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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

OBTAINING AND STUDY OF NITROGENOUS AND PHOSPHORUS DERIVATIVES OF METHYLCYCLOPENTYLPHENOLS

Speciality: 3321.01 – Oil-gas-coal processing and technology

Field of science: Technical sciences

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The work was performed at the "Chemistry and Technology of Cycloalkylphenols" laboratory of the Institute of Petrochemical Processes named after Academician Y.H.Mammadaliyev of the Ministry of Science and Education of the Republic of Azerbaijan.

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GENERAL DESCRIPTION OF WORK

The relevance of the topic and the degree of development. Despite the fact that more than 130 years have passed since the first research studies on phenol alkylation reactions began (the alkylation reaction of phenol was first conducted in 1890 by the German scientist Königs with isoamylene in the presence of sulfuric acid), the production of alkylphenols and their derivatives of various compositions is still one of the urgent and important problems of the chemical industry. It is no coincidence that 70-75% of antioxidants, additives, thermo- and photostabilizers, oxygenates, antiozonants, etc. added to polymeric materials, rubbers, oils, and fuels used today are obtained on the basis of alkylphenols. It is known from literature sources that as the alkyl group in alkylphenols increases from methyl to octyl, their antioxidant properties improve[1]. The problem here is that large alkyl groups (C_8-C_{12}) are not resistant to high temperatures, breaking down and acting as oxidants themselves. In this regard, cycloalkylphenols obtained on the bases of cyclic hydrocarbons are resistant to high temperatures, dissolve well in the objects in which they are used, and therefore are evenly distributed within them. This leads to an improvement in other quality indicators of the target products.

Alkylphenols are mainly obtained from alkylation reactions of phenol with various alkylating agents. Various homogeneous and heterogeneous catalysts are used in the alkylation process. [2] Although the process proceeds under mild conditions and the yield of the target product is high when using homogeneous catalysts, the process is intermittent, multi-stage, and equipment corrosion problems arise; this also creates economic and technological problems. In this regard, zeolite-containing catalysts allow the process to be carried out

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[1] Расулов Ч.К., Агамалиев З.З., Гасанова Г.Д., Нагиева М.В. Синтез алкилфенолов и применение их в реакциях аминометилирования, Баку: Муаллим, 2021, 197 с.

[2] Jin H., Ansari M.B., Park S.E. Chemoselective O- versus C-alkylation of substituted phenols with cyclohexene over mesoporous ZSM-5 // Applied Catalysis A: General, -2014, vol.472, p.184-190.

continuously. The main advantage of zeolite-containing catalysts is their mechanical strength and ability to be regenerated after a certain period of operation.

In this regard, the presented dissertation work is dedicated to a urgent issue – the study of cycloalkylation reactions of phenol with 1-methylcyclopentene, 1-methylcyclopentadiene, cyclopentadiene in the presence of various zeolite-containing catalysts, the determination of the areas of application of phosphorus- and nitrogen-containing derivatives obtained from the phosphination reactions of the obtained para-cycloalkylphenols with phosphorus trichloride and aminomethylation with aminoethylnonylimidazoline.

The object and subject of the research. The objects of the conducted scientific research are phenol, 1-methylcyclopentene, 1-methylcyclopentadiene, cyclopentadiene, their cycloalkylation reactions, selection of efficient zeolite-containing catalysts; the subject is to sythesize and to determine the efficient areas of use of phosphorus and nitrogen derivatives of *para*-cycloalkylphenols.

The aim and objectives of the research. The aim of the **research** is to examine the tri(*para*-cyclopentylphenyl)phosphites of para-methylcyclopentylphenols obtained from cycloalkylation reactions of phenol with methylcyclopentene in the presence of zeolite-containing catalysts, Mannix bases, and their compositions with alkylimidazolines as antioxidants in oils, surfactants, and bactericides and disinfectants against intestinal cocci in large and small horned animals.

The following research studies were carried out to achieve the goal:

-cycloalkylation reactions of phenol with methylcyclopentene in the presence of zeolite-containing catalysts Seokar-2, Seokar-2M, KH-30, KH-30M in intermittent and continuous devices were investigated, and the effect of kinetic factors (temperature, time, molar ratios of initial raw materials, amount of catalyst, volume velocity) on the yield of target substances and the selectivity of the process was studied;

-the reactions of phosphitization with phosphorus trichloride and aminomethylation with aminoethylnonylimidazoline of the obtained *para*-(cyclopentyl)phenols were conducted, and compositions with

alkylimidazoline and oxyethylated nonylphenol were obtained;
-the chemical structures, physicochemical properties and elemental compositions of the obtained products were determined;
-tri(*para*-methylcyclopentylphenyl)phosphites were tested in turbine oil T-46, compositions of *para*-(methylcyclopentyl)phenols modified with alkylimidazolines as high-temperature resistant antioxidants in M-8 engine oil, products obtained from the interaction of *para*-(1-methylcyclopentyl)phenols with formalin and aminoethylnonylimidazoline as bactericides and disinfectants against intestinal cocci in large and small horned animals, and compositions of *para*-(methylcyclopentyl)phenols with oxyethylated *p*-nonylphenol and alkylimidazolines as surfactants.

Research methods. Cycloalkylation reactions of phenol with methylcyclopentene were carried out in intermittent and continuous laboratory devices, phosphitization of the obtained *para*-(methylcyclopentyl)phenols with phosphorus trichloride, aminomethylation reactions with aminoethylnonylimidazoline, and preparation of the compositions were carried out in a three-necked flask under laboratory conditions.

Integrity **of the results.** The chemical structures and properties of the initial components, the obtained *para*-(methylcyclopentyl)-phenols, methylcyclopentylphenylphosphites, Mannix bases, and compositions were studied by modern methods – IR, ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, X-ray phase and chromatographic analyses.

The main provisions put forward for defense. Cycloalkylation reactions of phenol with methylcyclopentene in the presence of zeolite-containing catalysts Seokar-2, Seokar-2M, KH-30, KH-30M were studied in intermittent and continuous units; phosphitization reactions of the obtained *para*-(methylcyclopentyl)phenols with phosphorus trichloride, aminomethylation reactions with aminoethylnonylimidazoline were studied; compositions of *para*-(methylcyclopentyl)phenols with alkylimidazolines were obtained; tri-(methylcyclopentylphenyl)phosphites were tested in turbine oil T-46, compositions of *para*-cycloalkylphenols with alkylimidazolines as antioxidants in M-8 engine oil, 2-hydroxy-5(methylcyclopentyl)-

benzylaminoethylnonylimidazolines as bactericides and disinfectants against intestinal cocci in large and small horned animals, and compositions of para-(methylcyclopentyl)phenols with oxyethylated nonylphenol and alkylimidazolines as surfactants.

Scientific novelty of the research. For the first time, the cycloalkylation reactions of phenol with 1-methylcyclopentene, 1-methylcyclopentadiene and cyclopentadiene were studied by using zeolite-containing catalysts Seokar-2, Seokar-2M, KH-30, KH-30M, and the effect of kinetic factors on the yield of target products and the selectivity of the process were studied and material balances were compiled for each of the processes.

For the first time, the aminomethylation reactions of *para*-(methylcyclopentyl)phenols with formaldehyde and aminoethylnonylimidazoline, and phosphitization reactions with phosphorus trichloride were studied; compositions of *para*-(methylcyclopentyl)phenols modified with alkylimidazoline were obtained. 2 Azerbaijani patents were obtained for the results of research.

Theoretical and practical significance of the research: Compositions of *para*-(methylcyclopentyl)phenols modified with alkylimidazolines have been tested as high-temperature antioxidant in M-8 engine oil, tri-[*para*-(methylcyclopentyl)phenyl]phosphites obtained from the phosphitization reaction with phosphorus trichloride have been tested as antioxidant in turbine oil T-46, compositions obtained from the modification with oxyethylated para-nonylphenol and alkylimidazolines have been tested as surfactants, and Mannix bases obtained from the aminomethylation reactions with aminoethylnonylimidazolines have been tested as bactericides and disinfectants against intestinal cocci in large and small horned animals.

The technical and economic indicators of the process for obtaining a composition of alkylimidazoline and *para*-(1-methylcyclopentyl)phenol (in a ratio of 9:1) have been calculated. According to preliminary calculations, the cost of 1 ton of the composition is formed at 2878.52 AZN. As a result, the application of the proposed technology creates the basis for reducing the cost of 1 ton of commercial product by 134 manats compared to alkylimidazoline.

Approbation and its application. 26 scientific works on the dissertation work, including 2 Azerbaijani patents, 6 articles (4 of them in abroad), and 18 abstracts of international and republican level reports have been published.

The results obtained in the dissertation work were reported and discussed in the following conferences:

Republican scientific conference on "Modern problems of chemistry" (Sumgayit, 2021), International scientific conference on "Current problems of modern natural and economic sciences" (Ganja, 2021), XIV International scientific conference on "Current problems of chemistry" dedicated to the 98th anniversary of the national leader Heydar Aliyev (Baku, 2021), V All-Russian scientific conference "Actual problems of theory and practice of heterogeneous catalysts and adsorbents" (Ivanovo, 2021), XVII International scientific-practical conference "New polymer composite materials Mikitaevsky readings" (Nalchik, 2021), VIII International scientific-technical conference "Alternative sources of raw materials and fuel "AIST-2021"" (Minsk, 2021), the International Scientific and Methodological Conference "Integration of Science and Education in the Nodes of the Oil and Gas Profile-2022. Advanced Technologies and Modern Trends" (Salavat, 2022), the republican scientific conference on "Catalysts, olefin-based oils" dedicated to the 90th anniversary of Academician Nadir Mir-Ibrahim oglu Seyidov (Baku, 2022), Academician The republican scientific conference dedicated to the 110th anniversary of Ali Guliyev on "Multipurpose organic substances and composite materials" (Baku, 2022), the international scientific conference on "Current problems of modern natural and economic sciences" (Ganja, 2022), the 18th International scientific-practical conference "New polymer composite materials Mikitaevsky readings" (Nalchik, 2022), "Heteroatom Republican scientific conference on "Actual problems of chemistry of compounds" (Baku, 2022), II Republican scientific conference on "Chemistry and chemical technology" dedicated to the 100th anniversary of the birth of the national leader Heydar Aliyev (Baku, 2023), International scientific conference on "Actual problems of modern natural and economic sciences" dedicated to the 100th anniversary of the birth of the national leader Heydar Aliyev (Ganja, 2023), Scientific conference on "Petroleum chemistry, synthesis of polyfunctional monomers, oligomers and polymers" dedicated to the 90th anniversary of Academician Sahib Aliyev (Baku, 2023), Scientific conference on "Metal complex and metal-organic catalysis, synthesis and study of (co)oligomers, (co)polymers" dedicated to the 80th anniversary of Academician Akif Azizov (Baku, 2023).

The obtained main results were published in the following journals: News of higher educational institutions, Chemistry and chemical technology, Processes of Petrochemistry and Oil Refining, World of Oil Products, Oil Refining and Petrochemicals, Azerbaijan oil industry.

The name of the organization where the dissertation work performed: Institute of Petrochemical Processes named after Academician Y.H. Mammadaliyev of the Ministry of Science and Education of the Republic of Azerbaijan, “Chemistry and Technology of Cycloalkylphenols” laboratory (State registration No. 0114Az2005. In 2022-2024).

Personal participation of the author. The results in the dissertation were obtained by the author. The formulation of the problems, the implementation of experiments and testing of the obtained products, the systematization, generalization and analysis of the obtained results were carried out with the participation of the author.

Total volume of the dissertation with a mark, indicating the volume of the structural sections of the dissertation separately. The dissertation is 188 pages and consists of an introduction, 5 chapters, a conclusion, a list of 160 references, and appendices. The dissertation includes 37 tables, 14 graphs, 34 figures, 6 diagrams. The total volume of the dissertation work consists of 199907 characters (excluding tables, figures, appendices and references). Introduction 12790, chapter I 45440, chapter II 21805, chapter III 50930, chapter IV 29150, chapter V 35920, conclusions 3872 characters.

The **introduction** provides brief information about the relevance of the topic, the object and subject of the research, the aim and objectives, methods, the main provisions put forward for defense, the scientific novelty of the research, its theoretical and practical significance, the author's personal participation, approbation and application, the organization in which the dissertation was carried out, the scope of the work, and the chapters.

The I chapter examines the known literature sources relevant to the topic of the dissertation, provides an extensive analysis of the literature sources on the methods of obtaining cycloalkylphenols obtained from the alkylation process of phenol with aliphatic and cyclic hydrocarbons, their nitrogen and phosphorus derivatives obtained based on Mannix bases and phosphite reactions. At the end, a critical analysis of the literature review and justification of the direction of the conducted research work are reflected.

The II chapter presents the experimental part, the physicochemical properties of the initial raw materials, a description of the equipment used for the experiments, the raw materials used for the processes, the modified catalyst, and the analysis methods of the target products obtained after the reaction.

The III chapter discusses the study of cycloalkylation reactions of phenol with 1-methylcyclopentene, 1-methylcyclopentadiene and cyclopentadiene in intermittent and continuous units in the presence of zeolite-containing KH-30 and modified KH-30M catalysts.

In the IV chapter, the interaction reactions of phenol with 1-methylcyclopentene, 1-methylcyclopentadiene and cyclopentadiene in the presence of zeolite-containing Seokar-2 and modified Seokar-2M catalysts were studied in intermittent and continuous devices.

The V chapter discusses the preparation of synthesized cycloalkylphenols containing nitrogen and phosphorus and their application areas. This chapter presents the results of tests of nitrogenous compounds obtained as bactericides and disinfectants against intestinal cocci microbes in animals, compositions as antioxidants and surfactants for M-8 oil, and phosphorus derivatives as antioxidants for turbine oil T-46.

The completed dissertation work concludes with results, a list of references, appendices, and a list of abbreviations.

MAIN CONTENT OF THE WORK

Raw materials, reagents and devices used in the work

The raw materials used for scientific research were phenol, 1-methylcyclopentene, 1-methylcyclopentadiene, cyclopentadiene, formalin, aminoethylnonylimidazoline, polyethylpolyamine (PEPA), natural petroleum acid (NPA), alkylimidazolines, oxyethylated *para*-nonylphenol, and among phosphorus trichloride solvents such as toluene, heptane, and benzene.

The phenol was re-extracted and purified before the cycloalkylation process. After purification, phenol had the following physicochemical properties: boiling point –182ºC; melting point – 41ºC; n_D^{20}– 1.5403; ρ_4^{20} –1.0710 g/cm^3; molecular mass – 94.

Cyclopentadiene is obtained from the pyrolysis of the low-boiling fraction of petroleum and the coking of coal. Cyclopentadiene dimerizes at room temperature within a few hours. Dicyclopentadiene is monomerized by rectification at 150ºC and added to the cycloalkylation process. After rectification, cyclopentadiene has the following physicochemical properties: boiling point – 41ºC; melting point – -90ºC; n_D^{20}– 1.4430; ρ_4^{20} – 0.802 g/cm^3; molecular mass – 66.

1-Methylcyclopentene is obtained from the dehydration of cyclohexanol: molar mass 82, ρ_4^{20} –0.7782 g/cm^3, boiling point 75°C.

1-Methylcyclopentadiene is obtained from the dehydrogenation of methylcyclopentene: molar mass 80, ρ_4^{20} –0.9527 g/cm^3, boiling point 86 °C.

PCl_3 – molar mass 137, ρ_4^{20} –1.574 g/cm^3, boiling point 76°C.

Formalin is a solution (30%) of formaldehyde (formaldehyde) in water.

Aminoethylnonylimidazoline: empirical formula – $C_{14}H_{30}N_3$; average molecular weight – 240; n_D^{20} – 0.9860; ρ_4^{20}– 0.1098.

PEPA: average molecular weight – 230, ρ_4^{20}– 0.1009, boiling point – 206-288ºC, n_D^{20} – 1.5110.

NPA: average molecular weight – 220, ρ_4^{20}– 0.8840 g/cm^3, boiling point– 110-220ºC, n_D^{20} – 1.4772.

Alkylimidazoline (by taking NPA:PEPA in a 2:1 molar ratio): density at 20°C, ρ_4^{20} –1.001 g/cm^3; n_D^{20} – 1.5110, kinetic viscosity at

100°C – 243.31 mm^2/s; ash content – 0.02%; freezing temperature – minus 20 °C.

Oxyethylated nonylphenol (ONP) (Russian Federation, Republic of Tatarstan, Nizhnekamsk city, ATSC "Nijnekamskneftekhim" (TU 2483-077-05766801-98))– ρ_4^{20} – 1.0630 g/cm^3; kinetic viscosity, mm^2/s, at 100°C – 363.81; n_D^{20} – 1.4903.

In order to conduct the alkylation process, a KU-23 (GOST 20298-74) with a high average effective pore radius (250-600Å) and a zeolit-Y catalyst impregnated with orthophosphoric acid were used as a catalyst. Orthophosphoric acid impregnated zeolite-Y catalyst is prepared by thoroughly mixing aluminogel and cracking catalyst (Grace Davison) (Zeolite-Y, $SiO_2 : Al_2O_3$ = 4.8, ion exchange degree 97%).

Also, KH-30, Seokar-2 and their 10% HCl modified KH-30M, Seokar-2M zeolite-based catalysts were studied as heterogeneous catalysts. KH-30 catalyst is manufactured according to TU 2177-011-07622236-2008, and Seokar-2 is manufactured according to TU-38-101483-77 based on an environmentally friendly high-silica zeolite system, does not contain heavy metals. Seokar-2M and KH-30M were prepared by modifying Seokar-2 and KH-30 catalysts with 10% HCl solution.

DLS spectra of catalyst samples were recorded at room temperature (24°C); the average particle size measurement in modified Seokar-2M, KH-30M catalyst samples differs from Seokar-2, KH-30 catalyst samples (Table 1).

It can be seen from Table 1 that the average particle size is inversely proportional to the diffusion coefficient and amplitude. It is observed that as the average particle size decreases, the values of other parameters increase.

The elemental composition and distribution of elements in layers near the surface of each of the four catalyst samples were determined by scanning electron microscopy (SEM) and X-ray fluorescence (XRF) microscopy.

The Seokar-2 and KH-30 samples were dried in a drying oven at 110°C for 2 hours, and thermal and X-ray phase analyses were carried out.

Table 1

Results of DLS analysis of Seokar-2, KH-30 and their modified catalyst samples

Catalysts	Average particle size (median), nm	The mean value of the distribution, nm	Maximum of the particle size (mode), nm	Diffusion coefficient, m^2/s	Amplitude
Seokar-2	1049.0	1032.9	1075.6	2.4719 E-13	0.68
KH-30	798.8	817.7	813.6	3.2425 E-13	0.60
After modification with 10% HCl					
Seokar-2M	501.2	501	482.6	5.1753 E-13	0.70
KH-30M	440.2	462.7	475.6	5.8862 E-13	1.09

The structure of the catalyst samples was studied by X-ray phase analysis (Figures 1, 2).

In Figure 1, it is observed that the sample is amorphous from the curves of Seokar-2 drawn in the 2θ(theta-theta) angle range from 5 to 85° at room temperature.

It should be noted that initial information about the condition of the catalyst can also be obtained from the appearance of the X-ray curves. As can be seen from the X-ray diffraction pattern of KH-30 (Figure 2), narrow and highly diffraction peaks characteristic of silicate E (SiO_2) with mainly well-crystallized, intense maxima 00-047-0715 are observed.

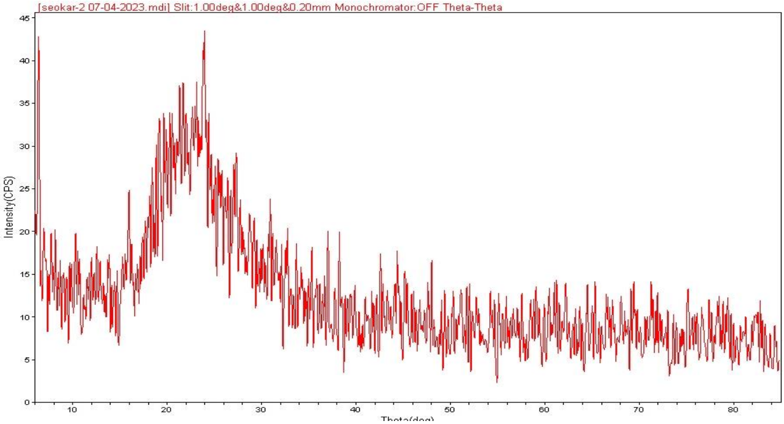


Figure 1. Radiogram (X-ray pattern) of Seokar-2 sample

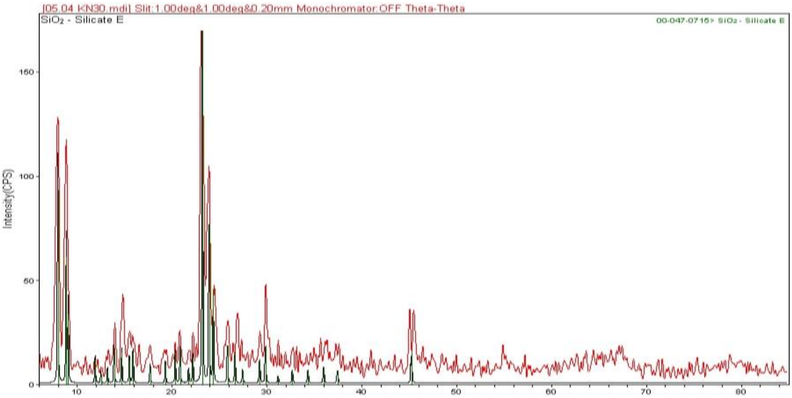


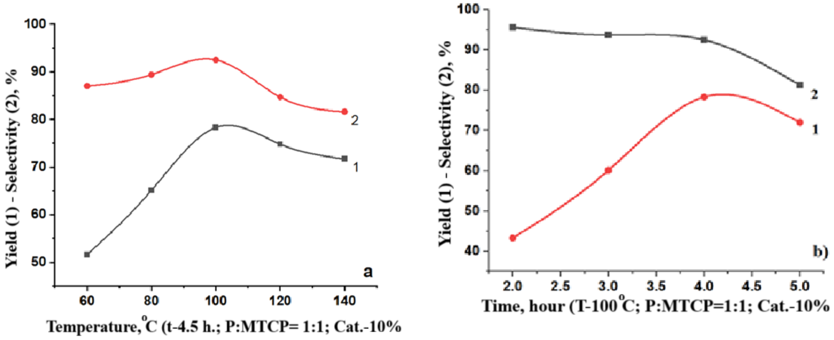
Figure 2. Radiogram (X-ray pattern) of KH-30 sample

The cycloalkylation reactions of phenol with cyclopentadiene, 1-methylcyclopentadiene and 1-methylcyclopentene in the presence of zeolite-containing KH-30 and modified KH-30M catalysts

Catalytic cycloalkylation reactions of phenol with cyclopentadiene, 1-methylcyclopentadiene, and 1-methylcyclopentene in the presence of KH-30 catalyst were studied in intermittent and continuous pilot plants.

Alkylation reactions were studied in a intermittent device at temperatures of 60-140°C, experimental times of 2-6 h, molar ratios of phenol to cyclopentenes ranging from 2:1 to 1:2, and catalyst consumption ranging from 5-15%.

For example, the results of the cycloalkylation reactions of phenol with MTCP in a batch plant are given in Figure 3.



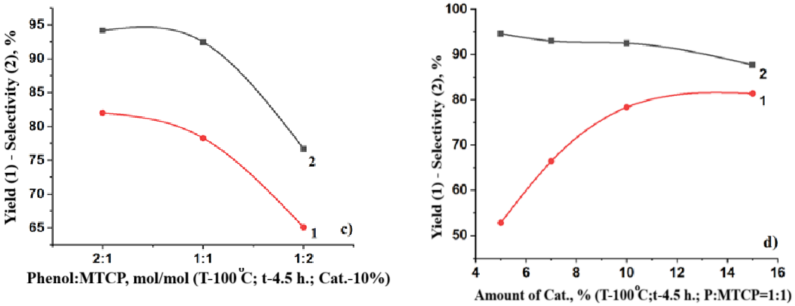


Figure 3. Dependence curves of the yield (1) and selectivity (2) of *para* – (1-Methylcyclopentyl) phenol on temperature (a), time (b), molar ratio of initial components (v) and amount of catalyst (c)

It can be seen from the figure that it is possible to achieve efficient yield and selectivity of the target product at a reaction temperature of 100°C and a reaction time of 4.5 h.

According to the indicators in Figure 3, it can be concluded that high yield (82.0%) and selectivity (94.2%) of the target product can be achieved at a 2:1 mol/mol ratio of phenol to 1-methylcyclopentene. Achieving a 3-4% increase in the yield and selectivity of the target product by doubling the concentration of phenol in the initial raw material mixture is not economically and technologically efficient. The figure shows that at a 1:1 molar ratio of phenol to MTCP, the yield of the target product relative to the phenol taken is 78.3%, and the selectivity is 92.5% relative to the target product. The yield and selectivity decrease sharply, when the concentration of MTCP in the initial component mixture is doubled. This is explained by the formation of 2-mono-, 2,4-, 2,6-di- and 2,4,6-trimethylcyclopentylphenols in the final product.

As a result of the conducted research, effective conditions were found for the cycloalkylation reaction of phenol with 1-methylcyclopentene in a intermittent device in the presence of a zeolite-containing KH-30 catalyst: temperature - 100°C, reaction time - 4.5 h, molar ratio of phenol to MTCP 1:1 mol/mol, catalyst amount 10% based on the taken phenol. Under these conditions, the yield of the target product - *para*-(1-methylcyclopentyl)phenol - is 78.3%

based on the phenol extracted, and the selectivity is 92.5% based on the target product.

The IR, ^{1}H and ^{13}C NMR spectra of *para*-(1-Methylcyclopentyl)phenol were recorded and its chemical structure was confirmed; at the same time, the physicochemical properties and elemental compositions of the substance were determined (Figures 4, 5).

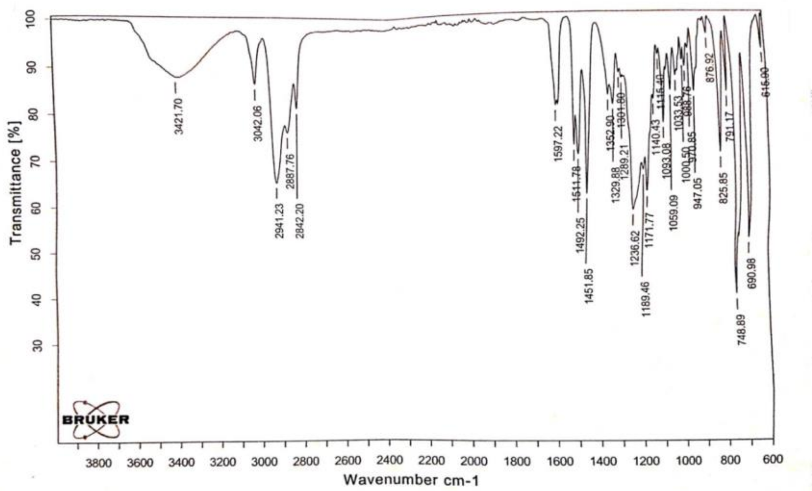


Figure 4. IR spectrum of *para*-(1-Methylcyclopentyl)phenol

The absorption bands observed in the IR spectrum are: 825 cm^{-1} para-substituted benzene ring, 690-947 cm^{-1} valence vibration of the C–H bond of the HC=C- group of unsaturated hydrocarbons, 1093-1236 cm^{-1} C-O bond, 1329-1492 cm^{-1} deformation vibration of the C-H bond of the CH_3-, CH_2- and CH- groups, 1511,1597 cm^{-1} C=C bond of the –HC=C– group, 2842-2941 cm^{-1} valence vibration of the C-H bond of the CH_3-, CH_2- and CH- groups, 3042 cm^{-1} valence vibration of the C-H bond of the -CH=C- group, 3421 cm^{-1} valence vibration of the O-H bond of the -COH group.

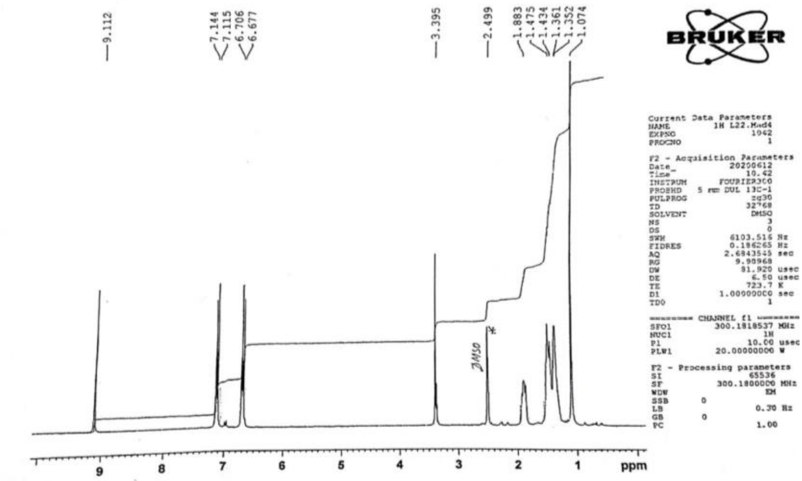


Figure 5. ^{1}H NMR spectrum of *para*-(1-Methylcyclopentyl)phenol

Results of ^{1}H NMR spectroscopic study: ($CDCl_3$, δ, ppm): 1.074(singlet, 3H, CH_3); 1.35-1.48 (multiplet; 8H, $4CH_2$); 1.88 (singlet, CH_3); 3.39 (singlet, OH); 6.67-6.70 (d, 1H, arom.); 7.11-7.14 (d, 1H, arom.); 9.11 (singlet, 12H, arom.).

Below is a step-by-step material balance of the process for the production of *para*-(1-methylcyclopentyl)phenol in a intermittent device under optimal conditions in the presence of a zeolite-containing KH-30 catalyst.

I. Cycloalkylation

Have been taken:	çəki,q	%-lə
Phenol	47.0	50.7
MTCP	41.0	44.2
KH-30 (10% due to phenol)	4.7	5.1
Total:	92.7	100.0
Have been obtained:		
Alkylate + cat.	91.2	98.4
Loss	1.5	1.6
Total:	92.7	100.0

II. Filtration

Have been taken:		
Alkylate + cat.	91.2	100.0
Total:	91.2	100.0

Have been obtained:		
Alkylate	85.1	93.3
Catalyst	4.3	4.7
Loss	1.8	2.0
Total:	91.2	100.0

III. Rectification

Have been taken:		
Alkylate	85.1	100.0
Total:	85.1	100.0
Have been obtained:		
Returned MTCP	5.5	6.5
Returned phenol	7.2	8.5
p-(MTCP)F	68.9	81.0
By-products	0.7	0.8
Residue	0.6	0.7
Loss	2.2	2.5
Total:	85.1	100.0

The stepwise material balance of the *para*-(1-methylcyclopentyl)phenol obtaining process shows that during the rectification of the obtained alkylate 68.9 g of the target product is obtained, this is 78.3% (based on the taken phenol) of its yield, 1.3 g of by-products and residue are obtained, which indicates a selectivity of 92.5% (based on the target product).

A regression mathematical model of the process of obtaining *para*-(1-methylcyclopentyl) phenol in the presence of KH-30 catalyst was developed and optimal operating parameters were found.

In order to develop a regression model of the process, a functional relationship was identified between the process parameters and this relationship was used for further prediction of the process.

As a result of optimization, the optimal values of the process were found: temperature - 115 °C, reaction time - 6 h, catalyst content - 12%, and in this case the yield of the intended product was 78, and the selectivity was 92%.

Similarly, the effect of kinetic factors on the direction of cycloalkylation reactions of phenol with 1-methylcyclopentadiene and cyclopentadiene was studied.

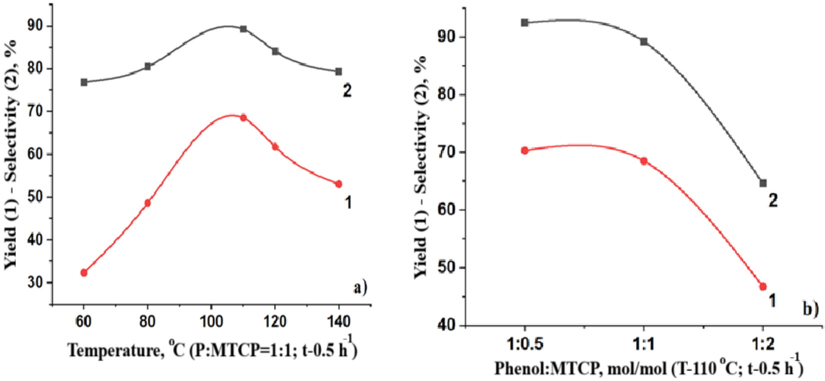
The physicochemical properties of *para*-(1-methylcyclopentyl)-[I], *para*-(1-methylcyclopentenyl)-[II], *para*-(cyclopentenyl)-[III]phenols are given below. [I]: boiling point 145-148°C/10 mmHg; melting point -90° C; m.m.-176; [II]: boiling point 136-139° C/10 mmHg; melting point -88° C; m.m.-174; [III]: boiling point 125-130°C/10 mmHg; melting point -86° C; m.m.-160.

Study of cycloalkylation reactions of phenol with methylcyclopentene in a continuous device

Cycloalkylation reactions of 1-methylcyclopentene and phenol in the presence of KH-30 catalyst were studied in a continuous-flow device.

In order to achieve efficient yield and selectivity of cycloalkylation reactions of phenol with methylcyclopentene in a continuous unit, the effect of the kinetic factors of the process - temperature, molar ratios of the initial raw materials, volume flow - on the direction of the cycloalkylation reactions and the composition of the obtained products was investigated. The cycloalkylation reaction was studied at a temperature of 80-140^{o}C, a molar ratio of phenol to cyclopentenes of 1:0.5÷2, and a volume rate of 0.2-1.0 h^{-1}.

Figure 6 presents the results of a study of the effect of kinetic factors on the yields and selectivities of the products of the cycloalkylation reactions of phenol with 1-methylcyclopentene in a continuous device for an example.



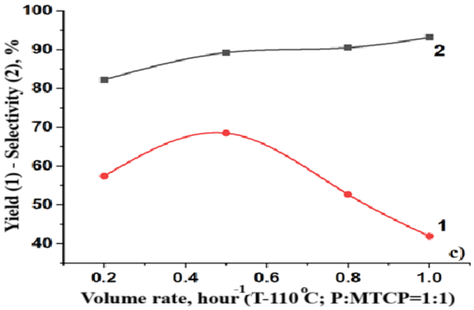


Figure 6. Dependence curves of the yield (1) and selectivity (2) of *para* – (1-Methylcyclopentyl)phenol on temperature (a), molar ratio of initial components (b), and volume velocity (c)

Efficient conditions were found for the cycloalkylation reaction of phenol with 1-methylcyclopentene in the presence of KH-30 catalyst in a continuously operating pilot device: temperature 110°C, molar ratio of phenol to MTCP 1:1, volume rate 0.5 h^{-1}. Under these conditions, the yield of *para*-(1-methylcyclopentyl)phenol is 68.5% based on the extracted phenol, and the selectivity is 89.2% based on the target product.

Similarly, cycloalkylation reactions of phenol with 1-methylcyclopentadiene and cyclopentadiene in the presence of KH-30 catalyst were studied in a continuously operating device, and optimal conditions for carrying out the process were found: reaction temperature 115°C, molar ratio of phenol to MTCPD (TCPD) 1:1 mol/mol, volume rate 0.5 h^{-1}. Under these conditions, the yield of *para*-(cyclopentenyl)phenols is 69.2-69.8% based on the taken phenol, and the selectivity is 92.0-92.3% based on the target product.

Cycloalkylation reactions of phenol with cyclopentenes in the presence of modified KH-30M catalyst

Cycloalkylation reactions of phenol with cyclopentenes in the presence of KH-30M catalyst were carried out in intermittent and continuous operating devices. KH-30M catalyst was obtained by treating KH-30 catalyst with 10% hydrochloric acid.

Cycloalkylation reactions of phenol with cyclopentenes using KH-30M catalyst in a intermittent device were carried out under the following conditions: temperature 100-105°C, reaction time 4-4.5 h, the molar ratio of phenol to cyclen is 1:1 mol/mol, and the amount of catalyst is 7.0% (due to the taken phenol). Under the optimal conditions found, the yield of the target products is 76.2-79.3% (due to phenol), and the selectivity is 94.6-95.6% (due to the target product). The target products are separated from the reaction mixture and their physicochemical properties and chemical structures are determined.

The interaction reactions of phenol with cyclopentenes in a continuously operating device were carried out by using the above-mentioned methodology.

As a result of the conducted scientific research, the effect of kinetic parameters (temperature, molar ratios of initial components, volume velocity) on the yield and selectivity of target products was investigated, and optimal conditions were found for each process: the molar ratio of phenol to cyclene is -1:1, and the volume velocity is -0.5 h^{-1}. Under these conditions, the yield of the target products is 74.7-76.8% (based on the taken phenol), and the selectivity is 93.2-96.2% (based on the target product).

The study of cycloalkylation reactions of phenol with cyclopentenes in the presence of Seokar-2 and Seokar-2M catalysts

Cycloalkylation reactions of phenol with 1-methylcyclopentene, 1-methylcyclopentadiene, and cyclopentadiene were carried out in intermittent and continuous device in the presence of zeolite-containing Seokar-2 and modified Seokar-2M catalysts.

Optimal conditions were found for the cycloalkylation process of phenol with MTCPD in a intermittent device in the presence of a zeolite-containing Seokar-2 catalyst: process temperature - 120°C, time - 5.5 h, molar ratio of phenol to MTCPD 1:1, catalyst consumption 10% of the taken phenol. Under these conditions, the yield of the main product - *para*-(1-methylcyclopentenyl)phenol - is 68.2% based on the taken phenol for the process and 82.7% based on the selectivity target substance.

Optimal conditions were achieved for the cycloalkylation process of phenol in a intermittent device with MTCP in the presence of the Seokar-2M catalyst: temperature -105°C, time-5 h, the molar ratio of phenol to MTCP is 1:1, and the catalyst consumption due to phenol is 10%. Under these conditions obtained for the cycloalkylation process of phenol with MTCP, the yield of *para*-(1-methylcyclopentyl)phenol is 75.7% relative to phenol, and the selectivity is 90.3% relative to the target substance.

The cycloalkylation reaction of phenol with MTCP in the presence of Seokar-2M catalyst was studied in a continuously operating device and optimal conditions were found: temperature -110°C, mole ratio of phenol to MTSP– 1:1, volume velocity – 0.5 h^{-1}. Under these conditions, the yield of the target substance - *para*-(1-methylcyclopentyl)phenol - is 71.3% based on the taken phenol, and the selectivity is 91.8% based on the target substance.

The material balance occurs under the found optimal conditions for the cycloalkylation reaction of phenol with MTCP in a continuous device by using the Seokar-2M catalyst:

Items	Weight, g	Weight, %
Have been taken:		
1. Fenol	47.0	53.4
2. MTCP	41.0	46.6
Total:	88.0	100.0
Have been obtained:		
1. Returned MTCP	6.5	7.4
2. Phenol (returned)	11.2	12.7
3. *para*-(MTCP)phenol	62.7	71.2
4. Di- and	3.4	3.9
trialkylphenols	2.0	2.3
5. Residue	2.2	2.5
6. Loss		
Total:	88.0	100.0

As can be seen, the alkylation of phenol with MTCP in a continuous device yields 62.7 g of *para*-(1-methylcyclopentyl)phenol;

this indicates a yield of 71.3% due to phenol. Under the found conditions, 3.4 g of by-products and 2.0 g of residue were obtained, so the selectivity is 91.8% to the target product.

Table 2 presents comparative results of catalytic cycloalkylation reactions of phenol with 1-methylcyclopentene in a continuous device.

Table 2

Comparative results of cycloalkylation reactions of phenol with 1-methylcyclopentene in a continuous-flow device

Reaction conditions	Catalysts			
	Seolit-Y	Seokar-2M	KN-30	KN-30M
Temperature, ^{o}C	110	110	110	105
Mole ratio of phenol to MTCP, mol/mol	1:1.5	1:1	1:1	1:1
Volumetric velocity, h^{-1}	0.5	0.5	0.5	0.5
Composition of the reaction mixture, wt. %				
Phenol	12.7	10.9	11.7	9.3
MTCP	9.2	8.5	7.8	7.0
Cycloalkylation products	78.1	80.6	80.5	83.7
Composition of cycloalkylation products, wt. %				
Methylcyclopentylphenyl ether	1.8	1.1	-	-
ortho-(1-Methylcyclopentyl)phenol	5.3	4.7	3.5	2.8
para-(1-*m*ethylcyclopentyl)phenol	89.0	91.8	93.8	95.8
Di-(1-methylcyclopentenyl)phenol	3.9	2.4	2.7	1.4
Ratio of *ortho- and para*-(1-methylcyclopentyl) phenols	16.8	19.5	26.8	34.2
Yield, %	64.7	71.3	68.5	76.8
Selectivity, %	88.3	91.8	89.2	93.4

As a result of the research, effective conditions were obtained for conducting cycloalkylation reactions of phenol with 1-methylcyclopentadiene in a continuously operating device in the presence of the Seokar-2M catalyst: temperature -110°C, molar ratio of phenol to MTCPD 1:1, volume velocity -0.5 h^{-1}. Under these conditions, the yield of cycloalkylphenol based on phenol is 69.8%, and the selectivity is 89.4% based on the target product.

Fenolun MTSPD ilə tsikloalkilləşmə reaksiyasının Seokar-2M katalizatoru iştirakında fasiləsiz işləyən qurğuda hesablanmış material balansı aşağıda verilmişdir. The calculated material balance of the cycloalkylation reaction of phenol with MTCPD in a continuous operation device in the presence of Seokar-2M catalyst is given below.

Have been taken:	Weight, g	Weight, %
Phenol	47.0	54.0
MTCPD	40.0	46.0
Total:	87.0	100.0
Have been obtained:		
1. MTCPD (returned)	7.1	8.2
2. Phenol (returned)	9.7	11.1
3. *p*-(Cycloalkyl)phenol	60.7	69.8
4. Di- and tri-substituted cycloalkylphenols	5.9	6.8
5. Residue	1.6	1.8
6. Loss	2.0	2.3
Total:	87.0	100.0

As can be seen, in the cycloalkylation process of phenol with MTCPD, 60.7 g of *para*-(1-methylcyclopentenyl)phenol is obtained, which means that the yield is 69.8% of the phenol taken, by-products are 5.9 g, and the residue is 1.6 g, which indicates that the selectivity for this target substance is 89.4%.

Similarly, cycloalkylation reactions of phenol with TCPD were carried out in a continuous device in the presence of Seokar-2M catalyst. As a result of the studies, under the optimal conditions found for the cycloalkylation process, the yield of *para*-(cyclopentenyl)phenol relative to the phenol taken is 64.5%, and the selectivity is 94.0% relative to the target product.

Obtaining and application areas of nitrogen and phosphorus-containing derivatives of *para*-methylcyclopentyl- and cyclopentenylphenols

The aminomethylation reactions of *para*-(1-Methylcyclopentyl)-, *para*-(1-methylcyclopentenyl)- and *para*-(cyclopentenyl)phenols with formaldehyde and aminoethylnonylimidazoline, phosphitization reactions with phosphorus trichloride, compositions with alkylimidazolines, and oxyethylated nonylphenol were obtained and their applications were studied.

One of the important issues is the development of the technology for obtaining the amine-containing compounds we receive in order to recommend them to industry. For this purpose, a technological scheme of their acquisition process is proposed. The technological scheme is reflected in Figure 7. Phenol is placed in the container 1, and cyclopentene is placed in the container 2. The temperature in the phenol tank is always 45°C. Both reagents are transferred to the mixer 3 in the required weight and fed to the bottom of the mixing reactor (4). The initial raw material mixture is passed over the catalyst filled into the reactor and directed to a 5-atmosphere rectification column.

A temperature of 80-120°C is achieved in the reactor by means of a spiral wound around the reactor surface. It is separated from methylcyclopentene, which does not react with alkylate, in atmospheric pressure. The composition of the cyclenes returning from the reaction is determined and sent to the cyclene line. The alkylate separated from the cyclene is fed to the vacuum chamber (6). The pressure in the vacuum chamber constitutes 10 mmHg. The temperature at the upper part of the furnace is maintained at 150-210°C, depending on the alkylate composition, and at 180-240°C in the lower part. The separated phenol is returned to the container (1), and the main substance – *para*-cyclopentylphenol is sent to reactor 10 for aminomethylation. The required amounts of solvent (benzene), AIM, and formalin are added to the reactor (10) from additional containers 7, 8, and 9 and mixed at 80°C for 2 hours. Then the mixture is cooled to 40°C and sent to the 11-atmospheric rectification column. The temperature in the lower part of the furnace is maintained at 130-135°C, and in the upper part at 110°C. Meanwhile, the benzene taken into the process and the resulting water are discharged from the upper part of the boiler and are separated after being cooled in the cooler (12). At the end, the obtained main substance is removed from the lower part of the tank and directed to the park.

Nitrogen and phosphorus-containing derivatives of *para*-methylcyclopentyl- and cyclopentenylphenols have been tested in various fields. Nitrogen-containing derivatives of cyclopentylphenols have been tested as high-temperature resistant antioxidants in M-8 engine oil, as surfactants, and as bactericides and disinfectants against diseases of large and small horned animals in agriculture, and phosphorus-containing derivatives have been tested as antioxidants in turbine oil T-46.

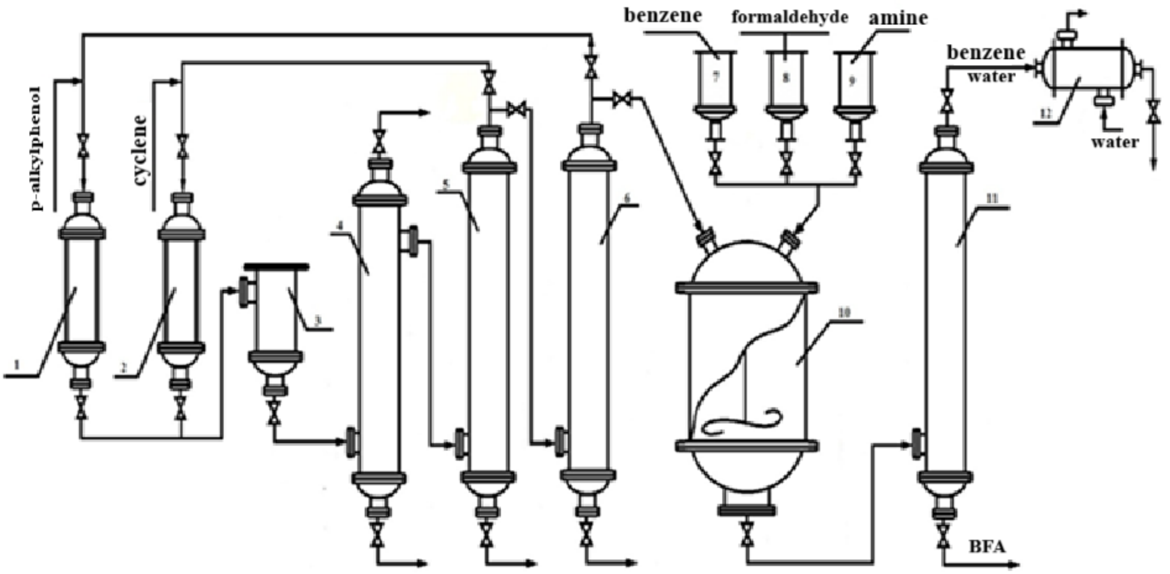


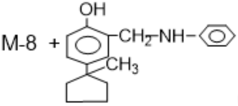
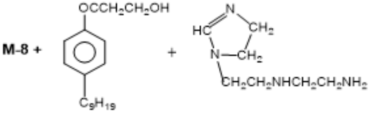
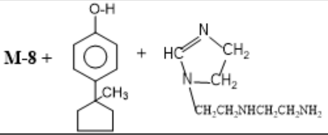
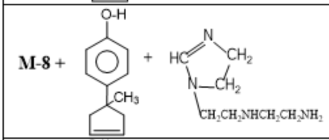
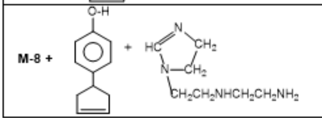
Figure 7. Technological scheme of the process of obtaining BAIs

1 - Container for phenol; 2 - container for cyclene; 3 - mixer; 4 - reactor; 5 - atmospheric rectification column; 6 - vacuum rectification column; 7 - container for benzene; 8 - container for formaldehyde; 9 - container for amine; 10 - mixing reactor; 11 - rectification column; 12 – cooler

The presented *para*-(methylcyclopentyl)phenols and alkylimidazoline compositions on the bases of [p-1-MTCAP]:[AIM] on the a mass ratio of 1:9, respectively, were prepared and tested as antioxidants in M-8 engine oil. The results are given in Table 3. The obtained compositions, when compared to the known AKI-21 and oxyethylated nonylphenol and alkylimidazoline-based antioxidants used in other industries, when added to M-8 engine oil at a rate of 0.5%, after 10 hours of oxidation at a temperature of 200°C, a slight (0.28-0.34%) sediment is obtained, and the increase in viscosity is 13.07-14.26%.

Table 3

The results of testing the compositions as antioxidants in M-8 engine oil

Substances	Containing of the composition	Sedi-ment, %	Viscosity, mm²/sec at 100° C The test Before	After	İncrease in visco-sity, Δ^{γ}, %
M-8 (Without adding AO)	-	4.47	7.95	9.23	16.10
M-8 + AKI-21 (known)	-	1.36	7.97	9.24	15.93
 (known)	-	1.24	7.96	9.19	15.46
 (known)	[ONP]: [AIM]= 1:9	0.58	7.94	9.11	14.73
	p-[1-MTCP]P : [APM]= 1:9	0.28	7.93	9.77	13.07
	p-[1-MTCP]P : [AIM]= 1:9	0.34	7.88	9.00	14.26
	p-[TCP]P: [AIM]= 1:9	0.30	7.95	8.99	13.08

The results of testing of the compositions (K-2 and K-3, respectively) of *para*-(1-methylcyclopentenyl), *para*-(cyclopentenyl)phenols on the bases of oxyethylated nonylphenol and alkylimidazoline as surfactants are given in Table 4.

Table 4

Surface tension values of aqueous solutions of ONP+AI+AP composition at the air interface

composition	Density of the substance, % (by wt.)											
	0.00025	0.0005	0.00075	0.001	0.0025	0.005	0.0075	0.01	0.025	0.05	0.075	0.1
	Surface tension at the water-air interface, mN/m (at 25°C)											
K-2	67.7	53.9	47.8	44.1	37.4	34.4	33.0	32.6	**30.9**	**30.5**	**30.3**	**30.1**
K-3	69.1	50.7	43.4	39.8	34.2	31.8	31.3	**30.5**	**30.1**	**29.9**	**29.9**	**29.8**

Note: Surface tension of water is 71.1 mN/m (without SAS)

As can be seen from the table, the values of the aqueous solutions of the compositions we present (from 0.01 to 0.1%) are satisfactory and can be used as SAS.

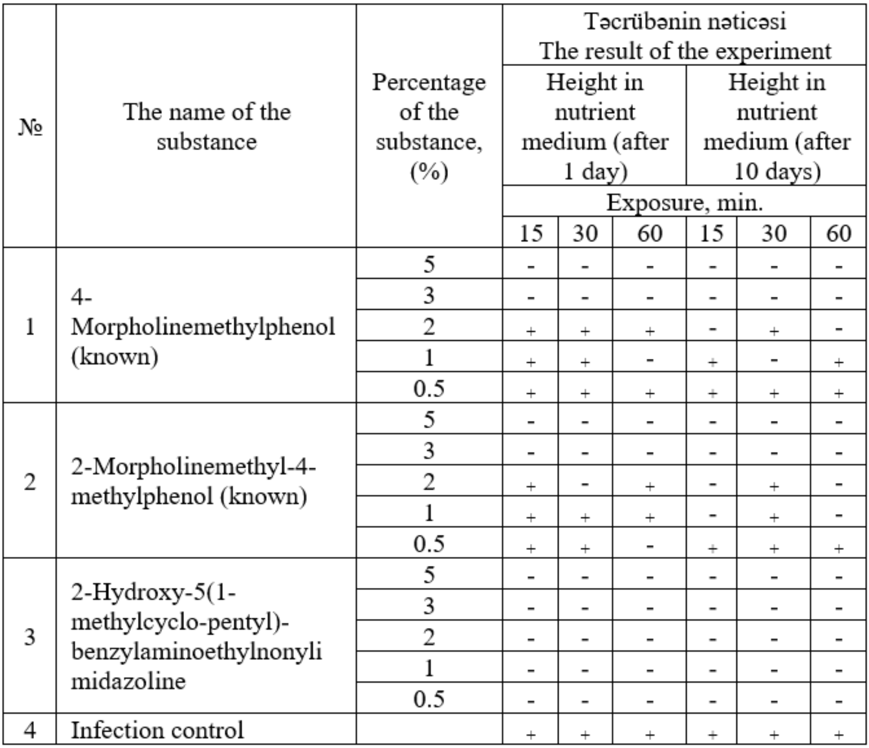
The synthesized 2-hydroxy-5(methylcyclopentyl)benzylamino-ethylnonylimidazolines were tested as bactericides and disinfectants against intestinal coccus microbes in large and small ruminants.

The studies have shown that 0.5, 1, 2, 3, 5% aqueous solutions of 2-hydroxy-5(1-methylcyclopentyl)-benzylaminoethylnonylimidazoline completely neutralize E. coli microbes on the mentioned wooden test objects at exposure times of 15, 30 and 60 minutes (Table 5), and 10% aqueous solutions at exposure times of 30, 60, 120, 180 minutes at a rate of 1 liter of solution per 1 m^2 of area, at a solution temperature of 18-20°C. It should be noted that the disinfectant we offer has high volatility, which leads to rapid air purification in an ecological way and does not cause any harm to animals.

Thus, 2-hydroxy-5(1-methylcyclopentyl)-benzylaminoethylnonylimidazoline substance can be proposed as a bactericidal and disinfectant agent against E.coli (intestinal cocci) microbe.

Table 5

The results of the tests of the 2-hydroxy-5(1-methylcyclopentyl)-benzylaminoethylnonylimidazoline as a bactericide



№	The name of the substance	Percentage of the substance, (%)	Təcrübənin nəticəsi The result of the experiment					
			Height in nutrient medium (after 1 day)			Height in nutrient medium (after 10 days)		
			Exposure, min.					
			15	30	60	15	30	60
1	4-Morpholinemethylphenol (known)	5	-	-	-	-	-	-
		3	-	-	-	-	-	-
		2	+	+	+	-	+	-
		1	+	+	-	+	-	+
		0.5	+	+	+	+	+	+
2	2-Morpholinemethyl-4-methylphenol (known)	5	-	-	-	-	-	-
		3	-	-	-	-	-	-
		2	+	-	+	-	+	-
		1	+	+	+	-	+	-
		0.5	+	+	-	+	+	+
3	2-Hydroxy-5(1-methylcyclo-pentyl)-benzylaminoethylnonylimidazoline	5	-	-	-	-	-	-
		3	-	-	-	-	-	-
		2	-	-	-	-	-	-
		1	-	-	-	-	-	-
		0.5	-	-	-	-	-	-
4	Infection control		+	+	+	+	+	+

Tri-[*para*-(cyclopentyl)oxyphenyl]phosphites were tested as antioxidants (AO) in turbine oil T-46.

As a result of the use of cyclopentylphenylphosphites as 0.5% antioxidant in turbine oil T-46, the increase in viscosity ($\Delta\nu$) of the oil after 10 hours of oxidation at 100°C is 2.9-3.94%, and the amount of formed sediment is 0.17-0.32%; in base oil without AO addition, these indicators are 10.76 and 2.17%, respectively.

Thus, tri-[*para*-(cyclopentyl)phenyl]phosphites fully meet the requirements for antioxidant additives and can be recommended as an antioxidant for turbine oil T-46 according to GOST 11063-77.

THE RESULTS

1. For the first time, the effect of various kinetic factors (temperature, time, molar ratios of initial raw materials, amount of catalyst, volume velocity) on the yield and selectivity of the target products was studied in intermittent and continuous device of phenol with 1-methylcyclopentene, 1-methylcyclopentadiene, and cyclopentadiene in the presence of KH-30 and modified KH-30M catalysts. It was determined that under the optimal conditions found for cycloalkylation reactions of phenol in a intermittent device, the yield is 76.3–81.3% of the phenol obtained, and the selectivity is 90.6–92.8% of the target product, while in a continuous device, the yield is 61.5–64.7%, and the selectivity is 88.7–93.2%, respectively [1, 9, 16].

2. The effect of key factors on the yield and selectivity of *para*-arylalkylphenol have been studied in intermittent and continuous devices in the reaction of phenol with 1-methylcyclopentene, 1-methylcyclopentadiene, and cyclopentadiene in the presence of Seokar-2 and modified Seokar-2M catalysts. It was determined that under the optimal conditions found for arylalkylation reactions, the yield of the target product in a intermittent device is 78.2-83.2% based on the phenol taken, and the selectivity is 93.5-95.3% based on the target product, while in a continuous device, the yield is 65.4-67.8% and the selectivity is 91.9-96.3% [7, 13, 15, 22, 23].

3. Aminomethylation reactions of methylcyclopentylphenols with formaldehyde and aminoethylnonylimidazoline have been conducted. As a result of the reaction aminomethylation products (at 80°C, for 2 h) with a yield of 79.3-81.6% (based on the taken *para*-methylcyclopentylphenol) and a selectivity of 86.7-88.0% (based on the target product) [2, 4, 5, 12, 13, 19, 20].

4. Compositions were prepared in a mass ratio of 1:9 on the bases of *para*-(1-Methylcyclopentyl), *para*-(1-methylcyclopentenyl) and *para*-(cyclopentenylyl)phenols and alkylimidazoline, respectively, and their quality indicators were evaluated by the amount of formed sediment and the change in viscosity after oxidation of the oil at a temperature of 200^{o}C in M-8 engine oil in accordance with GOST 11063-77. These compositions in comparison with the known AKI-21

and antioxidant of the composition on the bases of oxyethylated nonylphenol and alkylimidazoline, that used in other industries, when added to M-8 engine oil at a rate of 0.5%, after oxidation at a temperature of 200^{o}C, a slight (0.28-0.34%) sediment is obtained, the viscosity increase is 13.07-14.26% [6, 21, 25].

5. The compositions have been obtained in a mass ratio of 5:5:90 of *para*-(1-Methylcyclopentenyl), *para*-(cyclopentenyl)phenols with alkylimidazoline and oxyethylated nonylphenol and tested as surfactants. The samples have showed high surface activity, reduced the interfacial surface tension from 71.1 mN/m to 30.9-29.8 mN/m.

6. 2-Hydroxy-5(1-methylcyclopentenyl)benzylaminoethylnonyl-imidazoline has been tested as a bactericidal and disinfectant drug against intestinal cocci in agriculture – poultry, large and small horned animals. It has been found that a 0.5% solution of the substance in water inactivates intestinal cocci microbes within 15 minutes. A 10% solution of the drug in water, at the rate of 1 liter per 1 m^2 of area, completely neutralizes E-coli microbes in wooden test objects at a solution temperature of 18-20^{0}C [26].

7. Tri[para-(methylcyclopentenyl)-oxyphenyl]phosphites were tested as antioxidants for turbine oil T-46. It was determined that when 0.5% phosphites were added to turbine oil T-46, the amount of sediment after oxidation at 100^{o}C for 10 hours was 0.17-0.32%, and the viscosity increase was 2.9-3.94%. [24].

8. Aceto-benzophenones and para-arylalkylphenolamine resins have been obtained by using *para*-methylcyclopentylphenols as raw materials in the reactions of acylation with benzoyl chloride, acetic acid, and aminomethylation with urotropine. They have been tested as a thermostabilizer and antirad against radiation in polyethylene, and as a coating agent in paint and varnish materials, respectively [3, 8, 10, 11, 14, 17, 18].

9. The technical and economic parameters of the composition of alkylimidazolines with *para*-(1-methylcyclopentyl)phenol (in a mass ratio of 9:1) were calculated. According to the preliminary calculations, the cost of 1 ton of the composition is 2878.52 AZN. The application of the proposed technology reduces the cost of 1 ton of the commodity product by 134 manat.

The main content of the dissertation is reflected in the following published scientific works:

1. Гасымова, Ф.И., Нагиева, М.В. Гасанова, Г.Д., Расулов, Ч.К. Фосфорсодержащие цеолиты-новые поколения катализаторов для реакций циклоалкилирования фенолов // V Всероссийской научной конференция "Актуальные проблемы теории и практики гетерогенных катализаторов и адсорбентов", – Иваново, – 30 июня-2 июля, – 2021, – с.286-287.
2. Гасымова, Ф.И. Синтез и свойства 2-гидрокси-5(1-метилциклопентил)-бензиламиноэтилнонилимидазолина // Нефтепереработка и Нефтехимия, – 2021. – № 6, – с.30-32.
3. Гасымова, Ф.И., Агамалиев, З.З., Гасанова, Г.Д., Расулов, Ч.К. Синтез *пара*-циклоалкилфеноламинных олигомеров-антиоксидантов к моторным маслам // VIII Международной научно-технической конференции "Альтернативные источники сырья и топлива «АИСТ-2021»", Минск, – 12-14 октября, – 2021, – с.110-112.
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