are characterized by an average number n [40]. Demulsifiers are mainly ether products of block copolymers based on ethylene and propylene oxides. Therefore, demulsifiers are also mixtures of oligomer homologues with specific values of n, which are expressed often by terms of the mass fraction of the oxyethylene chain in demulsifier molecules.

When the demulsifier is dosed in crude oil, oligomer homologues are redistributed in water-oil and oil-water emulsions. Monoesters with relatively low n values, i.e. the most hydrophobic components are distributed in water-oil emulsions, and components with relatively high values of n, i.e. relatively hydrophilic components pass into the oil-water emulsion. Due to a similar pattern of redistribution of oligomer homologues in crude oil, simultaneous destruction of water-oil and oil-water emulsions occurs and commercial oil is obtained with a water content of not more than 0.5%, as well as commercial waste water (formation water) with an oil content of not more than 50 mg/dm3 in accordance with existing standards [2, 6]. Therefore, demulsifiers of the ”IKHLAS” brand with a polynanostructure are designed for the simultaneous destruction of water-oil and oil-water [13]. The polynanostructure of demulsifiers, in general, contributes to the high intensity of the processes of destruction of both types of oil emulsion.

CONCLUSION

The results of the “Bottle Test” established the relatively high efficiency of nanodemulsifiers of the brand “IKHLAS-1” and “ES-03” relative to the basic demulsifiers “Randem-2208”, “Dissolvan-4795”, “F-929”, respectively, at the Karajanbasmunai deposits (50 % National Oil Company (NOC) “Kazmunaigas” of RK and 50% Chinese company Sinopec), “S.Balgimbaev” (“Embamunaigas” NOC “Kazmunaigas”) and Zapadnaya Prorva (“Embamunaigas” NOC “Kazmunaigas”). The nanodemulsifier “IKHLAS-1” is successfully introduced to the “S.Balgimbayev” field since July 1, 2019, and in 2022 it passed successful pilot tests at the “Karajanbasmunai” field, and in the future are planned, pilot tests of the nanodemulsifier “ES-03” at the "Western Prorva" field ". Reagents "IKHLAS-1" and "ES-03" are produced in Atyrau. For the first time, a mechanism for the simultaneous destruction of water-oil and oil-water emulsions was proposed.

REFERENCES

1. https://petrowiki.spe.org/Oil_demulsification
2. GOST 31378-2009. Oil. General technical conditions. M.: Standartinform. 2019,13 p
3. Markin, A.N. A.N. Markin, R.E. Nizamov, S.V. Sukhoverkhov. Petroleum chemistry Vladivostok: Dalnauka. 2011, 288 p
4. Croda oil and gas: [Electronic resource], URL: https://www.scribd.com/document/470657872/Kemelix-D510
5. Gasanov, A.A., Dashdiyeva, T.K., Dashdiyev, R.A. Evaluation of novel nanodemulsifier based on colloidal and non-colloidal surfactants for the removal of hydrocarbons from wastewater Kiev: Journal of water chemistry and technology. 2019. 41 (6), pp.377-383
6. OST 39–225–88 (OST 39–133–81). Water for flooding oil reservoirs. Quality requirements M.,2003,10 p
7. Appendix of AIESS Brief Review on ACG Phase 1: [Electronic resource], Baku, May 2003,30p. URL: https://www.bp.com/content/dam/bp-country/az_az/PDFs/ESIAs/ACG/ACG- Phase1-ESIA-executive-summary-addedndum-az.pdf

8. BP Azerbaijan Sustainable development report: [Electronic resource] ,Baku, 2017, 36 p. URL: https://www.bp.com/content/dam/bp/country-reports/bp-sr-az2017_az.pdf
9. The first gas was injected from the compressor and drilling platform: [Electronic resource], Baku, 2006, URL: https://www.bp.com/az_az/azerbaijan/home/news/press-releases1/kompressor
10. The first gas was injected from the compressor and water injection platform: [Elektron resurs], Baku, 2006, URL: https://www.bp.com/az_az/azerbaijan/home/news/environmental
11. BP's "Reservoir management and disposal project": [Electronic resource],Baku, 2006, URL: https://az.trend.az/business/energy/834278.html
12. Dashdiyeva, T.K. Development and application of nanodemulsifiers for the treatment of formation waters from oil in the conditions of preliminary oil preparation, Baku: Azerbaijan Journal of Chemical News. 2020, 2 (1), pp. 68- 76
13. Nugmanov, A.K., Demulsifier for the destruction of water-oil and oil-water emulsions, Patent № 30960, Republic of Kazakhstan. A.B.Orazbek., R.A.Dashdiev, T.K.Dashdieva [и др.], 2016
14. EIA "Early Oil". 1996, 374p. Ecological expertise and EIA procedure in Azerbaijan: Baku, 2011. 7 p.
15. Environmental and Socio-Economic Impact Assessment (ESIA) of the Azeri, Chirag and Deep Water Gunashli (ACG) oil fields. Scoping report: [Electronic resource], Baku, 2006,575 p. URL: https://www.bp.com/content/dam/bp/country-sites/en_az/azerbaijan/home/pdfs/esias/acg/acg_2ffd-esia.pdf
16. Yin, G., Dendritic reverse demulsifier and preparation method thereof, Patent №102233249, China Xu Ch., Li J., Zhao F. 2011. https://patents.google.com/patent/CN102233249A/en
17. Yin, G., Dendritic reverse demulsifier, Patent №102234526, China / Xu Ch., Li J., Zhao F. 2011 https://patents.google.com/patent/CN102234526A/en
18. Yin, G., Method for preparing dendrimer antiphase demulsifier, Patent № 102234374, China Xu Ch., Li J., Zhao F. 2011. https://patents.google.com/patent/CN102234374A/en
19. Yuan, Sh., Ingo, D. Perspectives in Liquid-Crystal-Aided Nanotechnology and Nanoscience. Basel: Applied sciences, 2019. 9 (12), pp. 1-47
20. Zhang, L. Preparation and characterization of nano-demulsifier ZIF- 8@CNTs based on MOFs for O/W emulsion demulsification: [Electronic resource] / L.Zhang, L.Wei, X.Jia [et al.]. Journal of Dispersion Science and Technology, Received 16 Mar 2022, Accepted 07 Jun 2022, Published online: 17 Jun 2022
21. GOST R 51858-2002 Oil. General specifications
22. Murzagaliev, R.S. Geological model of the «Karazhanbasmunai" field of high-viscosity oil and modern geotechnologies for its extraction: Abstract of the thesis. cand. those. sciences in geological and mineralogical sciences. Moscow, 2009, 25 p.
23. https://emba.kz/rus/press-centr/smi_o_nas/?cid=0&rid=766
24. Committee of Geology and Subsoil Use - Western Prorva http://www.investkz.com/journals/100/1285.html

25. Khasanov, B.K., Guzhikov, P.A., Kunzharikov, K.M. and others. Properties of high- viscosity oil of the eastern Moldabek field. Bulletin of the oil and gas industry of Kazakhstan, 2021. 1 (6), pp. 68-76
26. Ibragimova, S.T., Aikuldieva, S.A., Kurmanbaev, A.A., Faizulina, E.R. Influence of oil pollution on the enzymatic activity of soils of the Zhanatalap, Kumkol, Aktas fields. Izvestiya NAS RK. Biological series. 2009, № 1, pp. 21-25
27. Nugmanov, A.K., Gasanov, A.A., Dashdiyeva T.K. The results of the Experimental – industrial tests (EIT) of the nanoemulsifiers "IKHLAS" -1 and "IKHLAS"-2 at the shop primary preparatin of oil (ShPPO) and at the fields of oil and gas production department (OGPD) "Zhaikmunaigas" JSC "EmbaMunayGas" Scientific journal "Kazakhstan Innovations". 2018, 5 (9), pp.125-141
28. Dashdiyeva, T.K. Development and implementation of nanoemulsifiers for the purification of oil from formation water and formation water from oil in the conditions of the primary preparation of oil. IJMRME, 2019, 2(5), pp.1-8
29. https://www.linkedin.com/pulse/importance-bottle-test-petroleum-industry-procedure-
30. GOST 2477-2014. Oil and oil products. Method for determining the water content M .: Standartinform. 2018, 16 p.
31. GOST 21534-76. Oil. Methods for determining the content of chloride salts. M.: IPK Standards Publishing House. 2003, 33 p
32. GOST 6370-2018. Oil, oil products and impurities. Method for determining mechanical impurities. M. : Garnitura Arial. 2018, 6 p
33. Dashdiyeva, T.K. Development and implementation of nanodemulsifiers for the treatment of formation water from oil in conditions primary preparation of oil. Azerbaijan Journal of Chemical News. Baku 2020, №1 (2), pp.27-33
34. Dashdiyeva, T.K. Results of laboratory and industrial tests of "IKHLAS-1" nanodemulsifier on "Akkulka" field and the new mechanism of destruction of oil emulsions. Baku. Azerbaijani Chemistry Journal. 2020, №3, pp. 34-45
35. Evdokimov, I.N., Fesan A.A. Multi- step formation of asphaltene colloids in dilutes solutions. Colloid and Surfaces A: Physicochemical and Engineering Aspects. 2016, Vol.492. pp. 170–180
36. Evdokimov, I.N. Initial stages of asphaltenes aggregation in dilute crude oil solutions: studies of viscosity and NMR relaxation. I.N.Evdokimov, N.Yu.Eliseev, B.R.Akhmetov. Fuel. 2003, Vol. 82, № 7, pp. 817 - 823
37. Evdokimov, I.N. Rheological evidence of structural phase transitions in asphaltenes - containing petroleum fluids. I.N. Evdokimov, D.Yu.Eliseev, N.Yu.Eliseev. J.Petrol.Sci.Eng. 2001, T. 30, № 3-4, pp.199 -211
38. Gasanov, A.A., Dashdiyeva, T.K. Isolation and Identification of Individual Oxyethyl Esters of *n*-Aliphatic Acids Using Critical Nanoemulsion.Saint-Petersburg: Russian Journal of General Chemistry. 2017, 87 (8), pp. 1771-1774
39. Gumbatov, G.G. The use of surfactants for the elimination of emergency oil spills on the water surface. G.G.Gumbatov, R.A.Dashdiev. Baku: Elm, 1998, 210 p
40. Abramzon, A.A. Surface-active substances. Handbook. A.A. Abramzon, G.M. Gaeva L.: Chemistry. 1979, 376 p.

РЕЗУЛЬТАТЫ ИССЛЕДОВАНИЙ ПО ДЕЭМУЛЬСАЦИИ СЫРОЙ НЕФТИ В УСЛОВИЯХ ПЕРВИЧНОЙ ПОДГОТОВКИ НЕФТИ НЕКОТОРЫХ СЛОЖНЫХ МЕСТОРОЖДЕНИЙ РЕСПУБЛИКИ КАЗАХСТАН

A.A.Gasanov[0000-0002-0149-1943] *, T.K.Dashdiyeva*[0000-0001-7962-4323]
Азербайджанский Государственный Университет Нефти и Промышленности
turanamammadova15@gmail.com

В статье представлены сравнительные результаты лабораторных испытаний некоторых собственных нанодеэмульгаторов и базовых деэмульгаторов в условиях первичной подготовки сырой нефти некоторых сложных нефтяных месторождений Республики Казахстана ("Karajanbasmunai", «Западная Прорва», «С.Балгимбаева»). Результатами общепринятого метода "Bottle Test" установлены значительные преимущества нанодеэмульгаторов марки "IKHLAS-1", "ES-03" относительно зарубежным деэмульгаторам типа "Randem-2208" (Rauan-Nalco); Disolvan-4795 (Германия, Швейцария, "Clariant International Ltd"); F-929 (Япония). "IKHLAS-1" с 2019 года успешно внедряется на месторождение С.Балгимбава «Эмбамунайгаз» ННК «КазМунайГаз» с двухкратным снижением удельного расхода деэмульгатора, а в 2022 году успешно прошел ОПИ на месторождение «Karajanbasmunai". Впервые предложен механизм одновременного разрушения водонефтяных и нефтеводяных эмульсий.

Ключевые слова: *нанодеэмульгаторы, холодная деэмульсация, первичная подготовка нефти, полинаноструктура деэмульгаторов, нефтепромысловая нанотехнология, механизм одновременного разрушения водонефтяных и нефтеводяных эмульсий.*

QAZAXISTAN RESPUBLİKASININ BƏZİ MÜRƏKKƏB YATAQLARINDA XAM NEFTİN, NEFTİN İLKİN HAZIRLANMASI ŞƏRAİTİNDƏ DEMULSASİYA EDİLMƏSİ ÜZRƏ TƏDQİQAT NƏTİCƏLƏRİ

Ə.A.Həsənov[0000-0002-0149-1943] *, T.K.Daşdiyeva*[0000-0001-7962-4323]
Azərbaycan Dövlət Neft və Sənaye Universiteti
turanamammadova15@gmail.com

Məqalədə Qazaxıstan Respublikasının bəzi mürəkkəb neft yataqlarına ("Karajanbasmunai", "Qərbi Prorva", "S. Balqımbayev") uyğun neftin ilkin hazırlanması şəraitində müəlliflərə məxsus bəzi nanodeemulqatorların baza deemulqatorları ilə müqayisəli şəkildə laboratoriya sınaq nəticələri təqdim edilmişdir. Ümumən qəbul olunmuş "Bottle Test" metodunun nəticələri əsasında "İKHLAS-1", "ES-03" markalı nanodemulqatorların "Randem-2208" (Rauan-Nalco), "Disolvan-4795" (Almaniya, İsveçrə, "Clariant İnternational Ltd"), "F-929" (Yaponiya) tipli xarici demulqatorlara nisbətən əhəmiyyətli dərəcədə üstünlükləri müəyyən etmişdir. "İXLAS-1" 2019-cu ildən "KazMunayQaz" MNŞ, "Embamunaqaz" AC "S.Balqımbayev" yatağında demulqator xüsusi sərfinin ikiqat azaldılması şəraitində uğurla tətbiq edilir, 2022-ci ildə isə "Karajanbasmunai" yatağında keçirilən təcrübi - sənaye sınaq nəticələri müsbət oilmuşdur. İlk dəfə olaraq, su-neft və neft-su emulsiyalarının eyni zamanda parçalanma mexanizmi təklif edilmişdir.

Açar sözlər: *nanodemulqatorlar, soyuq deemulsasiya, neftin ilkin hazırlanması, polinanoquruluşlu demulqatorlar, neft- mədən nanotexnologiyası, su-neft və neft-su emulsiyalarının eyni zamanda parçalanma mexanizmi.*

AJCN, Vol .5, No. 2, 2023, pp. 30-36
https://doi.org/10.32010/AJCN04022023-30

UDC: 547. 592. 1. 543. 51: 620.197.3

SYNTHESIS OF N_1,N_1,N_3,N_3-TETRA(N'_1,N'_1-DIDEOXIMETHYLAZONE-N'-MONODEOXYMETHYLAZONE)QUANIDINE COMPOUND AND ITS RESEARCH AS A CORROSION INHIBITOR

G.İ.Bayramov[0000-0003-2561-0094]
Baku State University
qiyasbayramov@mail.ru

For the first time a new derivative of guanidine N_1,N_1,N_3,N_3-tetra(N'_1,N'_1-dideoxymethylazone-N'-monodeoxymethylazone)guanidine (conditionally QB-2) was synthesized by us. A research study was conducted to determine the corrosion inhibitor property of this compound in strong [3% NaCl + oil (10:1) + H_2S 500 mg/l; 0.3 N HCl + gasoline (1:7) + H_2S 1000mg/l] aggressive environments organized in laboratory conditions. During the research, it was determined that QB-2 compound even in concentrations 0.5; 1,0; 1,5; 2,0; 2,5; 3,0 mg/l the inhibitory efficiency was 99.92-100%. Due to the fact that this compound has a high boiling point and corrosion inhibitor properties, it is justified that it is of great ecological and economic importance in the corrosion protection of steel technological equipment operated in a strong aggressive environment in the oil-gas and petrochemical industries.

Keywords: *method, dideoxymethylazone, guanidine, synthesis, aggressive, environment, corrosion, inhibitor, oil-gas, petrochemical, industry, steel, technological equipment.*

INTRODUCTION

As it is known, one of the main reasons for the occurrence of environmental problems in the oil-gas and petrochemical industry is the corrosion of steel technological equipment operated in aggressive environments in that industry. Due to the fact that polyatomic nitrogen-containing organic substances have a higher inhibitory property in the corrosion protection of steel technological equipment operated in the production areas of that industry, such compounds have been used more in the industry for the last 70 years.

As is known from the technical literature [1] and the results of our long-term research [2-15] organic compounds with a lot of nitrogen atom, functional $ROCH_2$ -ether group, $-CH_2-$ group, double bonds that create electron density, C_6H_5 group are even, at the lowest concentrations 0.5; 1,0; 1,5; 2,0; 2,5; 3,0 mg/l the corrosion inhibitor efficiency of is 99.92-100%. In this regard, one of the substances we synthesized based on cheap raw materials according to our methods [2-15] is a new derivative of guanidine, unknown in the literature, N_1,N_1,N_3,N_3-tetra(N'_1,N'_1-dideoxymethylazone-N'-monodeoxymethylazone)guanidine (QB-2) compound, a research study was conducted to determine the corrosion inhibitor property.

That is, taking into account the explanations given above, the main purpose of the conducted research can be explained as follows:

- Synthesis of a new derivative of guanidine (compound QB-2), which contains nitrogen, carbon atoms, C_6H_5-group, azonyl group, $ROCH_2$-group, double bonds that increase the electron density.

- The main goal of the research was to determine the effective corrosion inhibitor properties of that compound for corrosion protection of steel technological equipment operated in high temperature and strong aggressive environments in the oil-gas and petrochemical industries

EXPERIMENTAL PART

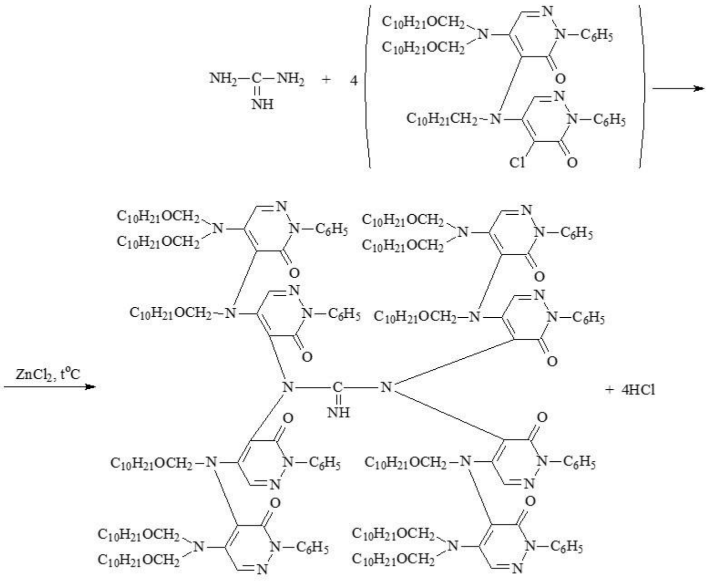
The synthesis of the above-mentioned QB-2 compound was carried out in accordance with the methods indicated in the literature [2-15] in the following sections. α-chlordeoxymethyl ether was obtained in the first stage:

$$C_{10}H_{21}OH+CH_2O+HCl \longrightarrow C_{10}H_{21}OCH_2Cl+H_2O$$

In stage II, the reaction of $C_{10}H_{21}OCH_2Cl$ ether with chlorazone (1:2) N'_1,N'_1-dioctoxymethylchloroazone ether was obtained. In stage III, the reaction of $C_{10}H_{21}OCH_2Cl$ ether (1:1) with chlorozone was carried out N'-monodesoxy-methylchloroazone ether was obtained. In stage IV, the reaction of N'_1,N'_1-dideoxymethylchloroazone with N'-monodeoxymethylchloroazone obtained in stages II and III was carried out N'_1,N'_1-dideoxymethylazone-N'-monodeoxymethylazone ether was obtained.

Elemental analyzes of the composition and structure of each substance synthesized in stages I and IV were carried out by the method indicated in the literature (Gelman.N.E and others 1987, p. 295). And the structure was determined by the spectrum taken with IQ spectrometer-Varian Scimitor 1000 FT-IR device and NMR H' BRUKER device.

In stage V, the reaction of N'_1,N'_1-dideoxymethylazone-N'-monodeoxymethyl-azone ether with gua;nidine was carried out.



The compound N_1,N_1,N_3,N_3-tetra(N'_1,N'_1-dideoxymethylazone-N'-monodeoxy-methylazone)guanidine (QB-2) was synthesized.

Synthesis of N_1,N_1,N_3,N_3-tetra(N'_1,N'_1-dideoxymethylazone-N'-monodeoxymethylazone)guanidine (QB-2) - The synthesis of compound QB-2 was carried out according to the method previously developed by us [2-15] in the following manner.

2 g of purified $ZnCl_2$ and 0.01 g-mol of guanidine are placed in the synthesis flask, 50 ml of C_2H_5OH spirit is added to it and mixed until the guanidine is completely dissolved. Then, 0.04 g-mol of N_1,N_1-dideoxymethylazone-N'-monododeoxymethylchloroazone is added to the mixture intermittently through a dropper. The reaction mixture was stirred at 70°C for 6 hours. After the completion of the reaction, 50 ml of 5% NaOH solution was added to the mixture at room temperature, mixed and washed with 200 ml of distilled water. Then, the finished reaction mixture from the synthesis flask is transferred to a separatory funnel, and 20 ml of diethyl ether is added to it and mixed several times. The obtained organic layer is separated from the water layer. The diethyl ether in the separated organic layer is pumped out with a water pump and dried over $CaCl_2$. The reaction product is then expelled in a vacuum unit. The synthesized compound N_1,N_1,N_3,N_3-tetra(N_1,N_1-dideoxymethylazone-N'-monodeoxymethylazone)-guanidine (QB-3) is a greenish-pink viscous liquid with a weak aromatic odor.

The structure and composition of the synthesized N_1,N_1,N_3,N_3-tetra(N'_1,N'_1 dideoxymethylazone-N'-monodeoxymethylazone)guanidine (QB-2) compound of guanidine, unknown in the literature, were determined by IR and NMR spectra (IQ spectrometer-Varian Scimitor 1000 FT-IR device and NMR H' BRUKER device) using known methods.The physico-chemical constants of that compound are shown in table 1.

In the IQ spectrum of the compound QB-2, the characteristic intense bands of the groups and bonds contained in it were obtained: C_6H_5- groups 700-780 sm^{-1}; $-CH_2-O-CH_2$ ether groups 1050, 1080 sm^{-1}; C-N bonds 1178,1310,1350 sm^{-1}; CH_2-groups 2950 sm^{-1}; CH_3-groups 1380,1460,2960,3030 sm^{-1}, C=C bonds in benzene nuclei (rings) 2810-3135 sm^{-1}, C=O bonds 1440-1465,1500-1510,1590-1610 sm^{-1}; in azone groups: C=C bonds 1680 sm^{-1}; C-H bonds 2810-3135 sm^{-1}; C=O bonds 1705-1720 sm^{-1}; CH=N-bonds 1640-1670 sm^{-1}; N-N bonds 1580 sm^{-1}; $-N-CH_2-O-$ groups 3400-3450 sm^{-1}.

Table 1

Derivation, physicochemical constants, elemental analyzes of the synthesized new derivative of guanidine N_1,N_1,N_3,N_3-tetra(N'_1,N'_1-dideoxymethylazone-N'-monodeoxymethylazone)guanidine (QB-2)

Conditional connection number	QB-2
Output%	98.64
$t_{b.p}$°C mm Hg	409-410 (2)
d_4^{20}	2.3215
n_D^{20}	2.8045
MR_D found/ computed	1072.85/1072.53
Brutto formula, mol. the whole	$C_{153}H_{154}N_{28}O_{21}Cl_{12}$
Elemental analysis % Calculated/ found	
C	$\frac{71.42}{71.38}$
H	$\frac{9.08}{9.05}$
N	$\frac{10.8}{10.42}$

The following characteristic signals were observed in the NMR' H spectrum of N_1,N_1,N_3,N_3-tetra(N'_1,N'_1-dideoxymethylazone-N'-monodeoxymethylazone)guanidine (QB-2): NMR' H, b, m.d.: 0.88-0.89 s. (36 H, 12 CH_3; 12-$C_{12}H_{25}$ in the group); 1.34-1.85 4 t. (in the group 216 H,108 –CH_2– 12 $C_{10}H_{21}$); 3.25-3.49 two t. (48 in H,12 –CH_2–O–CH_2-group); 6.68-6.70 s. (in the 6 H,6 -N=CH group in azone rings); 7.42-7.49 m. (1 H, >C=NH in guanidine group); 7.80-7.85 d. (40 H, 8 in the C_6H_5 group).

A scientific research work was carried out in laboratory conditions to determine the corrosion inhibitor properties of the new synthesized guanidine derivative QB-2 compound. of QB-2 combination of "Cm.3" brand steel plates in strong [3% NaCl + oil (10:1) + H_2S 500 mg/l; 0.3 N HCl + gasoline (1:7) + H_2S 1000mg/l] aggressive environments organized in those laboratory conditions corrosion rate was determined at concentrations of 0.05; 0.10; 0.20 mg/l. The research was conducted mainly in those environments in 4-necked flasks at 85-90^{0}C for 6 hours with 600 revolutions/min of stirring and metal mass loss based on the "gravimetric" method according to the rules specified in the literature [2-15].

Based on the results of the research, it was determined that the synthesized N_1,N_1,N_3,N_3-tetra(N'_1,N'_1-dideoxymethylazone-N'-monodeoxymethylazone)guanidine (QB-2) compound at concentrations of 0.5; 1,0; 1,5; 2,0; 2,5; 3,0 mg/l in the above environments corrosion inhibitor efficiency is 99.92-100%. The results of the study on determining the inhibitory efficiency of that compound are shown in table 2.

Table 2

The results of the investigation of the synthesized new derivative of guanidine N_1,N_1,N_3,N_3-tetra(N'1,N'1-dideoxymethylazone-N'- monodeoxymethylazone)guanidine (QB-2) as a corrosion inhibitor

Conventional name of the combination	The concentration of the inhibitor, mg/l	3% NaCl+oil(10:1), H_2S 500 mg/l		0,3N HCl+gazolin(1:7)+ H_2S 1000mg/l	
		Corrosion rate g/sm^2 x hour	Inhibitor efficacy %	Corrosion rate g/sm^2 x hour	Inhibitor efficacy %
Without inhibitor	-	2.56	-	3.65	-
QB-2	0.05	0.0006	99.96	0.0005	99.96
	0.10	0.0004	99.98	0.0002	99.99
	0.20	0.0001	100		100
A[10]	200	0.038	98.51	0.073	98

As mentioned in literature [22], the inhibitory efficiency of the modern effective corrosion inhibitor "AMDOR IK-7" is 98% at the highest concentration.

RESULTS AND DISCUSSION

The corrosion inhibitor effectiveness of the new synthesized derivative of guanidine, QB-2, can be theoretically explained in the following way, taking into account the data and explanations mentioned in our previous research studies and literature [2-16].

Due to the presence of 27 nitrogen atoms, 12 functional $C_{10}H_{21}OCH_2$ ether groups, 8 C_6H_5 groups, 8 heteroatom azonyl groups, 49 double bonds that increase the electron density, internal Van der Waals forces increase. As a result of this, it is likely that "nitrogen-metal", "$C_{10}H_{21}OCH_2$-metal", "C_6H_5-metal", "azonyl group-metal" coordination bonds are formed on the metal surface, and due to the adsorption of that compound, forming a very thin layer on the surface of the metal reduces the corrosion rate of that metal to zero.

According to the research conducted by us, it was determined that compared to inhibitor substances known in the technical literature and awarded an invention patent (except for our research works and invention patents), as well as corrosion inhibitors used in the oil-gas and petrochemical industry, the QB-2 substance has 4-5 times the economic and ecological advantages.

Thus, a new derivative of synthesized guanidine, unknown in the literature, N_1,N_1,N_3,N_3-tetra(N'_1,N'_1-dideoxymethylazone-N'-monodeoxymethylazone)guanidine (QB-2) is aggressive in the oil-gas and petrochemical industries. it can be considered scientifically justified to use it as an inhibitor, which has a very high efficiency in the corrosion protection of steel technological equipment operated in the environment. This combination does not have a negative impact on the quality of production products and meets modern environmental safety requirements.

CONCLUSION

The reaction of N'_1,N'_1-dideoxymethylchloroazone with N'-monodeoxymethylchloroazone ether gave N'_1,N'_1-dideoxymethylazone-N'-monodeoxymethylchloroazone ether. The reaction of this ether with guanidine was carried out, as a result of which a new derivative, unknown in the literature, was synthesized (conventionally designated as QB-2). Studies have been carried out to determine the inhibitory efficacy of the synthesized new guanidine derivative N_1,N_1,N_3,N_3-tetra(N'_1,N'_1-dideoxymethylazone-N'-monodeoxymethylazone)guanidine compound QB-2, which has 27 nitrogen atoms, 12 functional $C_{10}H_{21}OCH_2$, 8 C_6H_5 – groups, 8 heteroatom azonyl groups and 49 double bonds.

In the process of research in the most highly aggressive environments [3% NaCl + oil (10:1) + H_2S 500 mg/l; 0.1 N HCl + gasoline (1:7) + H_2S 1000 mg/l] compiled in laboratory conditions, 99.92-100% inhibitory efficiency of this compound was established at its concentration of 0.5; 1,0; 1,5; 2,0; 2,5; 3,0 mg/l. The inhibitory efficiency of the synthesized new derivative of guanidine QB-2 is several times higher than that of the inhibitors currently used in all industrial enterprises to protect steel processing equipment in the most aggressive environments.

REFERENCES

1. Rachev H, Stefanova S. Handbook of corrosion. M.: Mir. 1982, pp. 62
2. Bayramov G.I. Synthesis of new derivatives of diphenylguanidine and their study as corrosion inhibitors. Scientific and technical production and educational-methodical journal. RAS Moscow, Science and Technology, Journal of Corrosion metal, sewn up. № 1, 2010, pp. 54-57
3. Bayramov G.I. Synthesis of sulfur-, as well as nitrogen and sulfur-containing new organic compounds based on 1-methyl-1-chloro-2-octoxymethyl-cyclohexane. Zhur. Chemical Issues. Baku. № 1, 2008, pp. 96-99

4. Hajiyeva S.R, Bayramov G.I, Alieva T.I. Synthesis and study of a new derivative of sulfadimesine based on dioxymethylchlorazone ether as an environmentally effective inhibitor. Young scientist, International scientific journa. № 6, 2019, part III, pp. 1-5
5. Shikhmamedbekova A.Z, Mamedyarova I.F, Bayramov G.I, Mamedalieva G.G. N, N' – diphenyl – N' - octoxymethyl-guanidine as a steel corrosion inhibitor in a two-phase system. Author. Certificate USSR, .№1031141, 1983, A C07 C129/12; C23 F 11/14
6. Hajiyeva S.R, Bayramov Q.I, Cafarova N.M, Veliyeva Z.T, Rafiyeva H.L, Samadova A.A. Synthesis and Investigation of New Sulphadimezine Compounds Based On α-Chloroalkyl and Acyloxymethyl Ether. Internatinal Journal of Scientific & Engineering Research (IJSER).Vol.10, Issue7, July 2019, pp. 258-261
7. Hajiyeva S.R, Shamilov N.T, Bayramov Q.I, Huseynov F.E, Aliyeva T.I, Rafiyeva H.L, Samadova A.A, Veliyeva Z.T, Jafarova M.M, Gullerly G.G. Synthesis and research of new compaunds of guanidine on the basis of α-chlorether and chlorazone. Annali α-Italia Scientific Journal of Italy. Chemical Sciences 50134, Via Carlo Pisacane, 10, Florence, Italy. Vol. 1, №8, 2020, pp. 10-17
8. Frolova L.V, Agafankin F.V. and others. Inhibition of hydrogen sulfide corrosion of carbon steels by N-ethanolbutyleneamine and its mixtures with tertiary amine. Journal of corrosion: materials, protection. M .: Publishing house of Science and Technology LLC. №1, 2010, pp. 15
9. Shel N.V, Tsygankova L.E, Kimya R. New generation of metal corrosion inhibitors for the oil and petrochemical industries. XVIII Mendeleev Conference on General and Applied Chemistry, M.Nauka. 2007, pp. 1608
10. Marshakov A.I, Nenasheva T.A. Kinetics of dissolution of hydrogenated iron in an acidic chloride electrolyte. Zhur. Protection of metals, M. Nauka.Vol.42. №2, 2006, pp. 1-8
11. Avdeev Ya.G, Belinsky P.A. High-Temperature Steel Corrosion Inhibitor in Sulfuric Acid Solutions. Zhurn. Corrosion: materials, protection. M.: ed. LLC "Science and Technology". № 1, 2010, pp. 27
12. Khudyakova L.P. The system for ensuring the safety of operation of oil and gas equipment and pipelines operating in aggressive environments. GUP. IPTER, Ufa. 2008, pp. 39
13. Study of the effect of hydrogen sulfide on corrosion processes in the operational characteristics of structural elements of pipelines and tanks. Problems of collection, preparation and transport of oil and oil products: Sat. scientific papers, IPTER. Issue 65, 2005, pp. 27-40
14. Khudyakova L.P, Spashenko A.Yu, Antipov Yu.N. Assessing the degree of danger of stress-corrosion cracks - NTZ "Problems, collection, preparation and transport of oil and oil products", IPTER.Ufa. Issue 3(69), 2007, pp. 39-41
15. Khudyakova L.P, Spashenko A.Yu. and others. Estimated assessment of the rate of corrosion-mechanical cracking of oil and gas equipment and pipelines. STJ "Problems, collection, preparation and transport of oil and oil products", IPTER.Ufa. Issue 3(69), 2007, pp. 61-63
16. Gurvich L.M, Sherstiev N.M. Multifunctional compositions of surfactants in technological operations of oil production. M.: VNIIOENG, 1994, pp. 268

СИНТЕЗ N_1,N_1,N_3,N_3-ТЕТРА(N'_1,N'_1-ДИДЕЗОКСИМЕТИЛАЗОН-N'-МОНОДЕЗОКСИМЕТИЛАЗОН)ГУАНИДИННОГО СОЕДИНЕНИЯ И ИССЛЕДОВАНИЕ КАК ИНГИБИТОРА КОРРОЗИИ

Г.И.Байрамов[0000-0003-2561-0094]
Бакинский Государственный Университет
qiyasbayramov@mail.ru

Новое соединение гуанидина N_1,N_1,N_3,N_3-тетра(N'_1,N'_1-дидецоксиметилазон-N'-монодецоксиметилазон)гуанидин (условно QB-2) было синтезировано нами впервые. Были проведены исследования по определению ингибиторных свойств этого соединения в сильно [3% NaCl + масло (10:1) + H_2S 500 мг/л; 0,3 Н HCl + бензин (1:7) + H_2S 1000мг/л] агрессивных средах, осуществленных в лабораторных условиях. В ходе исследований установлено, что у соединения QB-2 даже в концентрации 0.5; 1.0; 1,5; 2.0; 2,5; 3,0 мг/л ингибирующая эффективность составляет 99,92-100%. В связи с тем, что данное соединение обладает высокой температурой кипения и свойствами ингибитора коррозии, оправдано, что оно имеет большое экологическое, экономическое значение при защите от коррозии стального технологического оборудования, эксплуатируемого в сильно агрессивной среде в нефтегазовой и нефтехимической промышленности.

Ключевые слова: *метод, дидецоксиметилазон, гуанидин, синтез, агрессивная, среда, коррозия, ингибитор, нефтегазох, нефтехимия, промышленность, сталь, технологическое оборудование.*

N_1,N_1,N_3,N_3-TETRA(N'_1,N'_1-DIDESOKSİMETİLAZON-N'-MONODESOKSİMETİLAZON)QUANİDİN BİRLƏŞMƏSİNİN SİNTEZİ VƏ KORROZİYA İNHİBİTORU KİMİ TƏDQİQİ

Q.İ.Bayramov[0000-0003-2561-0094]
Bakı Dövlət Universiteti
qiyasbayramov@mail.ru

Tərəfimizdən ilk dəfə olaraq quanidinin yeni törəməsi N_1,N_1,N_3,N_3-tetra(N'_1,N'_1-didesoksimetilazon-N'-monodesoksimetilazon)quanidin (şərti olaraq QB-2) sintez edilmişdir. Laboratoriya şəraitində təşkil edilmiş güclü [3% NaCl + neft (10:1) + H_2S 500 mq/l; 0,3 N HCl + benzin (1:7) + H_2S 1000mq/l] aqressiv mühitlərdə bu birləşmənin korroziya inhibitor xüsusiyyətini müəyyən etmək üçün tədqiqat işi aparılmışdır. Tədqiqat zamanı müəyyən edilmişdir ki, QB-2 birləşməsinin hətta 0,5; 1,0; 1,5; 2,0; 2,5; 3,0 mq/l konsentrasiyalarda inhibitor effektivliyi 99,92-100% təşkil etmişdir. Bu birləşmənin yüksək qaynama temperaturuna və korroziyaya qarşı inhibitor xüsusiyyətlərinə malik olması səbəbindən neft-qaz və neft-kimya sənayesində güclü aqressiv mühitdə işləyən polad texnoloji avadanlıqların korroziyadan qorunmasında böyük ekoloji və iqtisadi əhəmiyyət kəsb etməsi elmi əsaslandırılır.

Açar sözlər: *metod, didesoksimetilazon, quanidin, sintez, aqressiv, ətraf mühit, korroziya, inhibitor, neft-qaz, neft-kimya, sənaye, polad, texnoloji avadanlıq.*

AJCN, Vol. 5, No. 2, 2023, pp. 37-44
https://doi.org/10.32010/AJCN04022023-37

UDC 544

COMPREHENSIVE SANITARY AND ENVIRONMENTAL EXAMINATION OF THE BAKU COASTAL WATERS OF THE CASPIAN SEA

Kh.F.Mammadov$^{0000-0002-2509-1215}$, *M.Sh.Javadly*[2],
A.H.Huseynova$^{0000-0003-0399-0815}$, *E.I.Guliyev*[1]
[1]*Institute of Radiation Problems of the Ministry of Science and Education of the Republic of Azerbaijan,* [2]*Azerbaijan State Oil and Industry University*
xagani06@mail.ru

The widespread introduction of offshore methods of oil production has led to the pollution of the seawater of the Baku water area. To assess the current state, we carried out a comprehensive sanitary and environmental research of the Baku water area of the Caspian Sea, determined the concentrations of mineral salts (sulfates, chlorides, calcium carbonates, nitrates, nitrites), heavy metals (Sr, Fe, Mn, Zn, As) and radionuclides (Na^{22}*,* K^{40}*,* Fe^{60}*,* Co^{57}*,* Zn^{65}*,* Sr^{91}*,* $Eu^{152,154}$*,* Ra^{226}*) in sea water. Comparative analysis of the results of researches made it possible to conclude that there is a tendency to improve the ecological state of the Absheron Peninsula. The chemical composition of seawater, seaweed and sea sand samples shows that they can be used as beach sand and beach water, respectively. However, the study of microbiological indicators of seawater indicates the presence of pathogenic microorganisms on some beaches of the Caspian Sea, which requires the introduction of a certain restriction in the resolution of the beach season. Since pathogenic Salmonella bacteria have been found in the water of some beaches, according to sanitary and hygienic requirements, it is not advisable to swallow water when swimming, and after bathing, it is advisable to rinse with clean water. The concentration of mineral salts and heavy metals in the Caspian Sea water is many times higher than the corresponding indicators in drinking water sources. But, the concentration of radionuclides in sea water is 2-3 times lower than the concentration of radionuclides in drinking water sources, seaweed and sea sand.*

Keywords: *seawater, types of pollution, algae, sandy beach, coastal soil, mineral composition, radionuclides, radioactive background.*

INTRODUCTION

The presence of natural sources of energy, the uncontrolled production of gaseous and liquid hydrocarbons in the early stages of the development of the oil industry in Azerbaijan, the cases of spontaneous eruption and the spread of the oil over semi-desert plains, low-tech crude oil processing have led to large-scale contamination of the soil cover of the city of Baku. The capital of Azerbaijan, Baku, is located on the Absheron Peninsula, which has always been famous for its large oil fields. On the territory of the Absheron archipelago and adjacent territories there are numerous oil production facilities, huge oil storage facilities and metal tanks of various capacities for storing oil products, oil refining and petrochemical production facilities that are still functioning. These areas are characterized by high seismic activity. During natural disasters in these territories, man-made accidents occur, oil and petroleum product spills spread to adjacent territories, and pollution of land, water basins and atmospheric air occurs. Oil and most petroleum products have high viscosity and properties that evaporate easily; light fractions of oil have a high saturated vapor pressure. Consequently, their bottling leads to the spread of petroleum products over large areas, polluting water bodies and atmospheric air in adjacent areas. The development and implementation of offshore oil production methods have led to the pollution of the coastal waters of the Baku water area of the Caspian Sea. The above processes have become the causes of large-scale disturbances in the balance of natural processes occurring in interconnected objects of nature, irreversible deterioration of the ecological state of the environment. The closure of old production facilities and their replacement with new, relatively high-tech, sometimes waste-free production facilities only partially stopped environmental pollution, but did not completely eliminate the negative consequences of the environmental catastrophe [1-4]. To assess the current state of the Baku coastal area of the Caspian Sea, we carried out a comprehensive sanitary and environmental survey of this zone.

EXPERIMENTAL PART

An external examination in a stationary laboratory condition of the water samples taken was carried out and the presence of suspended particles and sediments was assessed, which were further isolated by filtering the water sample. Next, organoleptic, physicochemical and microbiological studies were carried out step by step.

When conducting organoleptic and express analyses, taste, smell, turbidity, transparency, color, chemical analysis using standard tests, active reaction, i.e. pH of water were determined.

Physical-chemical studies were carried out by determining the mineral composition with evaporation of water and obtaining a white mineral salt deposit, conducting analytical-chemical, X-ray fluorescence, atom-adsorption and activation analyses.

Microbiological studies were carried out by counting the number of colonies of microorganisms under a mesh magnifying glass, by counting microorganisms grown from a certain amount of water on standard microbiological test wipes or over a nutrient medium in Petri dishes, by comparing them with data from the corresponding microbiological atlases.

Minerals, heavy metals and radionuclides were analyzed using X-ray fluorescence (Expert-3L - Ukraine, XRF - USA), atomic absorption (AA-6800 - Shimadzu, Japan) and gamma spectrometry (Canberra with HPGe detector - USA).

Microbiological analyzes were carried out by growing colonies of microorganisms on selective standard nutrient media "Hi-Media" - India, "Condalab" – Spain [4-7].

To carry out systematic radiometric measurements and monitoring, a Thermo Eberline R020 SI dosimeter (Thermo Electron Co., USA) was used, the presence of alpha, beta, gamma, neutron, X-ray types of radiation and the intensity of radiation were assessed using a PRM gamma counter. -470CG" (Tesla Systems Ltd., USA), radiometer-dosimeter "InSpector 1000" (Canberra Co., USA-France), radiometer-counter alpha, beta, gamma, neutron radiation "Radiagem 2000" (Canberra Co., USA - France), search gamma-neutron radiometer-dosimeter ISP-RM1401K-01 IP65 (POLIMASTER, Minsk, Belarus) and for the determination of isotopes used the radiometer "IdentiFINDER" (Thermo Scientific Co., Germany-USA) and "GR-135 Plus" (Exploranium Co., USA-Canada) [6 - 9].

RESULTS AND DISCUSSION

After centrifugation, filtration and evaporation of seawater, it was determined that the compositions of the obtained mineral residues are identical for all seawater samples taken in the Baku area. The results of complex organoleptic, physicochemical and microbiological analyzes of seawater samples are shown in table1

Table 1

Results of the analysis of water samples taken from the beaches of the Caspian Sea on 02.05.2023

№	Parameters	Requirements of the standard (2874-82)	Actual results				Note
			1	2	3	4	
1	2	3	4	5	6	7	8
1.	Transparency, cm	>10	30	15	15	11	norm
2.	Turbidity, °	≤1,5	1,1	1,4	1,4	1,5	norm
3.	Sediment	0 or trace	trace	Trace	trace	trace	norm
4.	Color, °	≤20*					-
		≤40**-***	20	30	30	40	norm
5.	Smell at 20°C with points	≤2*					-
		≤3**-***	1	3	3	3	norm
6.	Taste at 20°C with points	≤2*					-
		salty**-***	salty	salty	salty	salty	norm
7.	Activity (pH)	6,0-9,0	7,8	7,6	7,8	7,6	norm
8.	Dry residue, mg/l	100÷1000*					-
		not normalized*** (>1000***)	13500	13500	13500	13500	norm
9.	Total rigidity, mmol/l	3,5-7,0*					-
		not normalized*** (>7.0)	30	30	30	30	norm
10.	Hydrocarbon concentration, mg-eq/l	<7*					-
		<15***	6	6	6	6	norm
11.	Zinc, mg/l	5	3-9	3-9	3-9	3-9	norm
12.	Nickel, mg/l	0*					-
		not normalized ***	0.001	0.001	0.001	0.001	norm
13	Residual chlorine, mg/l	0-0,5	0	0	0	0	norm
14	Free chlorine, mg/l	0	0	0	0	0	norm
15.	Nitrate, mg/l	45	0-2,5	0-2,5	0-2,5	0-2,5	norm
16.	Cadmium, mg/l	0*					-
		not normalized ***	0.001	0.001	0.001	0.001	norm
17.	Cyanides, mg/l	0	0	0	0	0	norm
18.	Copper, mg/l	1.0	0,19	0,19	0,20	0,20	norm
19.	Aluminum, mg/l	0.5	0	0	0	0	norm
20.	Iron, mg/l	0.3* 1**-100***	0,3-12	0,4-14	0,5-27	0,5-27	norm
21.	Lead, mg/l	0.03	0	0	0	0	norm
22	Manganese, mg/l	0.1	0	0	0	0	norm

Cont. of tab. 1

1	2	3	4	5	6	7	8
23.	Chromium, mg/l	0.5	0.01	0.01	0.01	0.01	norm
24.	Sulphates, mg/l	500	470-780	480-780	490-790	490-790	norm
25.	Phosphates, mg/l, (organic P)**	not normalized ***	0,01	0,02	0,02	0,03	norm
26.	E.coli number, number in 1 liter;	≤3* ≤9**					-
		300-5000***	55	900	700	2000	norm
27.	Coli-titr, the amount of water in which 1 unit is found, ml	>300* >100**					-
		>0,2-3***	18	1.1	1.4	0.5	norm
28	The number of saprophytic microorganisms in 1 liter:	≤100* ≤2000***	2	20	24	25	- norm
	-aspergillus niger	-	1	10	10	15	-
	-candida albicans	-	1	10	14	10	-
29.	Staphylococcus aureus, number in 1 liter	0* 10-500***	0	12	10	12	norm
30.	Staphylococcus epidermidis, number in 1 liter	0* 10-500***	0	100	80	100	norm
31	Micrococcus, number in 1 liter	0* 1000***	60	800	600	860	norm
32.	Streptococcus pyogenes,number in 1 liter	0* 10-500***	0	0	0	0	- norm
33.	Mold and yeast fungi, in 1 liter	-	3	22	25	28	-
34.	Total microbial count, in 1 ml	100*					-
		5000***	5	160	100	170	norm
35	Number of pathogenic microorganisms, including Salmonella in 1 liter	0 * not allowed in 10% of samples ***	0	6	4	10	norm (high)

Note: * - norm for drinking water [8, 9],
** - norm for tap water,
*** - norm for seawater.

1. Sea water samples taken at a distance of 5 and 20 m from the shore at Shuvalan beach;
2. Sea water samples taken at a distance of 5 and 20 m from the coast of Novkhani beach;

3. Sea water samples taken at a distance of 5 and 20 m from the shore of Shikh Beach;

4. Sea water samples taken at 5 and 20 m from the shore of Hovsan seaside jetty.

The chemical composition of the obtained mineral (dry) residue of seawater and seaweed consists mainly of the following components:

- as can be seen from Table No. 1, the total salinity in seawater is 13500 mg/l, of which the amount of sulfates is 751 mg/l, the amount of chlorides is 4300 mg/l, the amount of total calcium carbonates is 1416 mg/l, and the amount of nitrate and nitrite compounds is practically zero;
- the samples of seawater are characterized by the same indicator, and the amount of trace elements are Na 2603 mg/l, K 12 mg/l, I 62 mg/l, Sr 18 mg/l, Fe 27 mg/l, Mn 32 mg/l, 9 Zn mg/l and As 0.28 mg/liter;
- the seawater samples are characterized by the same trace amounts of radionuclides, such as $_{22}\text{Na}^{11}$ 0.50 Bq/l, $_{19}\text{K}^{40}$ 0.08 Bq/l, $_{26}\text{Fe}^{60}$ 0.30 Bq/l, $_{27}\text{Co}^{57}$ 0.25 Bq/l, $_{30}\text{Zn}^{65}$ 0.06 Bq/l, $_{38}\text{Sr}^{91}$ 0.10 Bq/l, $_{63}\text{Eu}^{152,154}$ 0.16, 0.24 Bq/l and $_{88}\text{Ra}^{226}$ 0.2 Bq/liter;
- the amount of sulfates in samples of seaweed (algae) taken from the sea sand near the village Bibiheybat of Sabail district is 300 mg/kg, the amount of chlorides is 330 mg/kg, the amount of total calcium carbonates is 1634 mg/kg, and the amount of nitrate and nitrite compounds is 6 mg/kg and 0.9 mg/kg respectively;
- the samples of seaweed (algae) are characterized by the same indicator, and the amount of trace elements are Na 261 mg/kg, K 2860 mg/kg, I 4.3 mg/kg, Sr 10 mg/kg, Fe 10 mg/kg, Mn 3 mg/kg, 2 Zn mg/kg and As 0.02 mg/kg;
- the seaweed (algae) samples are characterized by the same trace amounts of radionuclides, such as $_{22}\text{Na}^{11}$ 1.0 Bq/kg, $_{19}\text{K}^{40}$ 0.8 Bq/kg, $_{26}\text{Fe}^{60}$ 0.56 Bq/kg, $_{27}\text{Co}^{57}$ 0.5 Bq/kg, $_{30}\text{Zn}^{65}$ 0.12 Bq/kg, $_{38}\text{Sr}^{91}$ 0.2 Bq/kg, $_{63}\text{Eu}^{152,154}$ 0.30, 0.46 Bq/kg and $_{88}\text{Ra}^{226}$ 0.38 Bq/kg;
- the amount of sulfates in samples of sea sand taken near the village Bibiheybat of Sabail district is 310 mg/kg, the amount of chlorides is 1355 mg/kg, the amount of total calcium carbonates is 3645 mg/kg, and the amount of nitrate and nitrite compounds is 34 mg/kg and 1.2 mg/kg respectively;
- the samples of sea sand are characterized by the same indicator, and the amount of trace elements are Na 115 mg/kg, K 3960 mg/kg, I 1.8 mg/kg, Sr 28 mg/kg, Fe 162 mg/kg, Mn 6 mg/kg, Zn 2.1 mg/kg and As 0.004 mg/kg;
- the sea sand samples are characterized by the same trace amounts of radionuclides, such as $_{22}\text{Na}^{11}$ 1.5 Bq/kg, $_{19}\text{K}^{40}$ 0.8 Bq/kg, $_{26}\text{Fe}^{60}$ 0.95 Bq/kg, $_{27}\text{Co}^{57}$ 0.75 Bq/kg, $_{30}\text{Zn}^{65}$ 0.19 Bq/kg, $_{38}\text{Sr}^{91}$ 0.3 Bq/kg, $_{63}\text{Eu}^{152,154}$ 0.44, 0.62 Bq/kg and $_{88}\text{Ra}^{226}$ 0.59 Bq/kg.

The concentration of mineral salts and heavy metals in the Caspian Sea water is many times higher than the corresponding indicators in drinking water sources, the concentration of radionuclides in sea water is 2-3 times lower than the concentration of radionuclides in drinking water sources.

The obtained analysis results show that the concentration of salts in the water of the Caspian Sea is 13.5 g/liter, which is higher than the values for many other seas. Qualitative indicators (heavy metals, radionuclides, chemical compounds, E_{coli} number, Coli titer) in sea water do not exceed the maximum permissible values standardized by international standards.

However, some pathogenic microorganisms have been found in seawater, the presence of which is not desirable. Relatively large numbers of these pathogenic microorganisms are found especially in the autumn and spring months.

CONCLUSION

1. The concentration of salts in the water of the Caspian Sea is 13.5 g/liter, which is higher than the values for many other seas.
2. Despite the fact that the concentration of mineral salts and heavy metals in the Caspian Sea water is many times higher than the corresponding indicators in drinking water sources, the concentration of radionuclides in sea water is 2-3 times lower than the concentration of radionuclides in drinking water sources, seaweed and sea sand.
3. The chemical composition of seawater, seaweed and sea sand samples shows that these sea sand and seawater are suitable for use as beach sand and as beach water. However, the microbiological indicators of those waters indicate the presence of pathogens on some beaches of the Caspian Sea, which means that there is a need to limit the beach season on those beaches. As of May 2, 2023, some microbiological indicators of seawater are not satisfactory for the beach season. Since the presence of Salmonella pathogen bacteria in water is rare, it is not advisable to swallow seawater according to sanitary and hygienic requirements, and it is advisable to rinse with clean water after swimming.

REFERENCES

1. Lebedeva N.E., Gorbatova E.N., Golovkina T.V. et al. Screening method for substances acting in ultra-low concentrations. Radiation biology. Radioecology. 2003, Vol. 43, № 3, pp.282-286
2. Aleksandrov A.A. Thermodynamic bases of cycles of thermal power plants. M. MEI, 2004, pp.523
3. Khafizov F.Sh., Krasnov A.V. Saturated vapor pressure for petroleum products Electronic scientific journal "Oil and Gas Business". 2012, № 3, pp.406-413
4. Levin M.N., Negrobov O.P.,Gitlin V.R.,Selivanova O.V., Ivanova O.A.,Radon. Tutorial. Publishing and Printing Center of Voronezh State University. 2008,40 p
5. Mahmudov H.M., Kuliyeva U.A., Kerimov V.K., Kurbanov M.A. Water radiolysis on the surface of Al_2O_3 nano-catalyst. European Journal of Analytical and Applied Chemistry. 2015, pp.58-62
6. Mamedov, Kh. F. Radiolysis and Photolysis of Water Solutions of Phenol.Kh. F. Mammadov.J. European Researcher. 2014, № 7-1, pp.1216-1236
7. Mamedov H.F. Radiolytic decomposition of zearalenone in wheat. Kh.F. Mammadov. Immunopathology, allergology, infectology. 2012, № 1, pp.1216-1236
8. Mammadov Kh.F., Khasayeva S.G., Mammadov R.Kh., Shiraliyeva H.N., Mammadov C. Kh, Quliyev E.İ., Garibov R.G., Mammadova A.A. Determination of sources of pollution of Araz river by inorganic xenobiotics and pathogenic microorganisms. News of Pedagogical University. Mathematics and Natural Sciences series. 2020, Vol.68, №3, pp.168-185

9. Mammadov, X.F. Preventive measures to neutralize the negative effects of the conditions in the liberated territories. X.F. Mammadov, R.G. Garibov, H.N. Shiraliyeva [et al.]. Radiological and chemical risks in territories liberated from occupation. Republican scientific and technical conference. ANAS FRTEB, RPI. 28-29.10.2022, pp.121-124

КОМПЛЕКСНОЕ САНИТАРНО-ЭКОЛОГИЧЕСКОЕ ОБСЛЕДОВАНИЕ БАКИНСКОЙ АКВАТОРИИ КАСПИЙСКОГО МОРЯ

Х.Ф.Мамедов$^{0000-0002-2509-1215}$ *, М.Ш.Джавадлы*[2]*,*
А.Х.Гусейнова$^{0000-0003-0399-0815}$*, Э.И.Гулиев*[1]
[1]*Институт Радиационных Проблем Министерства Науки и Образования Азербайджанской Республики* [2]*Азербайджанский Государственный Университет Нефти и Промышленности*
xagani06@mail.ru

Широкое внедрение морских методов добычи нефти привело к загрязнению морской воды Бакинской акватории. Для оценки современного состояния проведено комплексное санитарно-экологическое обследование Бакинской акватории Каспийского моря, определены концентрации минеральных солей (сульфаты, хлориды, карбонаты кальция, нитраты, нитриты), тяжелых металлов (Sr, Fe , Mn, Zn, As) и радионуклидов (Na^{22}*,* K^{40}*, Fe60,* Co^{57}*,* Zn^{65}*,* Sr^{91}*,* $Eu^{152,154}$*,* Ra^{226}*) в морской воде. Сравнительный анализ результатов исследований позволил сделать вывод о наличии тенденции к улучшению экологического состояния Апшеронского полуострова. Химический состав образцов морской воды, морских водорослей и морского песка показывает, что их можно использовать в качестве пляжного песка и пляжной воды, соответственно. Однако изучение микробиологических показателей морской воды свидетельствует о наличии патогенных микроорганизмов на некоторых пляжах Каспийского моря, что требует введения определенного ограничения в разрешении пляжного сезона. В связи с тем, что в воде некоторых пляжей обнаружены патогенные бактерии Salmonella, согласно санитарно-гигиеническим требованиям не рекомендуется заглатывать воду при купании, а после купания желательно ополаскиваться чистой водой. Концентрация минеральных солей и тяжелых металлов в воде Каспийского моря во много раз превышает соответствующие показатели источников питьевой воды. Однако, концентрация радионуклидов в морской воде в 2-3 раза ниже, чем концентрация радионуклидов в источниках питьевой воды, морских водорослях и морском песке.*

Ключевые слова: *морская вода, виды загрязнения, водоросли, песчаный пляж, прибрежная почва, минеральный состав, радионуклиды, радиоактивный фон.*

XƏZƏR DƏNİZİ BAKI SAHİL AKVATORİYASININ KOMPLEKS SANITAR-EKOLOJİ MÜAYİNƏSİ

X.F.Məmmədov$^{0000-0002-2509-1215}$*, M.Ş.Cavadlı*[2]*,*
A.H.Hüseynova$^{0000-0003-0399-0815}$*, E.İ.Quliyev*[1]
[1] *Azərbaycan Respublikası Elm və Təhsil Nazirliyinin Radiasiya Problemləri İnstitutu* [2] *Azərbaycan Dövlət Neft və Sənaye Universiteti*
xagani06@mail.ru

Dənizdə neft hasilatı üsullarının geniş tətbiqi Bakı akvatoriyasının dəniz suyunun çirklənməsinə səbəb olmuşdur. Mövcud vəziyyəti qiymətləndirmək üçün Xəzər dənizinin Bakı akvatoriyasında *kompleks sanitar-ekoloji tədqiqatlar aparılmış, mineral duzların (sulfatlar, xloridlər, kalsium karbonatlar, nitratlar, nitritlər), ağır metalların (Sr, Fe , Mn, Zn, As) və radionuklidlərin (Na^{22}, K^{40}, Fe^{60}, Co^{57}, Zn^{65}, Sr^{91}, $Eu^{152,154}$, Ra^{226}) konsentrasiyaları müəyyən edilmişdir. Tədqiqatların nəticələrinin müqayisəli təhlili belə qənaətə gəlməyə imkan vermişdir ki, Abşeron yarımadasının ekoloji vəziyyətinin yaxşılaşması tendensiyası müşahidə olunur. Dəniz suyu, dəniz yosunu və dəniz qumu nümunələrinin kimyəvi tərkibi onların müvafiq olaraq çimərlik qumu və çimərlik suyu kimi istifadə oluna biləcəyini göstərir. Lakin, dəniz suyunun mikrobioloji göstəricilərinin öyrənilməsi Xəzər dənizinin bəzi çimərliklərində patogen mikroorqanizmlərin olduğunu göstərir ki, bu da çimərlik mövsümünün elan olunmasında müəyyən məhdudiyyətin tətbiqini tələb edir. Bəzi çimərliklərin sularında patogen Salmonella bakteriyası aşkar olunduğundan, sanitar-gigiyenik tələblərə uyğun olaraq, çimərkən su udmaq məsləhət görülmür, çimdikdən sonra isə təmiz su ilə yaxalanmaq məqsədəuyğundur. Xəzər dənizinin suyunda mineral duzların və ağır metalların konsentrasiyası içməli su mənbələrinin müvafiq göstəricilərdən dəfələrlə çoxdur. Lakin, dəniz suyunda radionuklidlərin konsentrasiyası içməli su mənbələrində, dəniz yosunlarında və dəniz qumunda radionuklidlərin konsentrasiyasından 2-3 dəfə azdır.*

Açar sözlər: *dəniz suyu, çirklənmə növləri, yosunlar, qumlu çimərlik, sahil torpağı, mineral tərkibi, radionuklidlər, radioaktiv fon.*

AJCN, Vol . 5, No. 2, 2023, pp. 45-51
https://doi.org/10.32010/AJCN04042023-45

UDC: 542.952.52.128.66

THE INFLUENCE OF THE TECHNOLOGICAL PARAMETERS OF THE THERMAL PYROLYSIS PROCESS ON THE INTENSITY OF THE PROCESS

G.Ch.Dadayeva$^{0000-0001-6801-4255}$*, M.M.Gurbanov, R.B.Ahmadov*
Azerbaijan State Oil and Industry University
dadayeva750@list.ru

By adjusting the technological parameters in the thermal pyrolysis process, it is possible to increase the yield of the target products. Therefore, researches were conducted in the direction of intensification of the pyrolysis process and it was determined that it is possible to increase the yield of ethylene by controlling the temperature regime, which is the basis of the technological parameters, and residence time of the raw materials in the reaction residence and dilution the raw materials with water steam. Moreover, adjusting of these indicators enables to achieve process intensification and reduce the amount of coke formation in the reactor. It is possible to get up to 23.2% mass of ethylene and 13.8% mass of propylene by maintaining such optimal conditions at temperature 800°C and contact time 0.3 seconds. Dilution of raw materials with water vapor will to some extent prevent the formation of coke during the polymerization of high-molecular compounds at high temperatures in the reactor furnace.

Keywords: *pyrolysis, ethylene, propylene, hydrocarbon, acetylene, olefins, methane, disposable gasoline.*

INTRODUCTION

The main parameters that considerable affect the pyrolysis process are temperature, the residence time of the feedstock in the reactor, and the partial pressure of the interacting hydrocarbons. The effect of these important parameters used in industrial practice is determined according to the law on the thermodynamics and kinetics of hydrocarbon reactions during the pyrolysis process. The depth of pyrolysis of hydrocarbon raw materials is determined by the temperature level of its processing and the residence time of stay in the high temperature zone where the reaction takes place, as well as the dilution of the raw materials with water vapor. These indicators, which characterize the composition or properties of the products obtained from the reaction, can be considered as a measure of the depth (intensity) of raw material processing during pyrolysis. It was determined that it is possible to intensify the pyrolysis process by adjusting the mentioned indicators.

To carry out the mentioned intensification process, the conversion degree of conversion of raw materials is mainly taken into account. Sometimes, to characterize the conversion degree of conversion of pyrolysis of hydrocarbon fractions (for example, gasoline fraction), the degree of gas formation is used, such as, the total yield of $C_1 – C_4$ and hydrogen (H_2), sometimes C_1 - C_3 hydrocarbons [1]. However, this indicator can only be used for less severe conditions. At this conditions, gas formation reaches its maximum and the yield of liquid products decreases.

The ratio of propylene to ethylene product, which decreases as the process deepens, or in some cases the yield of ethylene, is used as an indicator of intensity. However, all these indicators have a negative feature: - their indicators depend on the type and composition of raw materials, therefore, only a relative idea is given about the intensity of the process. Moreover conversion rate of straigtrein gasoline, the yield of ethylene, 1,3-butadiene and acetylene increases with a decrease in the residence time of the feedstock in the reaction zone and twice increasing of acetylene yield is observed with production of residence time of the feedstock from 0.6 s to 0.2 [2]. One of the practically used indicators of pyrolysis intensity is the atomic ratio of hydrogen to carbon in the light part of the liquid pyrolysis product (30-180°C fraction, pyrobenzene). It indicates the degree of dehydrogenation of the liquid product and characterizes the degree of coke formation of the raw material during pyrolysis. This indicator should not be lower than 0.85.

EXPERIMENTAL PART

To carry out the process of intensification of the pyrolysis process, the gasoline obtained from the CDU/VDU unit operated at the Baku Oil Refinery was used as raw material. The density of the used gasoline fraction is 0.713 kg/m^3.

In laboratory conditions thermal pyrolysis process was carried out in the device is shown in figure 1.

During the pyrolysis process, it was determined that the amount of various radicals formed and subjected to decomposition in the first stage and the output of lower olefins depend on the temperature [3].

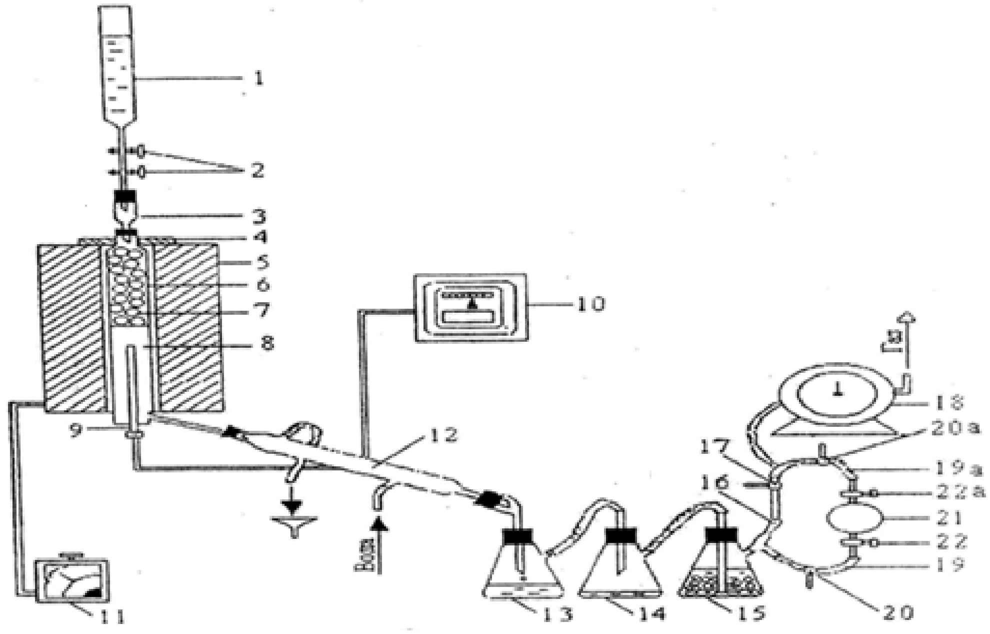


Fig. 1. Scheme of the thermal pyrolysis laboratory equipment
1- raw material burette; 2- valve; 3- allonge; 4- overlay; 5- electric stove; 6- reactor; 7- nozzles; 8- reaction zone; 9-thermocouple; 10-potentiometer; 11-thermoregulyator; 12- refrigerator; 13-receiver; 14-secend receiver; 15-absorber; 16-gasmeter outlet; 17-damp; 18-21-gasmeter; 19- gas inlett bypass; 19a- gas outlet bypass; 20-entrence damp; 22-22a valve of pycnometer.

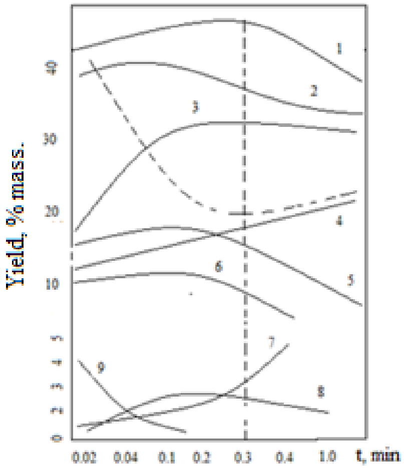


Fig. 2. Yield of pyrolysis products of straightreen gasoline dependence of τ on the residence time in the reactor at a temperature of 800°C
1 – sum of gaseous products (H_2 – C_4); 2 – olefins C_2 – C_4; 3 - ethylene;
4 – methane; 5 - propylene; 6 – C_4H_8; 7 - benzene; 8 - toluene; 9 – n-hexane.

It can be noted that the temperature of the process is a factor that determines both the degree of decomposition of the first hydrocarbons and the yield of pyrolysis products [4]. As a result of the initial reaction, the yield of low olefins, methane and hydrogen increases and alkanes decreases with increasing temperature. Despite the fact that the depth of decomposition of the initial hydrocarbons under conventional pyrolysis conditions is quite large, secondary reactions also take place deeper. This can also be explained by the decomposition of olefins and diolefins formed in the first stage and the addition type reaction. In this case, ethylene, which is the most stable of primary olefins, is formed. Propylene and butenes are decomposed in the second stage of the reaction in the presence of hydrogen. In addition to propylene and butene-1, the formation of ethylene continues. With increasing temperature, the formation of benzene occurs, the rate of secondary reactions increases, and with a significant increase in temperature, the formation of acetylene is accelerated [5,6]. As already mentioned, the most common pyrolysis raw material in industrial practice is direct firing gasoline. Its decomposition process starts at about 600 °C and continues at a noticeable rate with the formation of gaseous products at temperatures above 650°C.

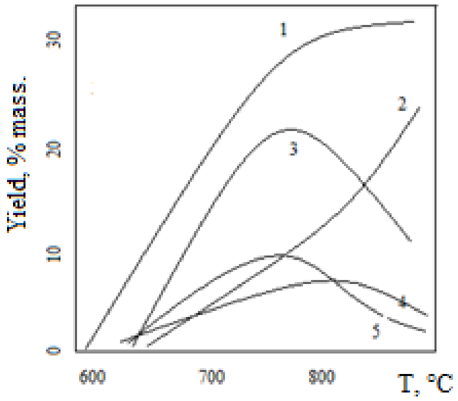


Fig. 3. Constant at different temperatures and reaction timevalues (about 0.3 s) of one-time expulsionyield of pyrolysis products of gasoline
1-C_2H_4; 2-CH_4; 3-C_3H_6; 4-C_4H_8; 5-C_4H_6

In the temperature range of 600 to 680°C, high olefins: - pentenes and hexenes are formed in significant amounts along with propylene and ethylene. At higher temperatures, the yield of lighter hydrocarbons increases and the yield of C_2 - C_4 olefins reaches a maximum. The stability of olefins increases with decreasing molecular weight, and their maximum yields shift toward higher temperatures.

During the pyrolysis process in industrial plants, the temperature of the processed feedstock is not uniform along the length of the reactor and usually reaches a maximum at the outlet of the furnace. Another important parameter of the pyrolysis process is the residence time of pyrolyzed hydrocarbons in the reaction zone, sometimes called the contact time. Contact time refers to the time the feedstock is in the reaction zone at temperatures where the pyrolysis reaction proceeds at a significant rate.

In the process of pyrolysis, the conventional temperature for the beginning of the participation of C_5-C_{10} hydrocarbons in the reaction can be considered 650°C. For a number of products (including ethylene and other olefins), yield curves pass through a maximum for each temperature as a function of reactor residence time. These dependences, which are characteristic for any primary oil fractions, are similar to the dependences of their productivity on temperature (fig. 3 and 4). The yield of hydrogen and methane increases continuously with increasing contact time.

Thus, it is likely that increasing the pyrolysis temperature with a corresponding decrease in residence time helps achieve higher yields of the target products, including ethylene. In the last few decades, the industrial pyrolysis process for the production of lower olefins, especially ethylene, has evolved towards increasing temperature and decreasing residence time in the reaction zone [7]. Temperature-dependent decomposition of the reactants along the length of the reaction reactor significantly affects the pyrolysis results. Figure 6 shows examples of temperature curves along the length of the reactor. For all three types of profiles, it is assumed that the starting point of the reaction in the reactor is combined.

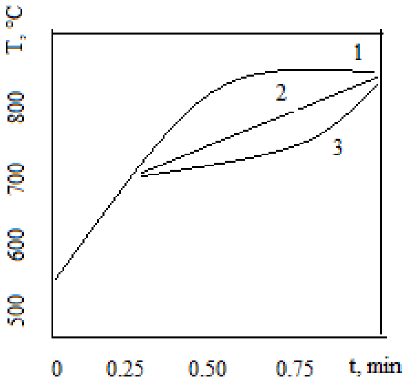


Fig. 4. Effect of temperature along the length of the pyrolysis reactor
1 - convex; 2 - straight; 3 – collapse

The convex shape of the curve helps to increase the depth of the pyrolysis process, leading to an increase in the yield of ethylene. The concave (slumped) shape leads to an increase in the yield of higher molecular weight olefins - propylene, butenes. If we consider, we can see that the yield of ethylene is slightly lower compared to the convex curve. The release of aromatic hydrocarbons increases with the rise in temperature.

In the process of pyrolysis of gaseous products, it is recommended to determine the selectivity as the ratio of ethylene formed to the amount of converted raw materials [8]. Practical determination of the degree of conversion of raw materials during pyrolysis of liquid raw materials is labor-intensive and not accurate enough [9]. In this case, it is appropriate to take the ratio of the yield of methane to the yield of ethylene (or C_2 - C_4 alkenes) as the quantitatively dominant byproduct as a measure of selectivity. Increasing the selectivity of the pyrolysis process is facilitated by the weakening of the secondary decomposition reactions with the sufficient implementation of the target products - olefins, their reactions [10]. This requires reducing the residence time of the raw material in the reaction zone and lowering the partial pressure of hydrocarbons.

RESULTS AND DISCUSSION

By adjusting the technological parameters in the thermal pyrolysis process, it is possible to increase the output of the target products. For this reason, researches were carried out in the direction of intensification of the pyrolysis process, and it was determined that it is possible to increase the yield of ethylene by adjusting the temperature regime and the duration of the raw materials in the reaction zone, which are the basis of the technological parameters, and by diluting the raw materials with water vapor. By adjusting these parameters, it is possible to achieve process intensification and reduce the amount of coke formation in the reactor.

Table 1

Yield of pyrolysis products at different temperatures

Product	Contact time, sec	Yield of product			
		785-800 °C	815-840 °C	840-870 °C	870-925 °C
CH_4	0.3	15,8	16,8	17.0	16,8
C_2H_4	0.3	23,2	26,1	29,5	33,5
C_3H_6	0.3	13,8	12,9	12,4	11,9
C_4H_6	0.3	2,4	4.0	4,4	5.0
C_5 and down	0.3	33.0	29,9	30.0	24.1
CH_4/C_2H_6	0.3	0,680	0,643	0,577	0,503
C_3H_6/C_2H_4	0.3	0,591	0,490	0,418	0,351

With the increase of dilution of hydrocarbons with water vapor, the formation of coke in the reactor decreases, because the rate of secondary and higher reactions leading to the formation of coke - high molecular compounds - decreases.

Ethylene and other lower olefins are formed as a result of the first primary reaction. In these reactions, the rate of conversion of raw materials is independent of pressure, olefins are further reacted to become polymerization or condensation products, and their conversion in these directions is partially proportional to pressure. An important and relatively easy (and often variable) factor that determines the partial pressure of hydrocarbons is the steam dilution of the hydrocarbon feedstock. The yield of ethylene, 1,3-butadiene and butenes increases with steam washing of raw materials (reduction of partial pressure of hydrocarbons). However, the productivity of aromatic hydrocarbons and methane decreases, the selectivity of pyrolysis increases.

Since the addition of water vapor reduces the rate of coke deposition on the inner surface of the pyrolysis tubes, the pressure drop in the tubes and the rate of surface temperature increase during operation are reduced. Thus, it is possible to increase the depth of the pyrolysis process and, accordingly, to increase the yield of ethylene, without reducing the selectivity of the raw material with steam.

CONCLUSION

1. The optimal conditions of the process were determined at a temperature of 800°C, a contact time of 0.3 seconds.
2. In the selected optimal parameters, 23.2% mass yield of ethylene and 13.8% mass yield of propylene was obtained.
3. Dilution of raw materials with water vapor to some extent will prevent the formation of coke during the polymerization of high-molecular compounds at high temperatures in the furnace.

REFERENCES

1. Current state and development trends of the pyrolysis process. Vestnik master's degrees. 2019,№ 11-3 (98), pp. 8-11
2. Akhmetov S. A. Technology of deep processing of oil and gas: textbook for universities. Ufa: Gilem.2002.672 p
3. Kuznetsov A. A. Calculations of the main processes and apparatus for processing hydrocarbon gases: a reference manual.M.: Chemistry.1983, 224 p
4. Khafizov I.F., Musin R.R. Current trends in the development of the pyrolysis process. Bulletin of the Technological University. 2017, T.20, № 21, pp 231-234
5. Minigaliev T.B., Yakupov A.A., DorozhkinV.P., Korobeynikova O.A. Pyrolysis of hydrocarbons. Guidelines for performing laboratory work. Nizhnekamsk Institute of Chemical Technology. 2010 , 40 p
6. Shekunova, V.M. Method of catalytic pyrolysis of hydrocarbon mixture C_1-C_4 into lower olefin C_2-C_4. Patent RF. № 2601864,2016
7. Shekunova, V.M. New catalytic systems for the pyrolysis of light hydrocarbons. V.M. Shekunova, E.I. Tsyganova, I.I. Didenkulova, Yu.A. Alexandrov. Bulletin of Nizhny Novgorod University N.I. Lobachevsky. 2014,T. 1,№ 1, pp. 92-103
8. Dadayeva G.Ch., A.A. Yusif-zade, S.A. Mamedkhanova. Catalytic Pyrolysis on Azerbaijan Zeolits. International Scientific Journal ISJ Theoretical&Applied Science Philadelphia, USA, Issue 02, Vol.82, published February 29, 2020, pp. 259-268
9. Dadayeva G.Ch, A.A. Yusif-zade, S.A. Mamedkhanova.Catalytic pyrolysis over modified zeolite-containing catalysts. Processes of petrochemistry and oil refining. Clarivate analytics. Vol.23, №2, 2022, pp.63-68, İSSN: online 2519-2876, oprint 1726-4685/ www.ppor.az

ВЛИЯНИЕ ТЕХНОЛОГИЧЕСКИХ ПАРАМЕТРОВ ПРОЦЕССА ТЕРМИЧЕСКОГО ПИРОЛИЗА НА ИНТЕНСИВНОСТЬ ПРОЦЕССА

Г. Ч. Дадаева$^{0000-0001-6801-4255}$*, М. М. Гурбанов, Р. Б. Ахмедов*
Азербайджанский Государственный Университет Нефти и Промышленности
dadayeva750@list.ru

К основным параметрам, наиболее влияющим на процесс пиролиза, относятся температура, время пребывания сырья в реакторе и парциальное давление взаимодействующих углеводородов. Влияние этих важных параметров, используемых в промышленной практике, определяется по закону термодинамики и кинетики реакций углеводородов в процессе пиролиза. Глубина пиролиза углеводородного сырья определяется температурным уровнем его переработки и временем пребывания в высокотемпературной зоне, где протекает реакция, а также разбавлением сырья водяным паром. Эти показатели, характеризующие состав или свойства продуктов реакции, можно рассматривать как меру глубины (интенсивности) переработки сырья при пиролизе. Определено, что можно интенсифицировать процесс пиролиза за счет корректировки указанных показателей.

Ключевые слова: *пиролиз, этилен, пропилен, углеводород, ацетилен, олефины, метан, одноразовый бензин.*

TERMİKİ PİROLİZ PROSESİNİN TEXNOLOJİ PARAMETRLƏRİNİN PROSESİN İNTENSİVLİYİNƏ TƏSİRİ

G.Ç.Dədəyeva$^{0000-0001-6801-4255}$*, M.M.Qurbanov, R.B.Əhmədov*
Azerbaijan State Oil and Industry University
dadayeva750@list.ru

Piroliz prosesinə ən çox təsir edən əsas parametrlərə temperatur, xammalın reaktorda qalma müddəti və qarşılıqlı təsirdə olan karbohidrogenlərin qismən təzyiqi daxildir. Sənaye təcrübəsində istifadə olunan bu mühüm parametrlərin təsiri piroliz prosesi zamanı karbohidrogen reaksiyalarının termodinamikasına və kinetikasına qanuna uyğun olaraq müəyyən edilir. Karbohidrogen xammalının pirolizinin dərinliyi onun emalının temperatur səviyyəsi və reaksiyanın baş verdiyi yüksək temperatur zonasında qalma müddətivə eləcədə xammalın su buxarı ilə durulaşdırılması ilə müəyyən edilir. Reaksiyadan alınan məhsulların tərkibini və ya xassələrini xarakterizə edən bu göstəricilər piroliz zamanı xammalın emalının dərinliyinin (intensivliyinin) ölçüsü kimi qəbul edilə bilər. Müəyyən olunmuşdur ki, qeyd olunmuş göstəriciləri tənzimləməklə piroliz prosesini intensivləşdirmək mümkündür.

Acar sözlər: *piroliz, etilen, propilen, karbohidrogen, asetilen, olefinlər, metan, birdəfəlik qovulma benzini.*

AJCN, Vol . 5, No. 2, 2023, pp. 52-58
https://doi.org/10.32010/AJCN04042023-52

UDC: 62.632.001.4

RECEIVING ETHYL TRIPLE BUTYL ETHER

G.F.Hajiyeva[1,2] *0009-0003-3646-5301*, *A.A.Hasanov*[1] *0000-0001-8953-4911*,
Ch.G.Rasulov[2] *0000-0003-4999-2955*
[1]*Azerbaijan State Oil And Industry University*[2] *Y.H. Mamedaliyev's Institute of Petrochemical Processes*
glsm.hcyv@mail.ru

The article deals with the study of the process of obtaining ethyl tert butyl ether from the etherification reaction of bioethanol with the C_4-fraction obtained in the process of pyrolysis of low-octane gasoline. H-form KU-2 cationite was used as a catalyst in the process. Divinyl-free (BDF) and divinyl-denatured (BIF) fractions of the C_4-fraction were used for the etherification reaction. The amount of isobutylene in BIF is 42.29%, while the amount of isobutylenes in BDF is 38.30%, and the amount of divinyl is 46.90%. After etherification reactions of ethanol with BDF, the amount of divinyl increases to 66.88%. As a result of the conducted studies, it was determined that the yield of ethyl tert butyl ether obtained as a result of etherification reactions of C_4-fraction (BIF and BDF) with ethanol at a pressure of 0.7-0.8MPa and a temperature of 70-75°C in a cationite-containing catalytic system is 65.6-71.6%. The chemical structure and physical-chemical properties of ethyl tert butyl ether obtained by both methods corresponded to the parameters of ether obtained by other known methods.

Keywords: *C_4-fraction, bioethanol, cationite, catalyst, etherification, ethyl tert butyl ether.*

INTRODUCTION

The tightening of environmental requirements for combustion products in car engines has given a strong impetus to the production of environmentally friendly gasoline containing oxygen-containing components-oxygenates.

Methyl tert-butyl ether (MTBE) and ethyl tert butyl ether (ETBE) are among the well-known oxygenates in the industry [1-8].

In the last 5 years, the countries of the European Union have consumed 110-120 million tons of gasoline per year. 6 million tons of different oxygenates (MTBE, ETBE) were used in the production of this amount of gasoline [9].

The presented article deals with the study of reactions of esterification of pyrolysis products with isobutylene-rich, divinylated (BIF) C_4 fraction and bioethanol in the presence of H-form KU-2 catalyst.

EXPERIMENTAL PART

C_4-fraction containing up to 38-42% isobutylenes and 99.8% pure bioethanol were used as primary raw materials for the etherification process of bioethanol with the C_4-fraction obtained during the pyrolysis process.Hydrocarbon compositions of BIF and BDF are given in tables 2 and 4.H-form KU-2 cationite was used as a catalyst. The catalyst is dried before use.The etherification process was carried out in a mini-device installed for this purpose.

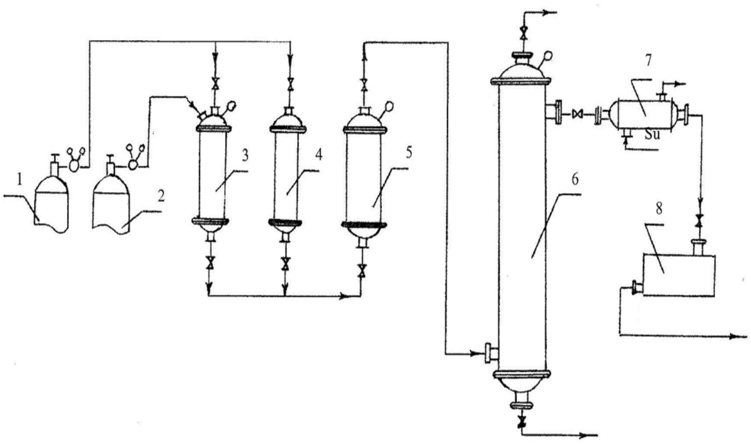


Fig 1. Technological scheme of the process of obtaining ethyl (methyl) tert butyl ether: 1-nitrogen tank; 2-C_4-fraction tank; 3-C_4-fraction container; 4-bioethanol container; 5-mixer; 6-reactor; 7-cooler; 8- ETBE (MTBE) tank

To carry out the process, first of all, the catalyst is filled in the reactor (6). For this purpose, the catalyst is filled inside the tube made of asbestos cloth in the diameter of the reactor and placed in the reactor (6). Bioethanol is fed from the container (4) and C_4-fraction from the tank (2) to the container (3) and from there to the mixer (5) in the calculated amount. The mixture of components passes over the catalyst in the liquid phase, exits from the top of the reactor, is cooled in the cooler (7), and then collected in the tank (8). The purchased product is sent from there for rectification.

The pressure in the system is constantly maintained due to the nitrogen supplied to the system.

RESULTS AND DISCUSSION

Experiments were carried out at different mole ratios of components, temperatures and volume velocities. The results are given in table 1.

Table 1

Results of etherification reactions of devinylized C_4-fraction with ethanol

Ethanol: BİF, mol	Temperature, °C	Pressure, MPa	Yield, % mass
1:3	60	0,8	49.3
1:3	70	0,8	63.7
1:3	80	0,8	57.2
1:4	70	0,8	65.6
1:3	75	0,8	62.7
1:4	80	0,7	56.1
1:5	75	0,7	58.4
1:5	60	0,8	47.6
1:4	75	0,7	63.3
1:4	80	0,7	60.7
1:2	70	0,8	23.1
1:2	80	0,7	24.4

Etherification reactions of ethanol with BIF were explored at the temperature of 60-80℃, the molar ratio of bioethanol to BIF from 1:2 to 1:4, and the pressure at 0.7-0.8 MPa. When the reaction temperature is 60℃, the yield of ETBE is 49.3%. At further increases in the reaction temperature, the yield of the target product is 63.7% at 70℃ and 57.2% at 80℃. As can be seen from the table, the yield decreases with increasing temperature. This is explained by the formation of side products with increasing temperature. It was observed that dimers, trimers, and tert butyl alcohol of olefinic hydrocarbons contained in BIF were obtained as side products. At a 1:3 mol ratio of bioethanol to BIF, the yield of ETBE is 62.7% at a temperature of 75℃. At values of 1:2 mole ratios, the yield of ETBE is 23.1-24.4%. At 1:4 and 1:5 mol ratios of bioethanol to BIF, the yield of the target product is 47.6-63.3%.

As can be seen from the table, the yield of ETBE is high when the conditions of the process are: temperature 70-75℃, pressure 0.7-0.8MPa, and the ratio of alcohol to BIF 1:3-4 mol.

As a result of the conducted research, it was determined that the interaction reaction of BIF with bioethanol in the KU type catalytic system is suitable for the purpose: temperature 70-75℃, pressure 0.7-0.8MPa, molar ratio of ethyl alcohol to BIF 1:3-4 mol. At this time, the output of ETBE is 63.7-65.6%.

The percentage amount of product obtained during the etherification process is shown below: ETBE-65%, C_4-fraction- 6.4%, alcohol- 12.8%, alkylate and dimers- 12.6%, heavy resin- 2.0%, loss- 1.2%. Table 2 shows the hydrocarbon composition before and after the etherification reaction of BIF with bioethanol.

Table 2

Hydrocarbon composition before and after etherification reaction of BIF with bioethanol

Hydrocarbon composition of BIF	Before the reaction, %	After the reaction,%
Propane	0,85	3.47
Propylene	0,17	0.53
Isobutane	4,14	9.37
Isobutylene	42,29	7.83
Butene-1	28,49	37.65
Butadiene- 1,3	0,50	1.08
n-butane	4,67	10.31
trans-butylene	9,46	15.27
cis-butylene	9,43	14.49
Total	100,00	100,00

It can be seen from table 2 that while the amount of isobutylene was 42.29% before the reaction, its amount decreased to 7.83% after the reaction. As a result, the amount of saturated hydrocarbons in the post-reaction hydrocarbon content of BIF is significantly increased, while the fraction's unsaturation is significantly reduced, and this fraction is offered as a household fuel.

At the same time, bioethanol was also studied in etherification reactions with BDF in the presence of cationite KU-2 catalyst.

Bioethanol and BDF are mixed in a 1:2-5 mol ratio and fed to the lower part of the reactor at a rate of 0.5 hour^{-1} volume. The temperature in the reactor is maintained at 60-80℃, and the pressure is 0.7-0.8MPa.

The results of the etherification reaction of BDF with bioethanol obtained under different conditions are given in table 3.

Table 3

Results of the etherification reaction of BDF with bioethanol under different conditions

Ethanol: BDF, mol	Temperature,℃	Pressure, MPa	Yield,% mass
1:3	60	0,8	58.5
1:3	70	0,8	69.7
1:3	80	0,8	63.2
1:4	70	0,8	70.8
1:3	75	0,8	68.3
1:4	80	0,7	64.9
1:5	75	0,7	65.6
1:5	60	0,8	54.0
1:4	75	0,7	71.6
1:4	80	0,7	67.1
1:2	70	0,8	29.3
1:2	80	0,7	28.7

It can be seen from table 3 that when the temperature of the esterification reaction is 60℃, the yield of the target product is 58.5%, and when the temperature is 70-75℃, the yield of ETBE is 68.3-70.8%. By raising the reaction temperature to 80℃, the yield drops to 63.2%. A 1:3 mole ratio of bioethanol to BDF can be considered effective. As can be seen from the table, the yield at this time is 69.7%.

If the amount of BDF in the mixture is taken as low, i.e. 1:2, the yield is 31.9-32.6%. Too much BDF in the reaction mixture does not give such an efficient result. Thus, at a 1:5 mol ratio of ethanol to BDF, the yield of the target product is 58.3-68.6%. The decrease in the yield of the target product is explained by the dimerization and oligomerization of the olefinic hydrocarbons contained in BDF, and the acquisition of their dimer and oligomer products.

As a result, it was determined that when the process conditions are 70-75℃ temperature, 0.7-0.8 MPa pressure, and the ratio of BDF to alcohol is 3-4:1 mol, the maximum yield of ETBE is 69.7-71.6% by mass.

The hydrocarbon content of the BDF used in the production of ETBE before and after the reaction is given in the following table 4.

It can be seen from table 4 that while the BDF taken for the reaction contains 38.30% isobutenes, after the reaction their amount decreases to 7.86%, the hydrocarbon content of the initial BDF is 46.90%, and after the reaction 65.88% butadiene-1.3. As a result, the amount of butadiene in the hydrocarbon content of BDF returning from the reaction increases to 18-20%.

Table 4

Hydrocarbon composition before and after etherification reaction of BIF with bioethanol

Hydrocarbon composition of BIF	Before the reaction, %	After the reaction,%
C_3	0.05	0.13
Iso-butane	3.50	4.66
n-butane	3.45	6.83
Butylenes	38.30	7.86
Cis-2-butylene	3.57	6.14
trans-2-butene	3.43	7.07
Butadiene-1,3	46.90	65.88
C_5	0.80	1.43
Total	100,00	100,00

Divinyl-enriched BDF is recommended as an efficient raw material in the production of divinyl.

ETBE was obtained by both proposed methods. T_{boil}=73°C, ρ_4^{20}=746 kq/m^3, $n_D^{20} = 1.3766$, the molar mass is 102.

Thus, as a result of the study of the esterification reaction of the olefin-containing C_4 fraction (BIF and BDF) with ethyl alcohol in the cationite containing catalytic system at a pressure of 0.7-0.8 MPa and a temperature of 70-75°C, it was determined that the yield of ethyl tert butyl ether under optimal conditions is 65.6-71.6%.

CONCLUSION

1. Etherification reaction with ethanol was carried out in the presence of the H-form KU-2 catalyst with the rich divinyl (BDF) and divinyl depleted (BIF) fractions of the C_4- fraction of the pyrolysis process.
2. Ethyl tert butyl ether was obtained with a yield of 65.6-71.6% as a result of the etherification reaction of the C_4- fraction of pyrolysis (BIF and BDF) with ethanol at a pressure of 0.7-0.8 MPa and a temperature of 70-75°C in the catalytic system containing cationite.

REFERENCES

1. Mirzoev V.G., Pushchik E.V.., European ethanol market, MTBE and ETBE. Eurasian chemical market. 2010, №6, pp.48-52
2. Chase J.D., Galvets B.B., Production of high-octane ether components.Oil, gas, and petrochemicals abroad. 1981, №3, pp.104-109
3. Rustamov M.I., Guseinova A.D., and others. A.s. 1401823 USSR. Method for producing methyl tert-butyl ether. and others.1987
4. Anichkin A.N., Dobrovsky A.A., Kolobrodov V.P. and others., Patent 2209811 RF. Method for producing alkyl-tert-alkyl ethers and high-octane gasoliners, 2003
5. Denisov A.G., Zubarev A.N., Gryadunov A.V. Patent 2286379 RF. Method for increasing the octane number of gasoline. 2004
6. Radchenko E.D., Engin B.A., Robert Yu.A. Methyl tert-butyl ether as a component of motor gasoline. Chemistry and technology of fuels and oils.1976,

№5, pp.6-9
7. Karpov S.A. Modern aspects of the use of anti-detonators in motor gasoline.Oil refining and petrochemistry. 2006, №10, pp.26-30
8. Saidhamedov S.I., Kapustin V.M. Octane-boosting composite additive based on ethanol. Chemistry and technology of fuels and oils. 2006, №6, pp.33-35
9. Mirzoev V.G., Pushchik E.V. What to add to gasoline. Russian oil. 2011, №8, pp.64-66
10. Rustamov M.I., Azizov A.N., Rasulov Ch.G.,Mirzayev V.H. Patent I 20070174 AZ. The method of obtaining ethyl tert butyl ethe. 2007
11. Rustamov M.I., Azizov A.N., Rasulov Ch.G., Mirzayev V.H. Patent I 2014030 AZ. The method of obtaining ethyl tert butyl ether. 2014

ПОЛУЧЕНИЕ ЭТИЛ ТРЕТ БУТИЛОВОГО ЭФИРА

Г.Ф.Гаджиева[1,2] 0009-0003-3646-5301*, А.А.Гасанов*[1] 0000-0001-8953-4911*,*
Ч.Г. Расулов[2] 0000-0003-4999-2955
[1]*Азербайджанский Государственный Университет Нефти и Промышленности*
[2]*Институт Нефтехимических Процессов Министерства Науки и Образования Азербайджана*
glsm.hcyv@mail.ru

В статье приведены результаты исследования процесса получения этил трет бутилового эфира этерификацией биоэтанола C_4-фракцией, полученной в процессе пиролиза низкооктанового бензина. В качестве катализатора в процессе использовали катионит КУ-2 в Н-форме. Для реакции этерификации использовали фракцию C_4, обогащенную дивинилом (БДФ) и фракцию C_4 после выделения дивинила (БИФ). Количество изобутилена в БИФ составляет 42.29%, а количество изобутиленов в БДФ – 38.30%. После реакций этерификации этанола с БДФ количество дивинила увеличивается от 46.90% до 66.88%. В результате проведенных исследований установлено, что выход этил трет бутилового эфира, полученного в результате реакций этерификации C_4-фракции (БИФ и БДФ) этанолом при давлении 0.7-0.8 МПа и температуре 70-75℃ в катионитсодержащей каталитической системе составляет 65.6-71.6%. Химическая структура и физико-химические свойства этил трет бутилового эфира, полученного вышеуказанными методами, соответствовали характеристикам эфира, полученного другими известными методами.

Ключевые слова: *фракция C_4, биоэтанол, катионит, катализатор, этерификация, этил трет бутиловый эфир.*

ETİL ÜÇLÜ BUTİL EFİRİNİN ALINMASI

G.F.Hacıyeva[1,2] 0009-0003-3646-5301*, Ə.A.Həsənov*[1] 0000-0001-8953-4911*,*
Ç.Q.Rəsulov[2] 0000-0003-4999-2955
[1]*Azərbaycan Dövlət Neft və Sənaye Universiteti*
[2]*ARETN Neft-kimya Prosesləri İnstitutu*
glsm.hcyv@mail.ru

Məqalədə aşağı oktanlı benzinlərin pirolizi prosesində alınan C_4-fraksiyası ilə bioetanolun *efirləşmə reaksiyasından etil üçlü butil efirinin alınma prosesinin tədqiqindən bəhs edilir. Prosesdə katalizator kimi H-formalı КУ-2 kationitdən istifadə edilmişdir. Efirləşmə reaksiyası üçün C_4-frakiyasının divinil ayrılmadan (BDF) və divinilsizləşdirilmiş (BİF) fraksiyalarından istifadə edilmişdir. BİF-nin tərkibində izobutilenin miqdarı 42.29%, BDF-nın tərkibində isə izobutilenlərin miqdarı 38.30%, divinilin miqdarı 46.90% olur. BDF ilə etanolun efirləşmə reaksiyalarından sonra isə divinilin miqdarı 66.88%-dək artmış olur. Aparılmış tədqiqatlar nəticəsində müəyyən edilmişdir ki, kationit tərkibli katalitik sistemdə C_4-frakiyasının (BİF və BDF) etanol ilə 0.7-0.8MPa təzyiqdə, 70-75℃ temperaturda efirləşmə reaksiyaları nəticəsində alınmış etil üçlü butil efirinin çıxımı 65.6-71.6% təşkil edir. Hər iki üsul ilə alınmış etil üçlü butil efirinin kimyəvi quruluşu, fiziki-kimyəvi xassələri digər məlum üsullar ilə alınmış efirin göstəricilərinə uyğun olmuşdur.*

Açar sözlər: *C_4 fraksiyası, bioetanol, kationit, katalizator, efirləşmə, etil üçlü butil efiri.*

AJCN, Vol. 5, No.2, 2023, pp. 59-67
https://doi.org/10.32010/AJCN04022023-59

UDC: 541.64 : 547.566 : 661.894 : 661.8

STUDY OF THE MICROELEMENT COMPOSITION OF OIL FORMATION WATERS USING SORPTION AND FLAME IONIZATION METHODS

A. M. Maharramov[1] O97372019, M. R. Bayramov[1] 0000-0003-1640-3392,
Sh. J. Guliyeva[1] 0000-0002-9972-488X, G.M. Mehdiyeva[1] 0000-0003-4293-6555,
N.M. Sadıkhov[2], M. A. Agayeva[1] JDH-3658-2023, B. A. Babayeva[2]
[1]Baku State University [2]Institute of Geology and Geophysics
guliyevashahla@hotmail.com

By using of sorption and flame ionization methods, the microelement composition of formation waters associated with Azerbaijani oil fields (Lokbatan, Karadag district, well 260 and Bibiheybat, Sabail district, well 748, Baku) was studied. The sorbents used were cross-linked polymers obtained from co-oligomers of alkenylphenols (2-propenyl- and 4-isopropenylphenols), formaldehyde, maleic anhydride, and other compounds (three-dimensional structures of 4 types).Microelements were extracted from formation waters by sorption in static environment at room temperature and duration of 24 hours. Further, after pre-drying, the samples of copolymers with extracted microelements were included into an ICP MS 7700e apparatus (manufactured by Agilent, USA) and atomization and subsequent ionization of microelements were carried out and, based on the ratio of mass (m) to charge (Z), their content in the studied sample was calculated (in ppm). The influence of the structure of the sorbent and the composition of water on the degree of extraction of microelements was studied. It has been established that cross-linked polymers I and II obtained based on of 4-isopropenylphenol and maleic anhydride have the highest sorption properties compared to polymers III and IV. The degree of sorption of most cations in the first case is 99-100%, including environmentally hazardous ones; cross-linked polymers III and IV have a high selectivity with respect to K^+, Na^+, Ca^{2+} *and* Zn^{2+} *(the degree of their extraction is ~100%). The degree of extraction of other cations is on average up to 80%.*

Keywords: *oil formation waters, microelements, cross-linked polymers, alkenylphenols, ionization, sorption.*

INTRODUCTION

In modern technologies associated with the concentration and extraction of various heavy metals, radionuclides and other hazardous substances from water systems, sorption methods occupy one of the important places [1-5]. In this case, both natural and synthetic materials are used. Cross-linked copolymers obtained from large-capacity monomers - styrene, acrylonitrile, maleic anhydride, etc. - have found use as synthetic sorption materials [6].

Currently, the treatment of industrial and wastewater from environmentally hazardous heavy metals and radionuclides remains an urgent problem and, despite the numerous electrochemical and precipitation methods developed in this area, many issues have not been fully resolved. This is especially true for diluted solutions that are difficult to dispose of and have a harmful effect on humans and the environment [7].

Research in the field of creating new highly effective sorption materials based on available types of raw materials continues. In recent years, research on the synthesis of modified sorption materials of the phenol-formaldehyde type has expanded, which, obviously, can be explained by their availability compared to other types of synthetic sorbents. In particular, a carbon adsorbent with high sorption properties with respect to nickel (II) ions was obtained from waste from the production of phenol-formaldehyde resin [8].

333In another work, resorcinol-formaldehyde xerogels containing mercapto groups in their structures were used to extract dangerous mercury compounds [9].

For a number of years, we have carried out work on the synthesis of precursors - unsaturated co-oligomers of the phenol-formaldehyde type based on alkenylphenols, formaldehyde, maleic anhydride and other reagents, which can be cured thermally or in the presence of various cross-linking agents, with the formation of polymers of a three-dimensional structure with high sorption properties in terms of relation to various ions [10-14].

The aim of this article of the study cross-linked polymers based on 4-isopropenylphenols and 2-propenylphenols (I-IV) synthesized by us as sorption materials for the extraction of microelements from oil formation waters accompanying Azerbaijani oils (Lokbatan fields, Karadag region, well 260 and Bibiheybat, Sabail district, well 748, Baku) and their subsequent quantitative determination by the flame ionization method using an ICP MS 7700e (manufactured by Agilent, USA).

The flame ionization method has a high degree of accuracy and is widely used. For example, in [15] it was used to study the microelement composition of condensate from the Azerbaijan field.

Methods based on desorption-ionization processes have been successfully used in recent years to study complex formation processes, in particular, heterocyclic compounds with various metals [16,17].

EXPERIMENTAL PART

As an object of study, samples of formation waters accompanying Azerbaijani oils from the Lokbatan, Karadag district (well 260) and Bibiheybat, Sabail district (well K 748) fields were used (they are conventionally named waters A and B).

The formation waters used in the work, as was later revealed, differ somewhat in the content of microelements. Carrying out studies using water samples that differ in microelement composition and sorbents of different structures, in our opinion, will reveal their effectiveness and selectivity in relation to individual cations and express considerations regarding the possibility of using them for specific purposes.

Before use, samples of formation waters A and B were subjected to filtration (to remove clayey and other solids).

As sorbents we used 4 types of cross-linked polymers synthesized by us based on 4-isopropenylphenol and 2-propenylphenol:

I. 4-isopropenylphenol-phenol-formaldehyde cooligomer cross-linked with maleic anhydride and hydrolyzed.

II. Cooligomer 4-isopropenylphenol and maleic anhydride, cross-linked with ethylenediamin, formaldehyde and epoxyresin.
III. Cooligomer based on 2-propenylphenol and formaldehyde, cross-linked with maleic anhydride and hydrolyzed.
IV. Cooligomer based on 4-isopropenylphenol-phenol-formaldehyde, maleic anhydride and styrene, cross-linked with ethylenediamin.

In order to identify the possibility of using the above cross-linked copolymers I-IV as sorbents for the extraction of microelements from formation waters A and B, laboratory studies were carried out in a static mode as follows:

0.5 g of the tested cross-linked copolymer was placed in a beaker containing 300 ml of formation water (A or B), and the system was kept at room temperature for 24 hours. The sample with the extracted microelements was carefully removed from the aqueous medium and dried in a heating cabinet at a temperature of 70-80^{0}C. Next, it was fed in finely dispersed form into a flame ionization apparatus into a zone with argon plasma at a high temperature (3000-5000^{0}C) for the purpose of atomization and further ionization of the extracted microelements. In the analyzer, based on the ratio of the mass of an individual ion to its charge (m/Z), its quantitative content (in ppm) is calculated.

RESULTS AND DISCUSSION

Tables 1-3 present the results of studies on the influence of the structure of cross-linked copolymers used in the work (sorbents I-IV) and the microelement composition of waters A and B on the degree of their extraction from oil formation waters in a static mode. Obviously, the effective binding of cations from formation waters by these sorbents occurs due to the participation of certain functional groups in complexation with metal cations.

This is confirmed by the results of spectral studies, for example, of sorbent IV. In the IR spectra of the polymers, a change and shift in the absorption bands of the carbonyl, amine and C-H groups is observed before and after the sorption process. For example, while studying cross-linked polymer IV (fig.1 and fiq.2) by IR spectroscopy (“Varian 3600 FI-IR” Bruker and “Lumos” Bruker, Germany) before and after the sorption process, a clear change and shift in the absorption band of the carbonyl group is observed in the spectra (1770 cm-1 before sorption, ~1750 cm-1 after sorption) , amine fragment (C-N and N-H), which indicates the occurrence of the sorption process on the indicated functional groups.

A similar result was obtained in the case of cross-linked copolymer II, where in this case a change in the absorption band of the carbonyl group is observed. As in the previous copolymer, the absorption band in the region of 1463 cm-1 (II) and 1452 cm-1 (I) related to C-H clearly changes.

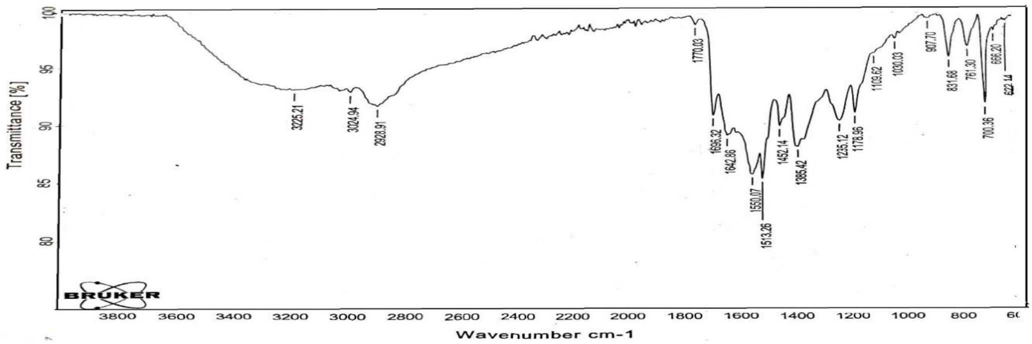


Fig. 1. IR spectra of copolymer IV before sorption

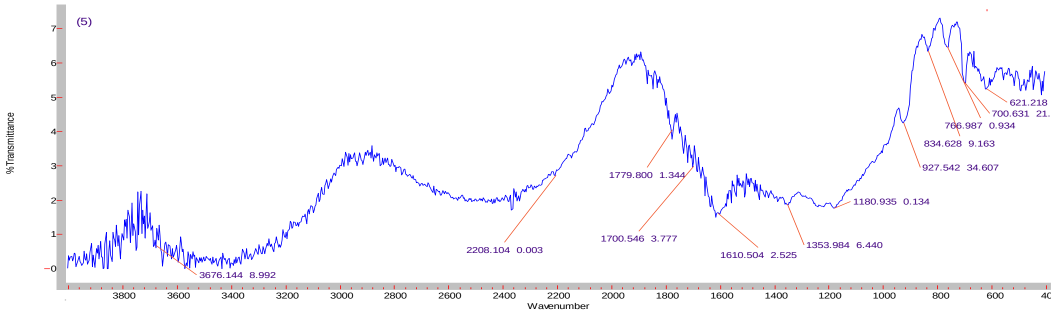
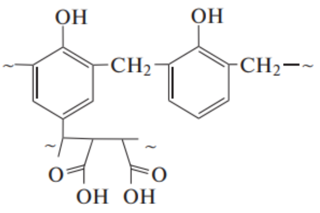
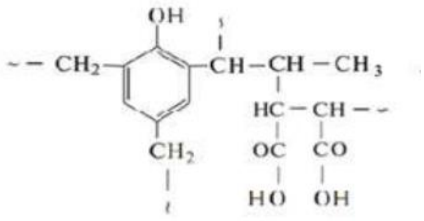


Fig.2. IR spectra of copolymer IV after sorption

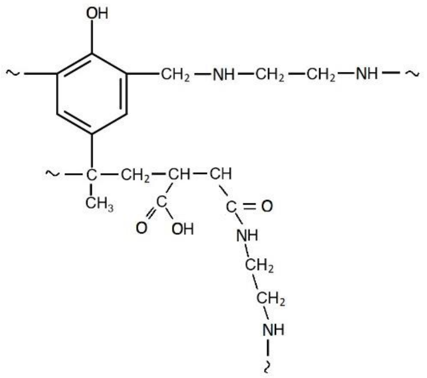
As can be seen from the data of comparative studies (tables 1 and 2), the structure of the cross-linked polymer used as a sorbent influences the process of extracting microelements from the water environment. Among the cross-linked copolymers used in the work, I and II have the best sorption properties, with the following structures:



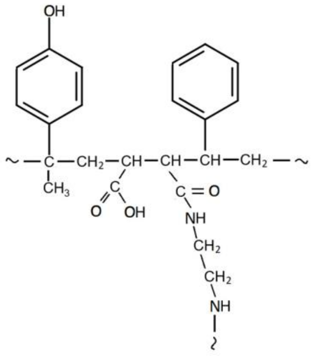
Polymer I



Polymer III



Polymer II



Polymer IV

Table 1

Results of studies on the extraction of microelements from oil formation waters A and B using sorbent

Micro-elements	Content of microelements in water A, ppm		Degree of extraction of microele-ments from water A, %	Content of microelements in water B, ppm		Degree of extraction of microelements from water B, %
	before sorption	after sorption		before sorption	after sorption	
K	28027.929	15321.225	45.3	10004.878	6122.9853	38.8
Na	31291.362	13541.654	56.7	12641.004	4164.281	67.0
Ca	8160.880	0	~100	6245.351	76.900	98.8
Ba	1076.850	375.433	65.1	1896.445	810.293	57.3
Zn	38.1760	0	~100	218.9100	2.18910	99.0
Cd	-	-	-	3.5430	3.0363	14.3
Cu	83.7480	0.3040	99.6	872.3800	38.3847	95.6
Hg	14.9210	0.3380	97.7	19.1810	2.0715	89.2
Fe	5998.198	0	~100	4806.253	26.451	99.4
Cr	505.3240	0.0190	~100	1224.6340	157.9777	87.1
Mn	87.7140	0.1820	99.8	119.4930	0.2389	99.8
As	20.3640	0.338	98.3	10.7400	2.7864	74.1
Se	63.4280	0.1820	99.7	87.2390	5.8450	98.3
Ni	-	-	-	11.8600	5.8350	50.8
Pb	-	-	-	27.2860	8.3220	69.5

As can be seen from the results of the studies, all 4 types of cross-linked polymers used as sorbents have good sorption properties, which can be explained by the presence in their structures of a nitrogen atom, phenolic hydroxyl and other active functional groups that promote complex formation with cations of various metals.

Table 2

Results of studies on the extraction of microelements from oil formation waters A and B using sorbent II

Micro-elements	Content of microelements in water A after sorption, ppm	Degree of extraction of microelements from water A,%	Content of microelements in water B after sorption, ppm	Degree of extraction of microelements from water B, %
K	39.6741	99.8	0	~100
Na	0	~100	0	~100
Ca	16.0330	99.7	0	~100
Ba	29.8160	97.2	68.2720	96.4
Zn	0	~100	0	~100
Cd	-	-	0.2267	93.6
Cu	0	~100	8.7238	99.0
Hg	0.0730	99.3	1.6303	91.5
Fe	0.5170	93.7	106.1709	98.3
Cr	0	~100	0	~100
Mn	0	~100	0	~100
As	0.0100	99.9	0.4620	95.7
Se	0	~100	0.6106	99.3
Ni	-	-	0.8538	92.8

Table 3

Results of studies on the extraction of microelements from oil formation waters B with sorbent III and IV

Micro-elements	Content of microelements in water B after sorption by sorbent III, ppm	Degree of extraction of microelements from water B by sorbent III, %	Content of microelements in water B after sorption by sorbent IV, ppm	Degree of extraction of microelements from water B by sorbent IV, %
K	0	~100	0	~100
Na	0	~100	0	~100
Ca	0	~100	0	~100
Ba	1099.9383	42	1276.3074	32.7
Zn	8.7564	96	0.2189	99.9
Cd	3.2879	7.2	1.5837	55.3
Cu	225.0740	74.2	165.5777	81.0
Hg	6.08030	68.3	9.7631	49.1
Fe	262.3047	93.8	1061.7096	83.0
Cr	366.16565	70.1	155.5285	87.3
Mn	55.3252	53.7	55.0862	53.9
As	1.7086	84.1	2.8476	73.5
Se	32.12891	62.3	32.4529	62.8
Ni	10.7095	9.7	2.1241	82.1
Pb	7.2853	73.3	26.3037	3.6

The process of sorption of metal cations when using I obviously occurs with the participation of carboxyl groups and phenolic hydroxyl. In this case, the degree of extraction of K, Na, Ca, Zn, Fe, Cr, Cu, Mn, As, Se from the aqueous medium is ~100%, the degree of extraction of Ba ions is low (~55%). Polymers III and IV have high selectivity (Z = 100%) and moderate sorption properties in relation to most other microelements, as evidenced by the test results given in table. 3.

CONCLUSION

Thus, the results of comprehensive studies of cross-linked polymers based on 4-isopropenyl and 2-propenylphenols (I-IV) for the extraction of microelements from formation waters by sorption and flame ionization methods, their quite high sorption activity, especially for copolymers I and II. It was found that polymers III and IV have high selectivity towards Ca and Zn ions.

Based on the results obtained, it can be concluded that the studied copolymers with a cross-linked structure can be recommended for the purification of oil field and formation waters from environmentally hazardous heavy metals.

REFERENCES

1. Lebedeva O.V., Sipkina E.I., Pozhidaeva Yu.N. Adsorption of platinum (IV) by a composite based on silica and a copolymer of 4-vinylpyridine with 2-hydroxyethyl methacrylate. Physical chemistry and protection of materials. 2017, №1, pp.75-80
2. Zhang Chenxi., Tang Ging, Mayes Richard. Poly (acrylonitrile)- Functionalized Porous Aromatic Frameworu Synt-hesized by AtomTransfer Radical Polymerization for the extraction of Uranium from Seawater. Jnd.and eng.Chem.Res. 2016, №15, pp. 4125-4129
3. Wang Fang-ping, Zhang Zun-ying, Li Wan-Xia. Prefaration of PBMA/GMA-SiO2 adsorbent and its effecient removal of lead ions. Zingxi huagong Fine chem. 2014, №4, pp. 486-492
4. Qiu Xuejing, Hu Huiping. Yang Zinpeng. Selective removal of copper from simulated nickel electrolyte by polysturene, supported 2-aminomethyl pyridine chelating resin. Chem. Pap. 2018, № 8, pp. 2071-2085
5. Chen Lili, Feng Shaojie, Zhao Donglin. Efficient sorption and reduction of U (IV) on zero - valent iron-polyanilino-graphene aerogel ternary composite. J. Colloid and Interface Sci. 2017, pp. 197-206
6. Magerramov A.M., Bayramov M.R.Chemistry of alkenylphenols. 2018, Moscow, Technosphere. 362 p
7. Trakhtenberg L.I., Gerasimov G.I., Gramov V.F., Bune E.V. Kinetic features of the sorption of metals from aqueous solutions by immobilized crown ethers. Zhur. Physchemistry. 2004, T 78, № 4, pp. 696-700
8. Dudarev V.I., Irinchinova N.V., Filatova E.G. Adsorption of nickel (II) ions from aqueous solutions by carbon adsorbents. Izv. universities Chemistry and chem. Technology. 2017, № 1, pp. 75-90
9. Motahari Siamak, Heidari Behzad Shiroud, Ieotlagh Chodratolla U Hashemi, Resorcind formaldehyde xerogels modified with mercap to functional groups as mercury adsorbent. Journal Appl. Polym. Sci. 2015, №37, pp. 182-189
10. Bayramov M.R., Maharramov A.M., Mehdiyeva G.M., Guliyeva Sh.J., Aghayeva M.A., Syntheses of carboxylate type sorbent based on coolıgomers of 2-propenylphenol and formaldehyde and study of the functional properties for sorptıon of uranyl ıons ın model systems. Chemical problems. 2023, № 1 (21), pp. 85-92
11. Bayramov M.R., Mehdiyeva G.M., Nagiev Dzh.A., Agaeva M.A., Kulieva Sh.Dzh. Studying the sorption of uranyl ions from aqueous solutions with the structured 4-isopropenylphenol-phenol-formaldehyde copolymer. Russian Journal of Physical Chemistry A. 2021, Vol. 95, № 4, pp.796- 774
12. Bayramov M.R., Guliyeva Sh.J., Mehdiyeva G.M., Agayeva M.A., Purıfıcatıon of water systems from uranium salts usıng acrylonıtrıle-structured triple co-olıgomers of 4-ısopropenılphenol, formaldehyde and 4-(1-methyl)-1-dımetoxsıphosphorylethyl)phenol. Azerbaijan Chemical Journal. 2023, № 1, pp. 155-161

13. Bayramov M.R., Magerramov A.M., Mehdiyeva G.M.,Kuliyeva Sh.J., Agayeva M.A., Syntheses and study of trıple co-olıgomers of 4-ısopropenylphenol, phenol and formaldehyde structured by maleıc anhydrıde . PPOR. 2021, Vol. 22, № 4, pp. 476-485
14. Bayramov M.R., Magerramov A.M., Mehdiyeva G.M.,Guliyeva Sh.J., Agayeva M.A., Synthesis of ternary coolıgomers of 4-ısopropenylphenol, formaldehyde, and 4-(1-methyl-1-dımethoxyphosphorylethyl)phenol and theır structurıng ın the presence of acrylonıtrıle. PPOR. 2022, Vol. 23, № 2, pp. 198-205
15. Guseinova B.A., Samedova F.I., Sadygov N.M., Gasanova G.M., Study of the microelement composition of condensate from the Azerbaijani “Bulla-Deniz” field. Oil refining and petrochemistry. 2017, № 7, pp. 13-15
16. Aung P.P., Veselova O.A., Troshkina I.D., Kinetics of scandium sorption by an impregnate containing phosphine oxide . Izv.vuzov, Chemistry and Chem. Technology. 2017, Vol.60, №8, pp. 28–30
17. Grechnikov A.A.,Borodkov A.S.,SimakinaYa.I.,Arabova Z.L.Complexation of heterocyclic azo compounds with transition metal ions data from the method of laser-induced desorption-ionization.Izv. RAS, Series Chem. 2016, № 12, pp. 2787-279

ИССЛЕДОВАНИЕ МИКРОЭЛЕМЕНТНОГО СОСТАВА НЕФТЯНЫХ ПЛАСТОВЫХ ВОД С ИСПОЛЬЗОВАНИЕМ СОРБЦИОННОГО И ПЛАМЕННО-ИОНИЗАЦИОННОГО МЕТОДОВ

А. М., Магеррамов[1] *O97372019**М. Р. Байрамов*[1] 0000-0003-1640-3392,
Ш. Дж. Кулиева[1] *0000-0002-9972-488X, Г. М. Мехтиева*[1] *0000-0003-4293-6555,*
Н. М. Садыгов[2]*, М. А. Агаева*[1] *JDH-3658-2023, Б. А. Бабаева*[2]
[1]*Бакинский Государственный Университет,* [2]*Институт геологии и геофизики*
guliyevashahla@hotmail.com

С использованием сорбционного и пламенно-ионизационного методов изучен микроэлементный состав пластовых вод, сопутствующих азербайджанской нефти месторождений (Локбатан, Карадагского р-на, скв. 260 и Бибиэйбат, Сабаилского р-на, скв. 748, г. Баку).В качестве сорбентов использовали сополимеры сшитой структуры, полученные на основе соолигомеров алкенилфенолов (2-пропенил- и 4-изопропенилфенолов), формальдегида, малеинового ангидрида и др. соединений (трехмерные структуры 4 видов) .Микроэлементы извлекались из пластовых вод методом сорбции в статическом режиме при комнатной температуре и продолжительности 24 час. Далее после предварительной сушки образцы сополимеров с извлеченными микроэлементами подавали в аппарат ICP MS 7700e (производства Agilent, США) и проводили атомизацию и последующую ионизацию микроэлементов и исходя из соотношения массы (m) к заряду (Z), вычисляли их содержание в исследованном образце (в ppm).Было изучено влияние структуры сорбента и состава воды на степень извлечения микроэлементов. Установлено, что наиболее высокими сорбционными свойствами обладают сшитые сополимеры I и II, полученные на основе 4-изопропенилфенола, малеинового ангидрида по сравнению с сополимерами III и IV. Степень сорбции большинства катионов в первом случае составляет 99-100%, в том числе и экологически опасных; сшитые сополимеры III и IV обладают высокой избирательностью по отношению к K^+*,* Na^+*,* Ca^{2+} *и* Zn^{2+}

(степень их извлечения ~100%) Степень извлечения других катионов составляет в среднем до 80%.

***Ключевые слова**: нефтяные пластовые воды, микроэлементы, сшитые полимеры, алкенилфенолы, ионизация, сорбция.*

SORBSIYA ÜSULU İLƏ NEFT-LAY SULARINDAN MİKROELEMENTLƏRİN TƏMİZLƏNMƏSİ

A. M. Məhərrəmov[1] O97372019, M. R. Bayramov[1] 0000-0003-1640-3392,
Ş. C. Quliyeva[1] 0000-0002-9972-488X, G. M. Mehdiyeva[1] 0000-0003-4293-6555,
N. M. Sadıqov[2], M. A. Ağayeva[1] JDH-3658-2023, B. A. Babayeva[2]
[1] Bakı Dövlət Universiteti,[2] Geologiya və Geofizika İnstitutu
guliyevashahla@hotmail.com

Sorbsiya üsullarından istifadə etməklə Azərbaycanın müxtəlif neft yataqlarından neftlə bərabər çıxarılmış lay sularından (Qaradağ rayonu, Lökbatan 260 saylı mədən və Səbail rayonu, "Bibiheybətneft" K748 nömrəli neft quyusunun lay suları) istifadə etməklə mikroelement tərkibi tədqiq edilmişdir Sorbent kimi alkenilfenolların (2-propenil- və 4-izopropenilfenollar) formaldehid, malein anhidridi və digər birləşmələrlə əmələ gətirdiyi sooliqomerlərindən sintez edilmiş tikili polimerlər tədqiq edilmişdir. Sorbsiya prosesi otaq temperaturunda, 24 saat müddətində gözlədilmişdir. Daha sonra məhlul süzülərək həm sorbent, həm də lay suyu analiz edilmişdir. Sorbentlərin lay suyunda sorbsiya prosesinin təsdiqi müxtəlif metodlarla, müxtəlif cihazlarda öyrənilmişdir: "İCP- MS 7300e". Mikroelementlər statik şəraitdə otaq temperaturunda, 24 saat müddətində sorbsiya yolu ilə lay sularından çıxarılmışdır. Daha sonra, sorbent nümunələri süzülmüş, qurudulmuş və analiz üçün ICP MS 7700e cihazına (Agilent, ABŞ istehsalı) verilmişdir. Sorbentin strukturunun və suyun tərkibinin mikroelementlərin sorbsiya dərəcəsinə təsiri öyrənilmişdir. Müəyyən edilmişdir ki, 4-izopropenilfenol və malein anhidrid əsasında alınmış I və II tikili polimerləri III və IV polimerləri ilə müqayisədə ən yüksək sorbsiya xassələrinə malikdir. Birinci halda əksər kationların sorbsiya dərəcəsi 99-100% təşkil edir, III və IV tikili polimerləri K^+, Na^+, Ca^{2+} və Zn^{2+} ionlarını digər ionlara nisbətən yüksək seçiciliklə sorbsiya edir (onların sorbsiya dərəcəsi ~100% təşkil edir). Digər kationların sorbsiya dərəcəsi demək olar ki, 80%-ə qədərdir.

***Açar sözlər:** neft-lay suları, mikroelementlər, tikili polimerlər, alkenilfenollar, ionlaşma, sorbsiya.*

AJCN, Vol. 5, No. 2, 2023, pp. 68-74
https://doi.org/10.32010/AJCN04022023-68

UDC: 4546.74.2+548.736

COORDINATION COMPOUNDS OF RHENIUM WITH ORQANOSULFUR LIQANDS

M.M Aghahuseynova[0000-003-2471-2136] , *T.A Guluzadeh*
Azerbaijan State Oil and İndustry University
terlanquluzade14@gmail.com

Method for the synthesis of coordination compounds of rhenium with N, N'-ethylenetiourea have been developed. The composition and structure of the complexes isolated in the crystalline state were established on the basis of a set of data from elemental analysis, IR and electronic spectroscopic methods and measurements of molar electrical conductivity. According to the results of the studies, the mono-dentate coordination of ethylenetiourea through the sulfur atom of the heterocycle was established The determing of molar electric conductivity indicate that the interaction of rhenium complexes with ethylenetiourea in polar solvent.

It has been shown that depending on the concentration of hydro halic acid and the Re: Tio ratio compound of various composition are formed. In the IR spectra of the synthesized complex compounds absorption bands of the valent vibrations of the C-S group, which are 30-50 cm-1 lower than the vibration of free thio group. The absorption bands related to the vibration of N-H groups are slightly shifted to the high-frequency region compared to the free ligand, which indicates the absence of a metal-nitrogen coordination bond.

Keywords: *tiourea derivatives, rhenium, coordination compounds, element analysis, molar electrical conductivity.*

INTRODUCTION

Urea derivatives are widely used in catalysis, analytical chemistry and as substances exhibity lightstabiliring and antistatia properties [1-7]. One of the tiourea derivatives is ethylenetiourea, which contains three donor atoms and can from complex compounds with some metals. However, the number of works devoted to the complexation of rhenium with this organic liqand in the world literature is practically absent

The literature also provides limited information on studying the influence of temperature and the nature of solvents on the stability of the obtained complex compounds in solutions.

The method of coordination of ethylenetiourea to the complexing agent - rhenium is largely influenced by its structure in free form and in solutions. In the work [8-9] complex compounds of Re with acetyltiourea were studied, in work [10-13] was described complexes of Cd (ll) with acetyltiourea. Information about synthesis of Re (V) with ethylenetiourea is of great interest. This work is devoted to the development of methods for synthesis and the study of their physicochemical properties.

EXPERIMENTAL PART

The starting materials $H_2[ReOG_5]$, where G – CI, Br and acetyltiourea were obtained according to the methods [2-3]. Rhenium was identified as nitrone perrhenate; chlorine and bromine were determined gravimetrically as AdG Nitrogen, carbon, sulfur and hydrogen by methods described in [3]. The electrical conductivity of solutions of the complexes was measured in a closed chamber using an alternating current bridge R-

5021. The IR spectra of the synthesized complexes were recorded in the region of 400-4000 cm on a Spekord-IR-75 device in the form of KBr tablets.

Synthesis of $[ReOL_2Cl_3]\ 2H_2O$. To 50 mL of 0.083 mol/L N_2 $[ReOCI_3]$ in 6 mol/L HCI, 2.44 g of ethylenetiourea was added in small portions with vigorous stirring. The resulting precipitate was filtered, washed with 6 mol/L HCI (100 mL), acetone (100 mL), and dried in a vacuum desiccator over solid KOH to constant weight. Productivity 68%. The complex is soluble in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). It is not soluble in benzene, 1,4-dioxane, ether, hexane.

Found, %: Re-31.86; Cl-19.55; S10.78; N-8.35. $2H_2O$ calculated for $[ReOL_2CI_3]$, %: Re 32.04%; Cl-18.35; S-11.02; N-9.65.Bromide complex containing $[ReOL_2Br_3]\ 2H_2O$ was obtained similarly to chloride complex in 5 mol/l HBr environment. The productivity of the complex is 72%. Found, %: Re-25.36; Cl-34.85; S-3.95; N-4.02. $2H_2O$ for $[ReOL_2Br_3]$ was calculated: Re 26.05; Br-33.61; S-8.96; N-7.84.

Synthesis of $[ReO(OH)_2L_2CI]$-$2H_2O$. 1.77 g of ethylenetiourea was added to 50 mL of H_2O with continuous stirring. Then, 25 mL of 0.12 mol/L $N_2[ReOCls]$ solution was added to this solution with vigorous stirring. The resulting dark brown precipitate was filtered, washed with 6 mol/L HCI (50 mL), ether (50 mL), and dried to constant weight over solid KOH in a vacuum desiccator. The complex is soluble in DMF, acetone, DMF. Productivity – 70%. Found, %: Re-33.00; Cl-7.25; N-9.89; S-4.70. Calculated for $[ReO(OH)_2L_2CI]\ 2H_2O$, %: Re 34.22; Cl-6.53; N-10.30; S-5.17.

Synthesis of $[ReO(OH)_2L_2Br]\cdot 2H_2O$. This complex was obtained similarly to the chloride complex. Productivity – 80%.Found, %: Re-30.74; Br-15.04; N-8.34; S-11.26. Calculated for $[ReO(OH)_2L2Br]\ 2H_2O$, %: Re- 31.63; Vg-13.60; N-9.52; S-10.88. Elemental analysis for C, H, N was performed on a Carlo Erba 1106 and Vario EL instrument. IR spectra were recorded on a Bruker IFS-85 Fourier spectrometer (KBr pellets).

RESULTS AND DISCUSSION

Studies have shown that when $H_2[ReOC1_3]$ reacts with ethylenetiourea in a ratio of 1:1 to 1:5 in 6 mol/l HCl, a consistent color change is observed, but only then does a precipitate form. The ratio of primary reagents is equal to 1:5. In this case, a dark brown compound is formed in which there are two chlorine atoms for one rhenium atom. Based on the elemental analysis data (table 1), this complex corresponds to the formula $[ReOL_2Cl_2]\ 2H_2O$. Like the chloride complex, the bromide complex was obtained in 5 mol/l HBr medium. A decrease in acid concentration leads to the formation of partially hydrolyzed complexes. Thus, we isolated and identified complexes of composition $[ReO(OH)_2G_2]\ 2H_2O$ in 5 mol/l NG medium, where G - Cl, Br.

Table 1

Elemental analysis for rhenium (V) complex compounds

Mixed	Calculated, %				Found, %			
	Re		N	S	Re		N	S
$[ReOL_3Cl_3]\ 2H_2O$	32.02	18.35	9.65	11.02	31.86	12.55	8.35	10.78
$[ReOL_2Br_3]\ 2H_2O$	26.05	33.61	7.84	8.96	25.36	34.85	6.98	9.67
$[ReCO(OH)_2L_2CI]\ 2H_2O$	34.22	6.53	10.30	5.17	33.00	7.25	9.45	4.73
$[ReO(OH)_2L_2Br]\ 2H_2O$	31.63	13.60	9.52	10.88	30.74	15.04	8.34	11.26

In order to determine the type of electrolyte to which the synthesized complex compounds belong, their electrical conductivity was studied in the temperature range of 25...65°C. Electrical conductivity of $[ReOL_2G]2H_2O$ containing complexes was measured only in DMF, acetone and DMF were used for $[ReO(OH)_2L_2G]2H_2O$ complexes.

Table 2

Values of molar electrical conductivity of rhenium (V) complex compounds with ethylenetiourea in DMF at different temperatures (C = 1-10 mol/l)

The composition of the complex					
	Temperature C°				
	25	35	45	55	65
$[ReOL_2Cl_3]\ 2H_2O$	69.64	81.54	98.68	114.23	130.09
$[ReOL_2Br_3]\ 2H_2O$	76.84	97.54	101.89	123.94	148.38
$[ReO(OH)_2L_2Cl]\ 2H_2O$	28.40	32.77	38.08	45.50	52.84
$[ReO(OH)_2L_2Br]\ 2H_2O$	35.87	45.90	50.25	62.83	76.24

Dimethylformamide solutions of rhenium(V) complex compounds obtained in 6 medium have electrical conductivity close to electrolytes of mol/l HCl and 5 mol/l HBr 1:1. With growth, there is a very rapid increase in the value of temperature for the above compounds. The polar electrical conductivity is probably related to the displacement of halide ions from the inner spheres of the complexes with solvent molecules, that is, the complexes dissociate at high temperatures. In the studied temperature range, hydroxyl-containing complexes behave like DMF and acetone non-electrolyte compounds.

In order to determine the degree of oxidation of rhenium in the synthesized complex compounds, potentiometric titration of solutions of complexes with potassium bichromate was carried out. It was determined that the oxidation state of rhenium in all synthesized compounds does not change and remains equal to five (table 3).

Table 3

Data on the determination of the oxidation state of rhenium in the synthesized complexes

Mixed	The volume of the oxidizer at the equivalent point, ml	The mass of the complex	The number of electrons	Oxidation state of rhenium
$[ReOL_2Cl_3]\ 2H_2O$	1.5	0.040	2.18	4.82
$[ReOL_2Br_3]\ 2H_2O$	1.5	0.045	1.90	5.1
$[ReO(OH)_2L_2Cl]\ 2H_2O$	1.0	0.027	1.99	5.01
$[ReO(OH)_2L_2Br]2H_2O$	1.2	0.037	2.01	4.99

To establish the coordination method of ethylenetiourea to rhenium (V), we studied the spectrum of free ethylenetiourea and the synthesized complexes in the 400-4000 cm region. Figure 1 shows the IR absorption spectrum of uncoordinated ethylenetiourea.

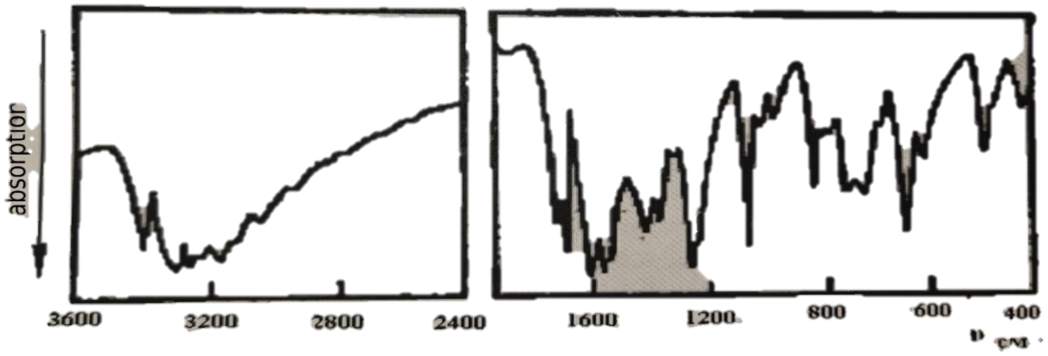


Fig. 1. IR absorption spectrum of ethyleneltiourea.

An interpretation of the vibrational spectra of crystalline ethylenetiourea was proposed in [2,10]. The authors of these works associate the 1710 and 1690 cm bands with the vibrations of the carbonyl group. The vibrations with the largest contribution from the C-S bond correspond to the 835, 732, and 620 cm bands. The disequilibrium of C-M bonds in ethylenetiourea molecules [11] indicates the presence of several stretching vibrational bands of CN bonds, which are (NCN), υ, (NCN), (NCC), (NCC). These fluctuations correspond to the 1550 and 1000 bands; 1370 and 835 cm. The bands at 1685 and 1700 cm” corresponding to the shoulder-shaped vibrations (CO), which decrease in intensity during the formation of complexes, appear in the same region as uncoordinated ethylene urea. Thus $[ReO(OH)_2L_2CI]$ $2H_2O$ composition complex shows bands at 1690 and 1700 cm^3 corresponding to stretching vibrations (CO), which reduce their intensity. This fact indicates the lack of coordination through the oxygen atom of the acetyl group.

In the IR spectrum of the complexes, the bands due to the vibrations of the C=S bond, which undergo a change, shift to the low-frequency region of 20-50 cm^2. Thus, in the IR spectrum of the $[ReO(OH)_2L_2CI]$-$2H_2O$ complex, the bands near 735 and 690 cm shift to the low-frequency region and appear as a single band at 670 cm, and the band at 620 cm shifts to the low-frequency region up to 600 cm passes

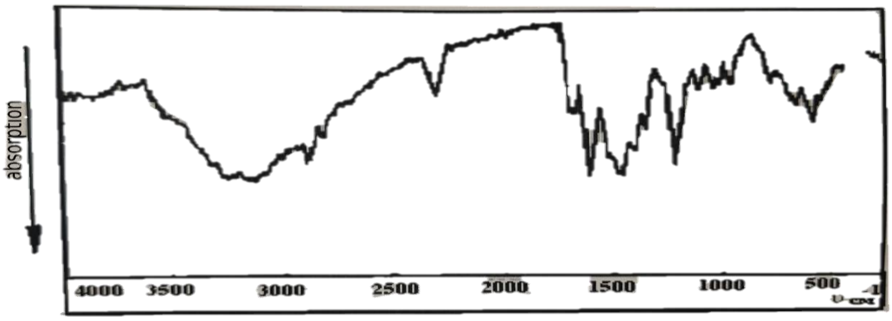


Fig. 2. IR spectrum of the $[ReO(OH)_2L_2CI]\cdot 2H_2O$ complex where L is ethyleneIthiourea

In the IR spectrum of the complex, the bands related to different vibrations of the CN group of ethyleneIthiourea [10] mainly undergo a high-frequency shift, and a change in frequency intensity is also observed. Thus, the v_2 (NCN) band visible in the spectrum of the free ligand at 1000 cm^{-1} is detected at 1029 cm in the spectrum of the complex; in the spectrum of the complex (NCC), the responsible bands appear at 1400 cm. In the IR spectrum of the complex, the bands responsible for $8(NH_2)$ and 6(NH) appear in the same region as free ethylenelthiourea. In the spectrum of the complex, the bands responsible for $c(NH_2)$ are mixed with the bands responsible for the vibration of the hydroxyl groups of water of crystallization molecules, so it is impossible to identify them unambiguously. Based on IR-spectroscopic studies, it can be assumed that ethylenethiourea in the synthesized complex compounds is monodentan tely coordinated to rhenium (V) through the sulfur atom.

CONCLUSION

The process of complexation of Rhenium with Ethylenetiourea has been studied. The influence of various factors (temperature, nature of solvents, concentration of hydrohalic acid) on the composition of resulting complex compounds has been established. The synthesized complexes were characterized by spectroscopic methods. A shift in the vibrational band of C-S bond towards higher wave numbers compared to the initial compounds was revealed. According to elemental analysis data, complex compounds are formed, in which there is one metal atom per ligand molecule. These complexes contain two water molecules, the presence of which was confirmed by IR-spectral data.

REFERENCES

1. Amindzhanov A.A., Karimova M.Kh., Vezen A.E. Study of the biological activity of complex compounds of rhenium (V) with benzoxazole and benzothiazole derivatives. Coordination connections and aspects of their application. Dushanbe.1991, 2 h.,46 p
2. Justin J. Wilson and Stephen J. Lippard. Synthetic methods for the preparation of Platinum Anticancer complexes. Chemical Review. 2014,114(8), pp. 4470-4495
3. Zhao Y. Woods J.A., Farrer N.J., Robinson K.S., Pracharova Y. Diarido mixed-amine platinum (4) anticancer complexes activatable by visible-light form novel DNA adducts Chemistry. 2013, №9, (29) pp. 9578-91
4. Bauer E.B., Haase A.A., Reich R.M., Crans D.C., Kühn F.E. Organometallic and coordination rhenium compounds and their potential in cancer therapy. Coord. Chem. Rev. 2019 h, 393, pp.7-11
5. Vishkaee T. S., Fazaeli R., Youseti M. Teoretical Analysis at Soluent Effect on the NMR. A Platinum-Based Anticancer Drug. Russ J. Inorg. chem. 2019 h, 64, pp.237-241
6. Ryashentseva M. A. Rhenium containing catalysts in petrochemistry. Bulletin of MITHT 2007, Vol.2, №2 pp. 12-26
7. X. F. He, C. M Vogels, A. Decken, S. A Westcolt Pyridil benzimidozole, benzoxarole and benzotiarole platinium complexes. Polyhedron 2004, pp. 155-160
8. Beloglazkina E.K., Majuga A.B.,Moiseeva A.A. 5.2 methylthio ethye-2 tiokso-3 phemieimsdazolin 4-one and its complexes with transition metals. News of the Academy of Sciences. 2007, pp.339–343
9. D. Bohle., A. Zafar., P. A. Goodson., D A. Zaeqer. Synthesis and characteriratim of Nickol Bis (alkil this) salen complexes. lnorg. Chem. 2010, 38, pp.712

10. D. Zhu, Y. Xu Y Meı, YSci, C. Tu, X You, FT - İR study of rare earth 4 -aminobentsulfonate complexes. J. Mol Struct. 2001, 559, pp.119-126
11. Spillane C.B., Morgan J.L., Fletcher N.C., Collins J.G., Keene F.R. İnert benzotiazole functionalized ruthenium (ll) complexes. Dalton. Trans. 2006, pp.3122- 3133
12. K Dey, S. Sarkar, S.Mukhopadhyay, S.Biswas, B. B Bhaumik. Synthesis, characterization and coordination behavior of 2- (1- carboxyl - 2- hydroxyphenyl) thiazolidine. Journal of Coordination Chemistry. 2006, 59, pp.565 - 583

КООРДИНАЦИОННЫЕ СОЕДИНЕНИЯ РЕНИЯ С СЕРОРОРГАНИЧЕСКИМИ ЛИГАНДАМИ

Агагусейнова М.М. $^{0000-003-2471-2136}$ *Гулузаде Т.А.*
Азербайджанский Государственный Университет Нефти и Промышленности
terlanquluzade14@gmail.com

Разработан метод синтеза координационных соединений рения с N,N'-этилентиомочевиной. Состав и строение выделенных в кристаллическом состоянии комплексов установлены на основании совокупности данных элементного анализа, методов ИК- и электронной спектроскопии, а также измерений молярной электропроводности. По результатам исследований установлена монодентатная координация этилентиомочевины через атом серы гетероцикла.Определение молярной электропроводности свидетельствует о том, что взаимодействие комплексов рения с этилентиомочевиной в полярном растворителе

Показано, что в зависимости от концентрации галогеноводородной кислоты и соотношения Re:Tio образуются соединения различного состава. В ИК-спектрах синтезированных комплексных соединений полосы поглощения валентных колебаний группы C-S, которые на 30-50 см-1 ниже колебания свободной тиогруппы. Полосы поглощения, связанные с колебанием групп N-H, несколько сдвинуты в высокочастотную область по сравнению со свободным лигандом, что указывает на отсутствие координационной связи металл-азот.

Ключевые слова: *производные тиомочевины, рениум, координационные соединения, элементный анализ, молярная электрическая проводность*

RENİUMUN ORQANOSÜLFÜR MALİLƏRİ İLƏ KOORDİNASİYON BİRLİKLƏRİ

M.M Ağahüseynova$^{0000-003-2471-2136}$ *T.A Quluzadə*
Azərbaycan Dövlət Neft və Sənaye Universiteti
terlanquluzade14@gmail.com

Reniumun N, N’-etileniokarbamid ilə koordinasiya birləşmələrinin sintezi üsulu işlənib hazırlanmışdır. Kristal vəziyyətdə təcrid olunmuş komplekslərin tərkibi və quruluşu elementar analiz, İQ və elektron spektroskopik üsullar və molar elektrik keçiriciliyinin ölçülməsi məlumatlarının toplusu əsasında müəyyən edilmişdir. Tədqiqatların nəticələrinə görə, etilenetiouranın heterosiklin kükürd atomu vasitəsilə mono-dentat koordinasiyası müəyyən edilmişdir. Molar elektrik keçiriciliyinin təyini renium komplekslərinin qütb həlledicidə etilenikarbamid ilə qarşılıqlı təsirinin olduğunu göstərir.

Göstərilmişdir ki, hidrohal turşusunun konsentrasiyasından və Re: Tio nisbətindən asılı olaraq müxtəlif tərkibli birləşmələr əmələ gəlir. Sintez edilmiş kompleks birləşmələrin İQ spektrlərində sərbəst tio qrupunun vibrasiyasından 30-50 sm-1 aşağı olan C-S qrupunun valent *vibrasiyalarının udulma zolaqları. N-H qruplarının vibrasiyası ilə əlaqəli udma zolaqları sərbəst liqandla müqayisədə yüksək tezlikli bölgəyə bir qədər sürüşür ki, bu da metal-azot koordinasiya əlaqəsinin olmadığını göstərir.*

Açar sözlər: *tiokarbamid törəmələri, renium, koordinasiya birləşmələri, element analizi, molar elektrik keçiriciliyi*

AJCN, Vol .5, No. 2, 2023, pp. 75-85
https://doi.org/10.32010/AJCN04022023-75

UDC 665.703.502

ECOLOGICAL PROBLEMS CAUSED BY THE FORMATION OF TOXIC COMPOUNDS DURING THE EXPLOITATION OF MOTOR FUELS AND THEIR SOLUTION METHODS

N.N.Javadzada, E.T.Zeynalov[0000-0002-5372-754]
Azerbaijan State Oil and Industrial University
njavadzada@mail.ru

Internal combustion engines will continue to be the primary source of power for ships, heavy-duty vehicles, and thermoelectric plants in the future, as they are today. The primary objective of engine suppliers is to find ways to reduce their negative impact on the environment and provide cleaner energy. A critical part of automotive engineering and environmental science is the study of techniques for reducing toxic emissions from diesel engines. While diesel engines are efficient, they generate pollutants that can harm air quality and human health. This paper examines exhaust gas recirculation (EGR) method that regulates emissions during their formation. The mechanism of exhaust gas production and its relationship to engine parameters were thoroughly investigated. Problems that developed when applying individual method for reducing emissions in specific engine operating circumstances were discussed. The effect of emission control systems on engine performance characteristics such fuel consumption, NO_x emissions, load reaction, and durability was investigated. It was demonstrated that only a systematic strategy to reducing diesel exhaust emissions using new technology will maintain their importance and enable truly cleaner engines that will not only satisfy but well below the legal emission requirements.

Keywords: *exhaust gas recirculation, emissions regulation, formation of emissions, NO_x emission, toxic emissions reduction.*

INTRODUCTION

The constant growth of demand for internal combustion engines as the primary source of propulsion in maritime and road traffic, as well as for the majority of heavy duty machines, and the desire to reduce global emissions of greenhouse gases, have set two new goals for manufacturers: to optimize efficiency as a market requirement, and to reduce emission gas pollution as an environmental sustainability requirement. On the other hand, there are significant challenges with limited resources, the efficiency of energy conversion systems, and the need for a smart-based strategy, [1]. Understanding how to mitigate the impact of pollutant emissions from heavy more y-duty diesel engines, which pose a significant threat to the environment and human health, makes it more feasible to develop traffic-related policy measures to limit the negative consequences, [2]. Internal combustion engines (ICE) are getting progressively more complex, with a growing number of control systems, in order to comply with Euro 6d vehicle regulations while also enhancing engine efficiency. Complex control systems make engines more versatile in terms of engine load and speed, which can contribute to lower emissions and fuel consumption. The main disadvantages of such systems are their high production and maintenance costs, as well as ever complex requirements for monitoring exhaust gases in order to develop a basis for automobile type approval and to monitor the function of all sections during operation. Authors such as [3], [4], [5], and [6] have addressed the aforementioned issues, which result in a disparity between emissions and controlled by legislation to type approval cars and emissions for everyday use. [7] also compare the homologation process to the issue of discrepancy with actual and homologated emissions, as well as the controversies linked with them. From an economic standpoint, an automobile powered by a diesel engine consumes 20-30% less gasoline due to its higher energy value per litre and higher efficiency. From an ecological standpoint, despite a complicated purification process, an automobile powered by a diesel engine emits less carbon dioxide CO_2, hydrocarbon HC, and carbon monoxide CO, however the soot emission PM and NOx emission are higher. 1 kg of diesel fuel produced about 3.1 kg of CO_2 and 1.3 kg of H_2O when burned. Despite the fact that the same energy equivalent of gasoline fuel produces about 8% less CO_2 emissions, due to the significantly greater efficiency, the average diesel car in Europe emits about 17% less CO_2 than a similar conventional gasoline car in the same vehicle segment, [8]. Aside from carbon dioxide and water, the combustion of gasoline within an engine produces around 1% of toxic gases, [9]. Along with the toxic substances such as NO_x, emission particles PM, unburned hydrocarbon HC, carbon monoxide CO, the amount of carbon dioxide is also taken into account, which does not pose a direct risk of harm to people but is considered to be a greenhouse gas that contributes to global warming problems. The Kyoto Protocol's goal was to reduce global CO_2 emissions in all economic sectors by 8% by the end of 2008 compared to 1990. According to the author [10], road traffic produces around 20% of total CO_2 emissions, with passenger automobiles and light commercial vehicles accounting for 15%. Since 2015, a target of 130 g/km has been applied to the EU fleet-wide emission of new passenger cars. The emission target for new automobiles in 2021 will be 95 g/km, and car manufacturers will be fined 95V for every excess gram produced by vehicles.

The introduction of more realistic methods of type approval testing, such as the WLTP cycle combined with real-world RDE testing, requires manufacturers to develop their strategy in one of two ways: the rapid development of even more efficient internal combustion engines while reducing emissions, or the development of alternative propulsion systems. Because alternative fuels, especially bio fuels and blend fuels, are becoming more prominent due to their availability and classification as a renewable energy source, the environmental aspect of their use, i.e. their specificity in terms of influencing the amount of harmful emissions, should be considered. s. According to [11] and [2], when compared to regular diesel fuels, quality blends of available bio fuels contribute to a significant reduction in CO and PM emissions while increasing NOx emissions. Compression ignition engines that apply tire pyrolysis diesel blends doped with nano additives as fuel can attain cleaner environments and economic sustainability, [12]. Thermoelectric generation could be a method for reducing gaseous emissions such as CO, CO_2, NO, NOX, and HC in internal combustion engines and recovering some of the wasted energy through exhaust, [13]. One of the most serious difficulties with diesel engines since the implementation of the first environmental emission standards has been the emissions of nitrogen oxides and particulate matter. After two decades of rigorous diesel engine research aimed at successfully reducing consumption and hence CO_2 emissions, there has only been limited satisfaction in terms of hazardous emissions, [14], followed by numerous emission scandals, of which Dieselgate marked the turning point in the direction of the further development of environmental standards, [15,4] report that Euro 6d standards for passenger cars and light commercial vehicles take a completely different approach to measuring type approval emissions, while emission limit values have remained virtually unchanged compared to earlier Euro 6 norms (except for temporary compliance factors). Because of much higher loads during type-approval testing, this technique will propel the development of an emission control system to the forefront of engine development. The first reason is the numerous increases in hazardous emissions that should be reduced to the originally specified limitations, and the second is the wide variety of loads to which systems running in relatively limited temperature ranges must adjust.

The fundamental cause for the rapid growth in diesel engine development is the higher standards for emission gas control and the demand for lower fuel consumption. Improvements to current systems, as well as the invention and implementation of new technologies, serve as the foundation for development. Further analysis is limited to systems whose major goal is to reduce hazardous emissions, with an emphasis on particulate matter and NO_x emissions.

The most widespread solution for reducing NO_x emissions in internal combustion engines is exhaust gas recirculation (fig.1). The fundamental distinction between EGR and other methods is that EGR reduces the creation of NO_x emissions during combustion, while other methods reduce the amount of NO_x emissions that have already been formed.

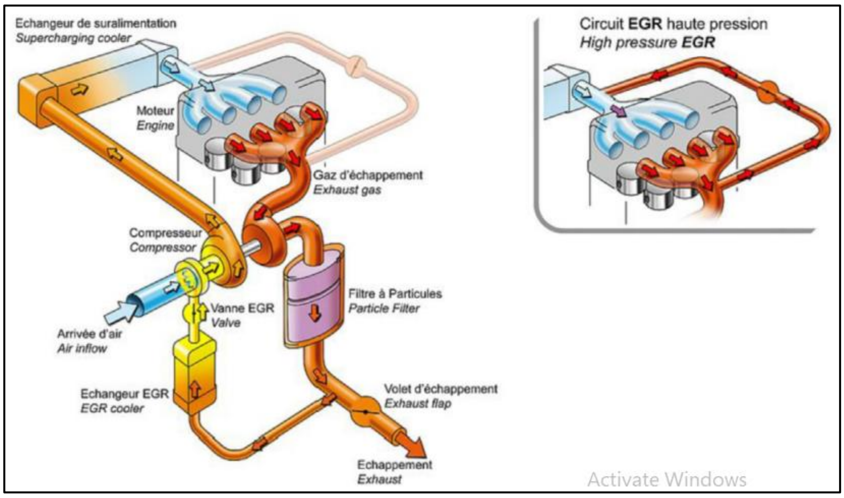


Fig.1. HP and LP EGR configuration

Nitrogen oxide emissions are currently the most serious problem with diesel engines. At room temperature, nitrogen and oxygen do not react, but at higher temperatures, they produce oxides such as NO, NO_2, N_2O, N_2O_3, and N_2O_5, which are commonly referred to as NO_x. As shown in fig.2, high combustion temperatures, oxygen excess, and their duration are solely responsible for NO_x emission generation. If the combustion process was to be observed, it is possible to notice a correlation between high efficiency combustion, which favors low consumption, CO_2 reduction, and toxic emissions such as CO, THC, and PM. The only exception is that NO_x emissions are higher. If the goal was to reduce NO_x emissions, it would be essential to lower the combustion temperatures within the cylinders, but this reduces engine performance and, as a result, increases fuel consumption.

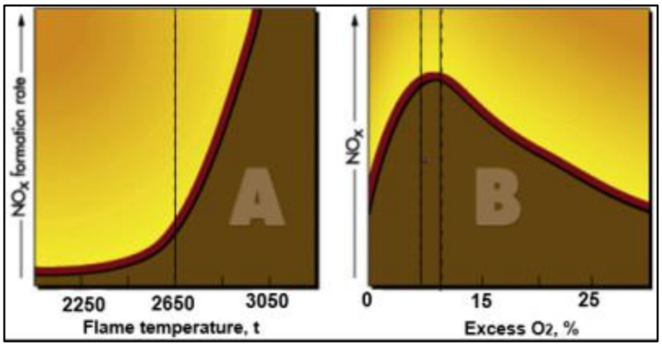


Fig. 2. Oxygen excess and combustion temperature influence on NO_x formation

Figure 3 represents the effect of air/fuel ratio on various emission forms. NO_2 and NO are the most major nitrogen oxides; approximately 90% of NO_x emissions are in the form of NO, but NO_2 has a significantly higher toxicity in terms of photochemical effects. When exposed to sunlight, it degrades into NO and extremely reactive O, which react with an oxygen O_2 molecule to form ozone O_3. In normal conditions, NO would instantly recombine into NO_2, but the presence of hydrocarbons slows the recombination, [16, 17]. Nitrogen oxides combine with moisture, ammonia, and other substances to generate a nitrogen acid vapor with fine particles. These particles easily penetrate into fragile lung tissue, resulting in a variety of lung diseases.

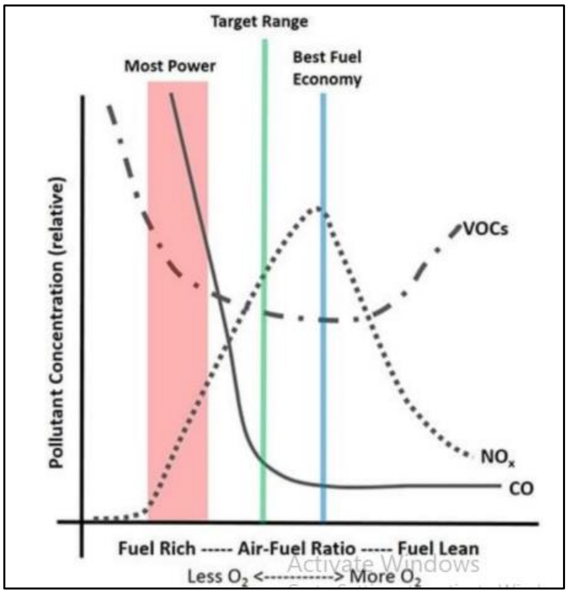


Fig. 3. Emission formation in function of fuel/air ratio

EXPERIMENTAL PART

We conduct the experiment using a diesel engine equipped with an EGR system. The heart of the experiment, the diesel engine, is instrumented with sensors to monitor critical parameters such as exhaust gas temperature, pressure, intake air temperature, engine speed, and fuel flow rate. The EGR system comprises an EGR valve, connecting pipes, and optionally, an EGR cooler. The EGR valve is electronically controlled and adjustable to regulate the EGR rate. Real-time data from the engine and EGR system are collected using a data acquisition system, which includes sensors, data loggers, and analysis software.

Our experiment commences by collecting baseline data with the diesel engine operating without EGR activation. We record emissions (NO_x, CO, CO_2, HC, and PM), engine performance (power output, fuel consumption), and exhaust gas temperatures. Then we activate the EGR system gradually, beginning with a low EGR rate and adjust the EGR valve to introduce controlled amounts of exhaust gas into the intake manifold. As a result, we conduct a series of tests with incremental increases in the EGR rate, make adjustments based on engine load, speed, and other relevant parameters and record emissions and engine performance data for each test.

The basic concept of our experiment is straightforward: we return a portion of the emission gases to the intake system, where it is combined with fresh air to reduce the amount of oxygen in the cylinder. Lower oxygen excess limits the potential of chemical interactions between oxygen and nitrogen, and thus NO_x generation, as seen in fig.2A. Recirculated gases reduce the peak combustion temperatures required to produce NO_x emissions inside the combustion chamber (fig. 2B). Lower peak combustion temperatures are caused by slowdown of combustion and a higher heat capacity in comparison to fresh air. Aside from lowering NO_x emissions, EGR technology is utilised in petrol engines to reduce losses during intake strokes and the likelihood of producing detonations during combustion strokes. With an appropriate exhaust valve phase, the EGR effect can also be accomplished internally within the combustion chamber. Standard HP (High Pressure) EGRs have been the primary technology for reducing NO_x emissions in diesel engines for a period of time.

These systems employ a portion of the exhaust gases from the exhaust manifold upstream of the turbocharger, if it exists, and route it through the EGR cooler into the intake manifold, where it is mixed with fresh air. EGR is introduced with the primary purpose of boosting the performance and efficiency of LP (Low Pressure). The LP collects EGR exhaust gases at low pressures in the exhaust system, downstream of the turbocharger and DPF filter, and drives them into the intake upstream of the compressor via a low pressure cooler. Both HP and LP EGR designs can be utilised separately or in conjunction, as shown in fig. 1. The presence of 15% exhaust gases in the cylinders reduces NO_x levels by 80%. Aside from NO_x emissions, EGR has an effect on HC, CO, and PM. Figure 4 represents the effect of the EGR rate on PM, NOx, HC, and CO. The calculations are from a Euro 2 truck engine at 10% load with fuel injection 6 before TDC (Top Dead Centre). EGR rates less than 43% have no major effect on engine performance, however EGR rates more than 37% significantly increase fuel usage.

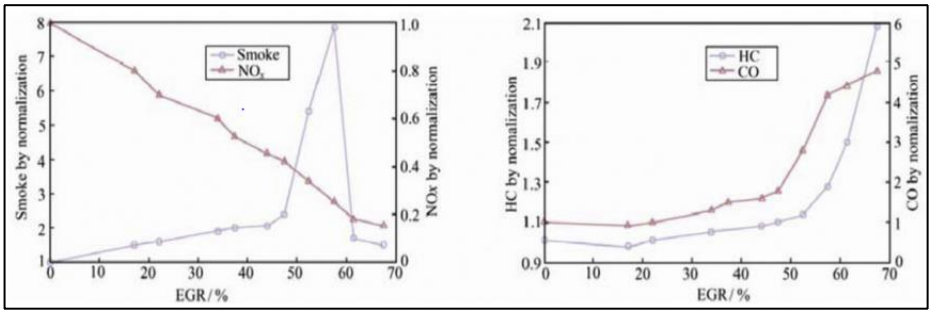


Fig.4. Effect of EGR rate on NOx, PM, HC and CO emissions

RESULTS AND DISCUSSION

The results of our experiment show that the effect of EGR on NO_x emission reductions is most pronounced at low loads, with a decrease of 85% measured in the NEDC test cycle, while at medium loads at constant speed, it decreases to 75% under normal load conditions, and with variable loads, the EGR efficiency under NO_x reduction is less than 50%. During normal driving conditions at medium loads, fuel consumption increases slightly, whereas at low loads, EGR systems reduce fuel consumption by 15%. Lowering the mean effective pressure during exhaust strokes results in lower fuel usage. We conducted a thermodynamic comparison of HP and LP EGR systems at various constant and transient loads. We also observed Brake Specific Fuel Consumption (BSFC), loses during exchange working medium and oxygen excess or air fuel ratio. As all of the observed values are dependent on the flow and pressure of gases in the intake and exhaust manifolds, which are controlled by variable geometry turbochargers, the results are shown and discussed on the compressor maps in fig.5. We see that at low engine load BMEP ¼ 2 bar, HP EGR shifts the compressor's operating point towards a lower compressor efficiency and reduced airflow (left side) with a low turbocharger speed, fig.5.

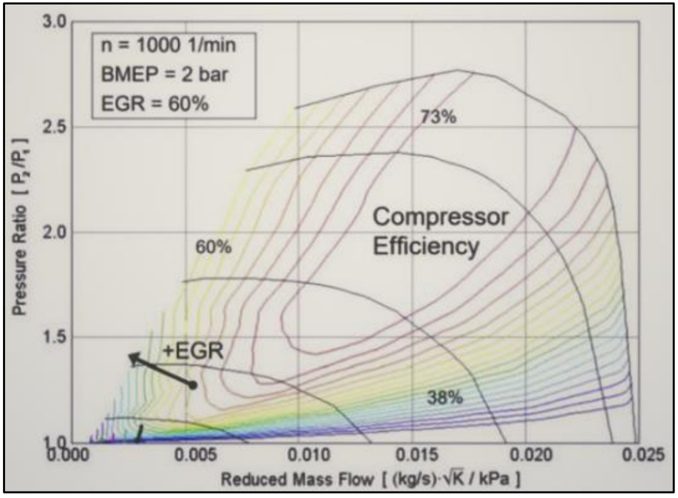


Fig. 5. HP EGR influence of compressor map

Fig.6 represents the effect of variable geometry turbocharger blade position and EGR HP/LP ratio ranging from 0 to 100% at medium engine load and medium engine speeds BMEP ¼ 12 bar n ¼ 2500 O/min with 30% EGR to the compressor behavior. With a constant amount of EGR, increasing the LP/HP EGR ratio increases the mass flow rate through the turbine and compressor, allowing the turbocharger to operate at a higher speed and efficiency. EGR cooling allows for lower compressor operating pressures with the same mass flow rate and more open turbine blades, as shown by the red arrows in fig.6.

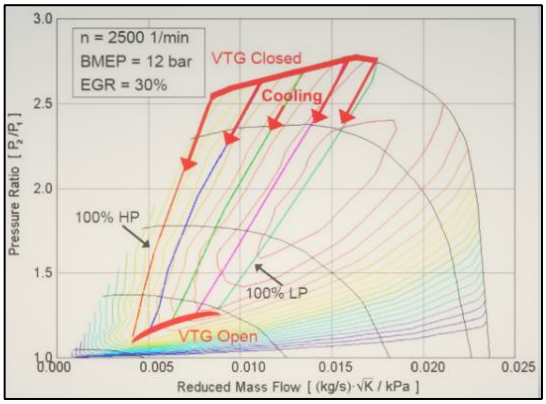


Fig.6. Influence of VGT and LP/HP ratio to compressor map

[18] conducted an experimental study on high-speed diesel engines at constant partial load and measured specific fuel consumption, NOx emissions and combustion characteristics in relation to LP/HP EGR. As shown in fig.7, the increase in relation to LP/HP has a positive impact on fuel consumption and NOx emissions [19] describes the behavior of HP/LP EGR in transient loads. Figure 8 represents the engine's response time with transient loads, ranging from a low load of 2 bar to a medium load of 9 bar BMEP. It can be seen that the amount of EGR at LP has no effect on engine response time; LP EGR provides better results for euro 4 and higher requirements.

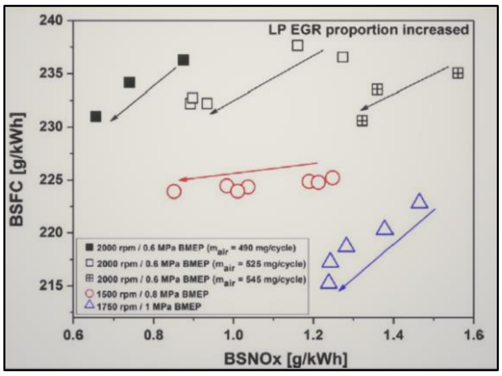


Fig. 7. BSFC and NOx emission in function of LP EGR

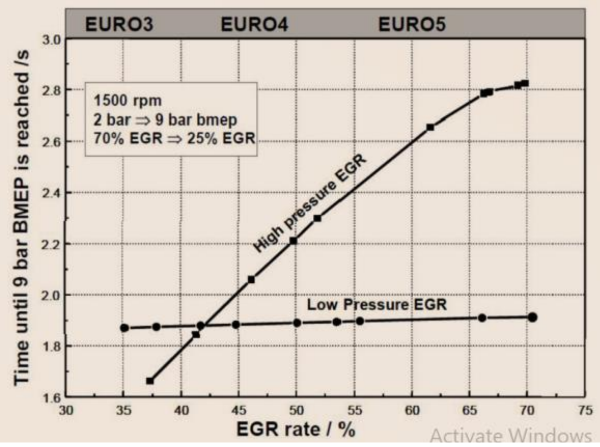


Fig. 8. Engine response at different Euro norms for HP and LP EGR

So far the dominant NOx emission reduction technique for passenger and light commercial automobiles, a high-pressure HP-EGR exhaust recirculation could only satisfy Euro 6b under laboratory test conditions according to the outdated NEDC type-approval cycle. With the advent of Euro 6d, which incorporates a new WLTP homologation cycle with real-world RDE testing, HP EGR is no longer sufficient but will be applied in the future in combination with other systems, particularly LP-EGR. When compared to other methods, LP-EGR develops promising results and is appropriate for use in smaller vehicles due to its cheaper cost and reduced space usage.

CONCLUSION

In conclusion, the concept of Exhaust Gas Recirculation (EGR) is a fundamental and effective strategy for reducing nitrogen oxide (NO_x) emissions in internal combustion engines, particularly in diesel engines. The primary principle behind EGR is to reintroduce a portion of exhaust gases into the intake system, where they combine with fresh air to lower the oxygen concentration in the combustion chamber. This reduction in oxygen limits the potential for chemical reactions between oxygen and nitrogen, thereby decreasing NO_x formation.

EGR technology plays a critical role not only in reducing NO_x emissions but also in improving the performance and efficiency of engines. It accomplishes this by lowering peak combustion temperatures, which, in turn, decreases the likelihood of detonations during combustion strokes. EGR is especially important in the context of diesel engines, where NO_x emissions are a significant concern.

High-Pressure (HP) EGR and Low-Pressure (LP) EGR systems are the primary technologies used in diesel engines. HP EGR collects exhaust gases from the exhaust manifold, routing them through an EGR cooler into the intake manifold for mixing with fresh air. LP EGR, on the other hand, collects exhaust gases downstream of the turbocharger and drives them into the intake system upstream of the compressor via a low-pressure cooler. These two EGR designs can be used separately or in combination to achieve the desired reduction in NO_x emissions.

EGR, while effective at lowering NO_x levels, also has effects on other emissions, including hydrocarbons (HC), carbon monoxide (CO), and particulate matter (PM). The specific impact of EGR on these emissions depends on the EGR rate, with higher EGR rates significantly affecting fuel usage.

In summary, EGR is a valuable technology in the effort to reduce harmful emissions from internal combustion engines, with a primary focus on mitigating NO_x. While it has proven effective in achieving this goal, it also has implications for engine performance and other emissions, requiring careful calibration and management to strike a balance between emissions reduction and engine efficiency.

REFERENCES

1. Brand, C. Beyond ‘Dieselgate’: implications of unaccounted and future air pollutant emissions and energy use for cars in the United Kingdom. PlumX Metrics. 2016,Vol.97, pp 1-12
2. Chen, Y., Borken-Kleefeld, J. Real-driving emissions from cars and light commercial vehicles e Results from 13 years remote sensing at Zurich. Atmospheric Environment. 2014, Vol.88, pp 157-164

3. Hooftman N., A review of the European passenger car regulations – real driving emissions vs local air quality. Renew. Sustain. Energy Rev. 2018, Vol.86, pp 1-21
4. Nižetić S., Smart technologies for promotion of energy efficiency, utilization of sustainable resources and waste management.Journal of Cleaner Production. 2019, September 10,Vol.231, pp 565-591
5. Ghotke P.R., Review of advanced EGR and breathing systems for high performance and low emission HSDI diesel engine.International Journal of Modern Engineering Research (IJMER). 2012,Vol.2, pp 3138-3142
6. Cheng, S., Zhang, Z., Peng, P., Yang, Z., Lu, F. Spatiotemporal evolution pattern detection for heavy-duty diesel truck emissions using trajectory mining: a case study of Tianjin, China. Journal of Cleaner Production. 2019, October 4, Vol.244, pp 1-11
7. O'Driscol, R., Stettler, M., Molden, N., Oxley, T., Apsimon, H.M. Real world CO2 and NOx emissions from 149 Euro 5 and 6 diesel, gasoline and hybrid passenger cars.Science of The Total Environment. 2018, April 15, Vol. 621, pp 282-290
8. Pouresmaeili, M.A., Aghayan, I., Taghizadeh, S.A. Development of Mashhad driving cycle for passenger car to model vehicle exhaust emissions calibrated using on-board measurements.Sustainable Cities and Society. 2018, Vol.36, pp 12-20
9. Kerbachi, R., Chikhi, S., Boughedaoui, M. Development of real exhaust emission from passenger cars in Algeria by using on-board measurement.Energy Procedia. 2017,Vol.136, pp 388-393
10. Nesbit, M., Fergusson, M., Colsa, A., Ohlendorf, J., Hayes, C., Paquel, K., Schweitzer, J-p. Comparative study on the differences between the Eu and Us legislation on emissions in the automotive sector.Policy Department A: Economic and Scientific Policy. 2016,Vol.3, pp 12-68
11. Díaz, S., Miller, J., Mock, P., Minjares, R., Anenberg, S., Meszler, D. Shifting gears: The effects of a future decline in diesel market share on tailpipe CO_2 and NOx emissions in Europe. The International Council on Clean Transportation. 2017, June 28,Vol.10, pp 1-40
12. Resitoglu, I.A., Altinisik, K., Keskin, A. The pollutant emissions from diesel-engine vehicles and exhaust aftertreatment systems. Springer,Clean Technologies and Environmental Policy. 2015,Vol.17, pp 15-27
13. Santos, G. Road transport and CO_2 emissions. Transport Policy. 2017,Vol.59, pp 71-74
14. Pardiwala, J.M., Patel, F., Patel, S. Review paper on catalytic converter for automotive exhaust emission.Institute of technology, Nirma university. 2011.Vol.3, pp 382-481
15. Nabi, M.N., Rahman, S.M.A., Bodisco, T.A., Rasul, M.G., Ritovski, Z.D., Brown, R.J. Assessment of the use of a novel series of oxygenated fuels for a turbocharged diesel engine. Journal of Cleaner Production. 2019, Vol.217, pp 549-558
16. Kumaravel, S.T., Murugesan, A., Vijayakumar, C., Thenmozhi, M. Enhancing the fuel properties of tyre oil diesel blends by doping nano additives for green environments. Journal of Cleaner Production. 2019,Vol.240, pp 118-128
17. Ramírez, R., Gutierrez, A.S., Eras, J.J.C., Valencia, K., Forero, J.D. Evaluation of the energy recovery potential of thermoelectric generators in diesel engines.

Journal of Cleaner Production. 2019,Vol.24, pp 118-412

18. Park, Y., Bae, C. Experimental study on the effects of high/low pressure EGR proportion in a passenger car diesel engine. Applied Energy. 2014,Vol.133, pp 308-316
19. Sillman, S. The relation between ozone, NOx and hydrocarbons in urban and polluted rural environments, Pergamon. Atmospheric Environment. 1999, Vol.33, pp 1821-1845

ЭКОЛОГИЧЕСКИЕ ПРОБЛЕМЫ, ВЫЗВАННЫЕ ОБРАЗОВАНИЕМ ТОКСИЧНЫХ СОЕДИНЕНИЙ ПРИ ЭКСПЛУАТАЦИИ МОТОРНЫХ ТОПЛИВ И МЕТОДЫ ИХ РЕШЕНИЯ

Н.Н. Джавададзе, Э.Т.Зейналов[0000-0002-5372-754]
Азербайджанский Государственный Университет Нефти и Промышленности
njavadzada@mail.ru

Двигатели внутреннего сгорания и в будущем останутся основным источником энергии для кораблей, тяжелых транспортных средств и термоэлектрических установок, как и сегодня. Основная цель поставщиков двигателей — найти способы уменьшить их негативное воздействие на окружающую среду и обеспечить более чистую энергию. Важнейшей частью автомобильной техники и экологии является изучение методов снижения токсичных выбросов дизельных двигателей. Хотя дизельные двигатели эффективны, они выделяют загрязняющие вещества, которые могут нанести вред качеству воздуха и здоровью человека. В данной статье рассматривается метод рециркуляции выхлопных газов (EGR), регулирующий выбросы при их образовании. Тщательно исследован механизм образования выхлопных газов и его связь с параметрами двигателя. Обсуждены проблемы, возникающие при применении индивидуального метода снижения выбросов в конкретных условиях работы двигателя. Было исследовано влияние систем контроля выбросов на рабочие характеристики двигателя, такие как расход топлива, выбросы NO_x, *реакция на нагрузку и долговечность. Было продемонстрировано, что только систематическая стратегия снижения выбросов дизельных выхлопных газов с использованием новых технологий сохранит их важность и позволит обеспечить действительно более чистые двигатели, которые не только будут соответствовать законодательным требованиям по выбросам, но и значительно ниже их.*

Ключевые слова: *рециркуляция выхлопных газов, регулирование выбросов, образование выбросов, выбросы* NO_x, *снижение токсичных выбросов*

MOTOR YANACAQLARININ İSTİSMARI ZAMANI ALINAN TOKSİKİ BİRLƏŞMƏLƏRİN YARATDIĞI EKOLOJİ PROBLEMLƏR VƏ ONLARIN HƏLLİ ÜSULLARI

N.N.Cavadzadə, E.T.Zeynalov[0000-0002-5372-754]
Azərbaycan Dövlət Neft və Sənaye Universiteti
njavadzada@mail.ru

Daxili yanma mühərrikləri bu gün olduğu kimi gələcəkdə də gəmilər, ağır nəqliyyat vasitələri və termoelektrik stansiyalar üçün əsas enerji mənbəyi olmağa davam edəcək. Mühərrik təchizatçılarının əsas məqsədi onların ətraf mühitə olan mənfi təsirlərini azaltmağın və daha *təmiz enerji təmin etməyin yollarını tapmaqdır. Avtomobil mühəndisliyi və ekologiyasının mühüm hissəsi dizel mühərriklərindən zəhərli emissiyaların azaldılması üsullarının öyrənilməsidir. Dizel mühərrikləri səmərəli olsa da, havanın keyfiyyətinə və insan sağlamlığına zərər verə biləcək çirkləndiricilər buraxırlar. Bu məqalə emissiyaların əmələ gəlməsini tənzimləyən üsul olan işlənmiş qazın təkrar dövriyyəsini (İQTD) araşdırır. İşlənmiş qazın əmələ gəlməsi mexanizmi və onun mühərrik parametrləri ilə əlaqəsi hərtərəfli öyrənilmişdir. Mühərrikin xüsusi iş rejimində individual emissiyaların azaldılması metodunun tətbiqi zamanı yaranan problemlər müzakirə olunur. Emissiyaya nəzarət sistemlərinin mühərrikin yanacaq sərfiyyatı, NO_x emissiyaları, yük reaksiyası və dayanıqlıq kimi performans xüsusiyyətlərinə təsiri araşdırılmışdır. Göstərilmişdir ki, yalnız yeni texnologiyalardan istifadə etməklə dizel qazı emissiyalarını azaltmaq üçün sistematik strategiya onların əhəmiyyətini saxlayacaq və nəinki qanuni emissiya tələblərinə cavab verən, həm də onlardan əhəmiyyətli dərəcədə aşağı olan həqiqətən daha təmiz mühərriklər təqdim edəcəkdir.*

***Açar sözlər:** işlənmiş qazın təkrar dövriyyəsi, emissiyaların tənzimlənməsi, emissiyaların əmələ gəlməsi, NO_x emissiyası, zəhərli emissiyaların azaldılması.*

ATTENTION FOR AUTHORS!

“Azerbaijan Journal of Chemical News” approved by the Higher Attestation Commission under the President of Azerbaijan Republic and it is included to the list of journals and periodicals that should be published by major scientific results of dissertations in Azerbaijan Republic.