REPUBLIC OF AZERBAIJAN

On the rights of the manuscript

ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

DEVELOPMENT OF AN EFFICIENT ALKYLATION PROCESS OF CRESOLS WITH 1- AND 2-PROPANOL

Speciality:	2314.01- Petrochemistry
Field of science:	Chemistry

Applicant: **Khayala Amiraslan Hajiyeva**

Baku – 2025

The work was performed at the Department of Petrochemistry and Chemical Engineering of Sumgayit State University.

Scientific supervisor: Doctor of Chemical Sciences, Professor **Akbar Ali Aghayev**

Official opponents: Doctor of Chemical Sciences, Professor **Chingiz Gnyaz Rasulov**

Doctor of Chemical Sciences, Professor **Gasim Zulfali Huseynov**

Doctor of Chemical Sciences, Professor **Sevinj Abdulhamid Mammadkhanova**

Dissertation council ED 1.16 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at academician Y.H. Mammadaliyev Institute of Petrochemical Processes of the Ministry of Science and Education of the Republic of Azerbaijan

Chairman of the Dissertation council:

______________ Doctor of chemical sciences, academician **Vagif Maharram Abbasov**

Scientific secretary of the Dissertation council:

______________ Doctor of chemical sciences, Assoc. Prof. **Lala Mahammad Afandiyeva**

Chairman of the scientific seminar:

______________ Doctor of chemical sciences, Assoc. Prof. **Fuzuli Akbar Nasirov**

GENERAL CHARACTERISTICS OF WORK

The relevance of the topic and the degree of elaboration. Propyl and isopropyl derivatives of phenol and cresols hold significant importance among their low molecular weight alkyl compounds. These valuable compounds are widely used in the production of resins, polymer materials, chemical toxic substances, antioxidants, vitamins, and pharmaceutical preparations, both as finished products and as intermediates[1].

It's known that primary raw material base for phenol and its methyl homologs is coal tar, but its reserves are diminishing[2].

C_3 and C_4 alkyl homologs are synthesized through the catalytic alkylation reaction of phenol and cresols with olefins, alkyl halides, and corresponding alcohols. However, conduction of the operation with alkenes and alkyl halides, the significant presence of side reactions, the use of metal halide catalysts, and alkyl halides as alkylating agents create environmental problems reducing efficiency of the process and complicate technology and management. Currently, obtaining and using new, efficient catalysts for these processes, along with the use of alcohols as alkylating agents, and the development of an efficient catalytic alkylation method are considered important directions and have attracted more attention in recent times.

The catalytic systems used in alkylation process of cresols with 1- and 2-propanols are also useful in the synthesis of *ortho (o-)* propyl and isopropyl derivatives. However, these catalytic systems exhibit low catalytic properties in the production of other isomers and target isomer mixtures. Therefore, there's a need to develop zeolite-based catalysts with adjustable acid-base properties and study alkylation process of cresols with C_3-saturated alcohols

The object and subject of the research. The object of the study is the catalytic alkylation process of methylphenols with propyl and isopropyl

---

1 Steve, C. Europe alkylphenols and cresylic asids Chemical Economics Hanbook. - 2015, -p.92-96.

2 Akhmetkarimova, J.S. Isomerization of phenols from coal tar fraction / J.S. Akhmetkarimova, M.I. Baykenov, M.G. Meyramov [et al.] // Chemistry of Solid Fuel –Moscow: – 2014.– No.3.– p.70-76.

alcohols. The development of an efficient method for the synthesis of propyl- and isopropyl derivatives of monomethylphenols in the presence of Pd-HSVM catalyst selected from palladium-containing zeolites is considered the subject of the study.

The goals and objectives of the research. The main goal of the dissertation work is studying the activity and selectivity properties of zeolite catalysts with different compositions in the alkylation process of methylphenols with 1- and 2-propanols, investigating the regularities of the process with the participation of selected palladium-containing zeolites, developing a kinetic model and a method for obtaining target products.

For the purpose of achieving the goal, the following issues were addressed and resolved in the dissertation:

- studying the effect of H-mordenite framework on the alkylation reaction of 2-methylphenol with propanols;
- regulating of the activity and selectivity of mordenite modified with palladium and nickel with selected framework modules;
- investigating the alkylation reactions of 2-, 3-, and 4-methylphenols with propanols using nickel- and palladium-modified H-mordenite;
- studying the process of synthesizing corresponding propyl and isopropyl derivatives of cresols through isomerization of propyl and isopropyl esters of 2-, 3-, and 4-methylphenols in the presence of an effective catalyst;
- identifying the main and side transformations occurring during the alkylation process, and developing an understanding of its chemistry and mechanism;
- conducting kinetic studies of the alkylation process, calculating the kinetic constants, and developing a kinetic model of the process;
- developing a method for obtaining 2,6-diisopropyl-4-methylphenol based on 4-methylphenol and 2-propanol.

Research Methods. The alkylation process of methylphenols with 1- and 2-propanols was studied in an extraction-type reactor equipped with a stationary layered catalyst. Modern physicochemical analysis methods, including gas-liquid chromatography and ^{1}H NMR spectroscopy, were used for determining the composition and structure of the alkylation products. Kinetic calculations were performed using MATLAB programs.

The main provisions defended:

- the study of the alkylation reactions of 2-, 3-, and 4-methylphenols with 1- and 2-propanols using H-mordenite, as well as its modifications with palladium and nickel, to determine the optimal composition and the study of the activity and selectivity of the zeolites;
- the study of the catalytic properties of palladium-containing pentasils (HSVM and ZSM-5) and PdCaY-type zeolites in the alkylation reactions of 2-, 3-, and 4-methylphenols with propanols;
- the determination of the chemistry of alkylation process, kinetic studies, key stages, and reaction pathways in the presence of Pd-HSVM zeolite, and the development of a low-error kinetic model;
- the study of the effective synthesis process of 2,6-diisopropyl-4-methylphenol based on the alkylation of 4-methylphenol with 2-propanol in the presence of the Pd-HSVM catalyst.

Scientific novelty of the research. The optimal module of H-mordenite (SiO_2/Al_2O_3=24) was determined by the alkylation reaction of 2-methylphenol with propanols, and modified with palladium and nickel. 1.0 wt % Pd, H-mordenite and 1.0 wt % Ni, H-mordenite were selected as an effective catalyst and their catalytic properties were determined. These were also studied in the alkylation reactions of other cresols with propanols, and the results were compared. Activity and selectivity of palladium-containing pentasils (HSVM, ZSM-5) and PdCaY zeolites were determined by the alkylation reactions of methylphenols with 1- and 2-propanols and their changes in catalytic performance were revealed. The Pd-HSVM zeolite with the highest results was studied in detail. It was determined that increasing the number of methyl groups in the phenol molecule enhances the conversion of the substrate and affects the selectivity of isopropyl derivatives formed in sterically hindered methylphenols and 3,4-xylenol. The synthesis of difficult-to-obtain propyl and isopropyl isomers in the alkylation reaction of monomethylphenols was achieved by isomerizing the propyl and isopropyl esters of 2-, 3-, and 4-methylphenols. In catalytic alkylation, it was established that the propyl and isopropyl esters of the obtained cresols are not intermediate compounds at high temperatures (T>340°C), with propanol side transformation resulting in the dehydrogenation of propanal. Reaction pathways, based on a sequential alkylation mechanism and a stepwise diagram, along with kinetic equations, were formulated in a low-error kinetic model. The effective synthesis of 2,6-diisopropyl-4-methylphenol in the alkylation of 4-methylphenol with 2-propanol using the Pd-HSVM zeolite was investigated, and a patent of the Republic of Azerbaijan (Invention i2021 0045) was obtained on this process.

Theoretical and practical significance of the research. As a result of studying Pd and Ni-modified mordenites, palladium-containing pentasils, and PdCaY zeolite in the alkylation reactions of 2-, 3-, and 4-methylphenols with 1- and 2-propanols, the activity and selectivity rankings of the catalysts were determined based on the substrates and alkylating agents. Methods for obtaining practical propyl and isopropyl derivatives of cresols were developed, and an effective process for the alkylation of 4-methylphenol with 2-propanol was achieved in the presence of Pd-HSVM zeolite, leading to the synthesis of 2,6-diisopropyl-4-methylphenol with 91.50-97.50% selectivity and 38.2-46.5% yield. The existing petrochemical raw material base in our country will allow for its future practical application.

Appropriation and application of the work. A total of 15 scientific papers have been published on the topic of the dissertation, including 8 papers in internationally renowned journals (3 of which are co-authored) and 6 conference materials. A patent of the Republic of Azerbaijan has been obtained. The published scientific works fully reflect the content of the dissertation.

Main results of the dissertation. The scientific results of the dissertation were presented at the following national and international conferences: the international scientific-practical conference dedicated to the 110th anniversary of Academician V.S. Aliyev on the topic "Innovative Development Prospects of Oil Refining and Petrochemistry" (Baku: 2018), the national scientific conference dedicated to the 110th anniversary of Academician M. Naghiyev titled "Naghiev Readings" (Baku: 2018), the international scientific conference dedicated to the 90th anniversary of Academician Y.H. Mammadaliyev Institute of Petrochemical Processes of ANAS on the topic "Current Problems of Modern Chemistry" (Baku: 2019), the collection of papers from the International Scientific Conference

"Mathematical Methods in Engineering and Technologies" (Saint Petersburg: 2020), the national scientific conference dedicated to the 60th anniversary of Sumgayit State University on the topic "Modern Problems of University Science and Education" (Sumgayit: 2022), the national scientific conference dedicated to the 90th anniversary of Academician Nadir Mir-Ibrahim oghlu Seyidov on the topic "Catalysts, Olefin-based Oils" (Baku: 2022).

The name of the institution where the dissertation work was performed. The dissertation work was carried out at the Department of Petrochemistry and Chemical Engineering at Sumgayit State University.

The applicant's personal contribution to the research conducted. The author is responsible for formulating and solving the main issues related to the execution of the core ideas of the dissertation, conducting the experimental research, performing the analyses, analyzing and systematizing the results and preparing the scientific papers and the dissertation itself at every stage.

The structure and volume of the dissertation. The dissertation consists of introduction, 5 chapters, conclusions, and list of referenced literature. Total volume is 147 pages, including 6 figures, 40 tables, and a list of 137 sources of literature. The overall volume of the dissertation (excluding figures, tables, graphs, and the list of literature) is 180 247 characters (introduction – 10 812 characters, the first chapter – 52 351 characters, the second chapter – 13 028 characters, the third chapter – 36 102 characters, the fourth chapter – 27 928 characters, the fifth chapter – 36 409 characters, conclusion – 3 617 characters).

Main content of the dissertation. The introduction (10,812 characters) justifies the relevance of the topic, outlines the object and subject of the research, the goals and objectives, the key provisions defended, the scientific novelty, the theoretical and practical significance, the approval and application of the work, and provides brief information on the structure and volume of the dissertation.

The first chapter is dedicated to the study of application areas of alkylphenols, methods for obtaining low molecular weight alkylphenols, particularly the alkylation of phenols to produce alkylphenols, the advantages of this method over other methods, and its widespread use as a competitive method in several countries. The heterogeneous catalytic route for the production of low molecular weight alkylphenols (C_1-C_4), the catalysts used in the process, and the scientific research work conducted in this field were systematically discussed and critically analyzed.

The second chapter studies physicochemical characteristics of substances used as raw materials and standard compounds in chemical analyses, as well as the synthesized alkylation products. The methodology of conducting experiments and analyses, the technological scheme and working principles of the devices used for the experiments, the methods for analysis of the obtained products, scientific information about the composition and preparation of catalysts, PMR spectra, and their analysis are also presented.

The third chapter presents the results of the study on the activity and selectivity of various zeolite catalysts in the alkylation reactions of 2-, 3-, and 4-methylphenols with 1-propanol and 2-propanol. Selection of the most effective catalyst is reflected on comparative analysis among palladium-containing zeolites.

The fourth chapter describes the results of the detailed study on the effective methods for obtaining the practically significant propyl and isopropyl derivatives of cresols.

The fifth chapter determines the nature of the main and side transformations occurring in the catalytic alkylation process, the kinetic studies of the alkylation reaction and discusses the work carried out in the direction of developing a kinetic model. Additionally, the results of the isomerization of propyl and isopropyl ethers of 2-, 3-, and 4-methylphenols and the production of their other C_3 derivatives are collected.

Conclusion is included in the dissertation.

THE MAIN CONTENT OF THE WORK

2-, 3-, and 4-methylphenols, 3,4-dimethylphenol, 1-propanol, 2-propanol, and propene were used in the research as raw materials and standard compounds in chemical analyses.

The experiments were conducted in a laboratory setup equipped with a flow-type reactor fitted with a stationary bed catalyst. The kinetic studies of the alkylation reaction were carried out in a reactor with a differential setup.

Modified samples of Y, mordenite, and pentasil zeolites were used in the research as well as the OMNIKAT-210P catalyst from the catalytic cracking unit at the Heydar Aliyev Baku Oil Refinery. Y and synthetic mordenites were synthesized using known methods. Initially, the optimal modulus of synthetic mordenite (SiO_2/Al_2O_3=24) was determined, and nickel was impregnated onto H-mordenite in the form of nickel cations using a nitrate solution. The catalyst also contained 20-25 wt% of aluminum oxide as a binder. The silica concentration was increased, and zeolites (HSVM and ZSM-5) were obtained through the high-temperature hydrothermal synthesis of organic and inorganic silica gels. Palladium-containing zeolites were prepared by ion exchange of palladium from its complex salt $[Pd(NH_3)_4]Cl_2$ aqueous solution.

The analysis of the reaction participants (raw materials, intermediates, and target products) was carried out using gas chromatography and PMR spectroscopy.

Study of the Activity of H-Mordenite-Based Catalysts in the Alkylation Reaction of 2-Methylphenol with 1- and 2-Propanol

Initially, mordenites with 18, 24, and 32 modules were synthesized as a result of de-cationization and dealumination of H-mordenites, and their catalytic properties were studied in the alkylation reaction of 2-methylphenol with 1- and 2-propanol. Based on the results obtained, higher yield and selectivity in the alkylation reaction of 2-methylphenol with 1- and 2-propanol were achieved with H-mordenite with a modulus of 24.

For the purpose of improving the performance properties, as well as the activity and selectivity of the selected H-mordenite catalyst, its modification with various ions (nickel, palladium) was carried out. The content of nickel and palladium ions in H-mordenite was varied within the range of 0.5-2.0 wt. %, and their effects on the results of the alkylation reaction of 2-methylphenol with 1- and 2-propanol were studied. The experimental results obtained are shown in Fig. 1 and 2. To ensure a visual comparison, the indicators obtained in the presence of H-mordenite with a modulus of 24 are presented on the ordinate axis. Analysis of these results reveals that H-mordenites containing 1.0 wt. % nickel or palladium show more favorable technological indicators in both reactions. The stable operating time of these catalytic systems also increased several times, reaching 200-240 hours.

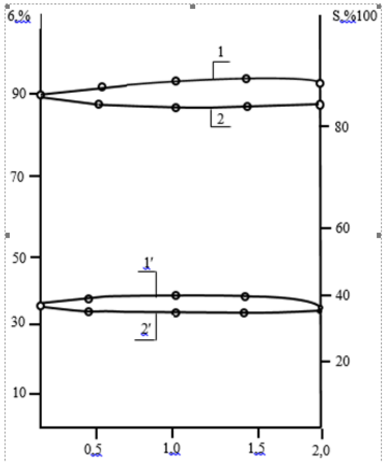


Fig. 1. Effect of the modifier concentration in H-mordenite on the yields of the converted (1, 2) and initial (1', 2') 2-methylphenol, obtained from the alkylation reaction of 2-methylphenol with 1-propanol, and the mixture of 2-propyl-6-methyl- and 4-propyl-6-methylphenols. 1, 1' - Pd, H-mordenite; 2, 2' - Ni, H-mordenite

The Study of the Alkylation Reaction of Cresols with 1-Propanol in the Presence of Ni, H-Mordenite and Pd, H-Mordenite Catalysts

The results of alkylation reaction of 2-, 3-, and 4-methylphenols with 1- and 2-propanol in the presence of Pd, H-mordenite and Ni, H-mordenite catalysts were thoroughly analyzed.

Thus, the results of the experiments show that Pd, H-mordenite catalyzes the alkylation of 2-, 3-, and 4-methylphenols with 1-propanol, resulting in the formation of *o*-isomers with selectivities of 75.5% and 80.5%, respectively. In contrast, Ni, H-mordenite catalyzes the *o*-alkylation to a significantly lower extent, with selectivities of 60.5%, 68.0%, and 78.5%, respectively. In the second case, the proportion of other isomers in the alkylates is higher (6.0-28.5%). The obtained results have practical significance and can serve as the basis for the development of technology.

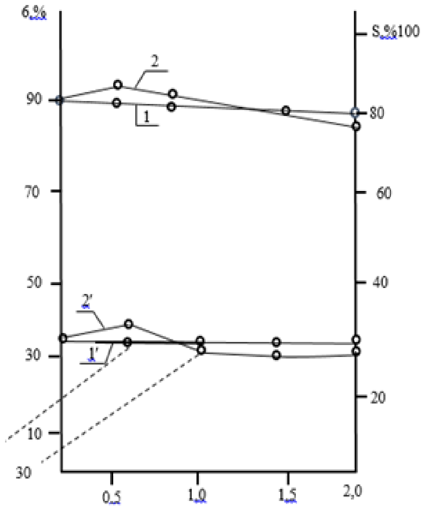


Fig. 2. Effect of the modifier concentration in H-mordenite on the yields of the 2-isopropyl-6-methyl- and 4-isopropyl-6-methylphenol mixture obtained from the alkylation reaction of 2-methylphenol with 2-propanol, calculated on the basis of the converted (1, 2) and initial (1', 2') 2-methylphenol. 1, 1' - Pd, H-mordenite; 2, 2' - Ni, H-mordenite

The selectivity of the monoproprуl derivatives obtained from the alkylation of cresols with 1-propanol in the presence of Pd, H-mordenite catalyst decreases in the following order: 2-methylphenol (96.5%) > 3-methylphenol (93.5%) > 4-methylphenol (84.0%). Analyzing of the results obtained from the alkylation of cresols with 2-propanol in the presence of the catalyst causes the following order: 3-methylphenol (90.5%) > 2-methylphenol (89.0%) > 4-methylphenol (82.5%). Alkylation with 1-propanol causes a decrease in selectivity in the following order for Ni, H-mordenite: 2-methylphenol (93.0%) > 3-methylphenol (91.0%) > 4-methylphenol (84.5%). Alkylation of cresols with 2-propanol, the decrease in selectivity is observed in the following order: 2-methylphenol (91.0%) > 3-methylphenol (88.5%) > 4-methylphenol (80.0%).

The analysis of the obtained results shows that among the cresols, 4-methylphenol is the most prone to successive propylation and isopropylation. The selectivity for the formation of 2,6-dipropyl-4-methylphenol in the presence of the studied catalysts is 12.5-14.5%, while for 2,6-diisopropyl-4-methylphenol, this value is 14.0-16.0%

Unlike some catalysts[3], palladium and nickel-modified H-mordenites partially carry out O-alkylation in the interaction of cresols with propanols, especially with 2-propanol. It's confirmed by the presence of monomethylphenols in the alkylate, as propyl and isopropyl ethers.

Thus, on the basis of experimental studies, more active H-mordenite with a determined module in the alkylation reaction of cresols with propanols was identified, and its palladium- and nickel-modified active and selective forms were discovered. A catalytic synthesis method for various propyl and isopropyl derivatives of monomethylphenols with practical significance, was proposed.

The alkylation reaction of cresols with propanols was also studied with other types of zeolites. The palladium-containing catalysts with 1.0 wt. % palladium include HSVM (x=40), CaY (x=4.7), and ZSM-5 (x=60).

The alkylation reactions of 2-methylphenol with 1- and 2-propanols were studied in the presence of the palladium-containing zeolites. As a result, from the interaction of 2-methylphenol with 1-propanol, all three catalysts exhibited *ortho* selectivity (63.5-68.0%) and *para* selectivity (22-24.5%). For the interaction with 2-propanol, the *ortho* selectivity was 57.5-66.0% and *para* selectivity was 24.0-27.5%. The highest overall selectivity (90.0-91.0%) and overall yield (52.6%) were observed for Pd-HSVM.

Thus, in the alkylation reaction of 2-methylphenol with propanols, the selective synthesis of propyl and isopropyl derivatives was achieved, and the activity of the palladium-containing HSVM, CaY, and ZSM-5 zeolites was confirmed.

In the alkylation reaction of other cresols with propanols, the overall selectivity and yield of monopropyl (isopropyl) derivatives were sufficiently high in the presence of Pd-HSVM catalyst.

---

[3] Agayeva, N.A. Catalytic Alkylation of 2-Methylphenol with 2-Propanol / N.A. Agayeva, K.M. Mutallimova, D.B. Tagiev // Journal of Chemical Problems – Baku: 2014. No. 4, pp. 377-380.

Practical Significance of Propyl and Isopropyl Derivatives of Phenols

Propyl and isopropyl derivatives of cresols expand the range of valuable intermediates that are effective and economically advantageous for the production of resins, pesticides, antioxidants, polymer materials, pharmaceuticals, and vitamins. Considering the existing raw material base and technological capabilities of the oil refining and petrochemical synthesis industries in our country, the production of valuable intermediates and products on the basis of propyl and isopropyl alcohols appears to be highly relevant. Examples of such processes include the catalytic alkylation of aromatic compounds based on local petrochemical raw materials, including phenol and cresols, with propanols to obtain mono- and dipropyl (isopropyl) derivatives.

The following are considered practical significant propyl and isopropyl derivatives of phenols:

– intermediates, which are inexpensive and similar in properties to the antioxidant ionol, such as 2,6-diisopropylphenol and 2,6-diisopropyl-4-methylphenol;

– isopropyl derivatives of phenols that can effectively prevent the formation of surface films during the air drying of protective coatings;

– phenol and cresol propyl derivatives obtained by dehydrogenation that are invaluable intermediates for the synthesis of specialty polymers, especially light-sensitive macromolecules;

– antioxidants obtained from the catalytic reactions of phenol and cresol with diiso- and di-tert-butyl derivatives, in the presence of bases, with beta and gamma unsaturated norbornene or alcohol, and applied in the synthesis of polyolefins.

Synthesis of 2,6-Diisopropyl-4-Methylphenol from 4-Methylphenol

Synthesis of 2,6-diisopropyl-4-methylphenol was studied in both one- and two-step processes by the alkylation of 4-methylphenol with 2-propanol: in the one-step alkylation process with 4-methylphenol and 2-propanol using Pd-HSVM catalyst, and the two-step alkylation reaction, where 2-isopropyl-4-methylphenol was first obtained from 4-methylphenol and 2-propanol in the first step and then alkylated with 2-

propanol in the second stage. The results obtained are shown in Tab. 1 and 2.

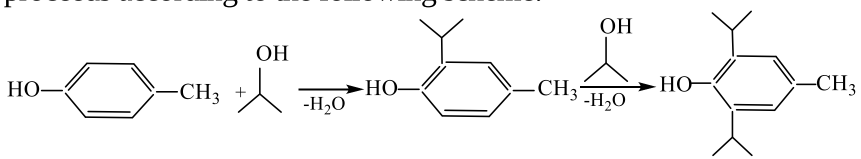
Table 1

The results of alkylation reactions of 4methylphenol with 2-propanol

Reaction conditions			Conversion of 4-methylphenol	The yield of the main reaction products calculated based on the converted 4-methylphenol, %		
T, °C	υ, st^{-1}	ν, mol/mol		2IP4MF	2,6DIP4MF	3IP4MF
340	1.0	1:1	45.0	82.0	12.5	3.0
360	1.0	1:1	53.5	76.0	17.5	4.0
360	1.0	1:2	66.5	68.0	24.0	2.5
360	1.0	1:4	80.0	55.0	35.2	3.5
380	1.0	1:1	61.1	66.0	25.0	6.5

In the resulting alkylates, the main products are 2-isopropyl-4-methylphenol (2IP4MF) and 2,6-diisopropyl-4-methylphenol (2,6DIP4MF). Small amounts of 3-isopropyl-4-methylphenol are also found. Alkylates obtained from experiments at high temperatures also contain some ethyl derivatives of 4-methylphenol and xylenols. These side products are also obtained by the alkylation of 2,6-diisopropyl-4-methylphenol (2IP4MF) with isopropyl alcohol, but they possess low concentration.

Thus, alkylation process of 4-methylphenol with 2-propanol mainly proceeds according to the following scheme:



Thus, it's possible obtaining a mixture of 2-IP4MF and 2,6-DIP4MF under specified conditions with overall selectivity ranging from 90.2% to 94.5% at various molar ratios (1:0.13÷0.40) by alkylation reaction of 4-methylphenol with 2-propanol in the presence of the Pd-HSVM catalyst. The selectivity for 2,6-DIP4MF is between 91.5% and 97.5% in the catalytic process performed based on 2-

IP4MF and 2-propanol, and the yield ranges from 38.2% to 46.5%. The purity of the obtained 2-IP4MF and 2,6-DIP4MF is approximately 99.0%.

Table 2

Results of the alkylation reaction of 2-isopropyl-4-methylphenol with 2-propanol

Reaction condition			Conversion of 2-isopropyl-4-methylphenol, %	The yield of the main reaction products calculated based on the converted 2-isopropyl-4-methylphenol, %	
T, °C	υ, st^{-1}	ν, mol/mol		2,6DIP4MF	Other products
340	1.0	1:1	44.0	91.5	5.6
360	1.0	1:1	50.5	92.0	6.0
360	1.0	1:0.75	40.0	95.5	2.5
360	0.8	1:0.5	39.5	97.5	1.0

Study of the Catalytic Properties of Pd-HSVM Catalyst in the Alkylation Reaction of 3-Methylphenol with Propanols

The study of the alkylation reaction of 3-methylphenol with 1- and 2-propanols in the presence of Pd-HSVM catalyst was carried out at temperatures of 310-400°C, volumetric flow rates of 0.7-1.3 st-1 h, and a molar ratio of cresol to alcohols ranging from 1:0.75 to 2. The effect of temperature, volumetric flow rate, and the molar ratio of components in the feedstock on the alkylation reaction, product yield, selectivity, and isomer composition was studied. The results obtained during the study are presented in Tab. 3 and 4.

Firstly, it should be noted that a large number of transformations occur during the interaction of 3-methylphenol with propanols. As is evident from Tab. 3, both *O*- and *C*-electrophilic substitutions occur in the alkylation reaction of 3-methylphenol with 1-propanol and the alkylates obtained include 3-methylphenol propyl ether (3MFPE), 2-propyl-5-methylphenol (2P5MF), 2-propyl-3-methylphenol (2P3MF), 4-propyl-3-methylphenol (4P3MF), and 2,6-

dipropyl-3-methylphenol (2,6DP3MF).

The propylation according to oxygen occurs at a lower temperature (310°C), and as the temperature increases, its selectivity decreases (340°C) and reaches a minimum (370°C). The main transformation in catalytic alkylation is the substitution according to carbon. Initially, monopropyl derivatives of 3-methylphenol (2P5MF, 2P3MF, and 4P3MF) are obtained, and as the temperature is increased and the molar ratio of alcohol in the feedstock is increased, the consecutive alkylation process is accelerated, raising the selectivity of the reaction for 2,6DP3MF from 11.0% to 14.5%

The analysis of the obtained results reveals that, in the alkylation reaction of 3-methylphenol with 1-propanol, the main products are the monopropyl derivatives of cresol (2P5MF, 2P3MF, and 4P3MF), and their yields calculated based on the converted cresol range from 83.0% to 97.5%, while the yields calculated based on the 3-methylphenol in the feedstock range from 33.9% to 66.9%.

The effect of temperature, volumetric flow rate, and the molar ratio of components in the feedstock on the alkylation reaction of 3-methylphenol with isopropyl alcohol was studied, and the results are set into Tab. 4.

As is evident from the table, the main products of the catalytic process are 3-methylphenol isopropyl ether (3MFIPE), 2-isopropyl-5-methylphenol (2IP5MF), 3-methyl-4-isopropylphenol (3M4IPF), 3-isopropyl-5-methylphenol (3IP5MF), and 2,4-diisopropyl-5-methylphenol (2,4DIP5MF). The catalytic alkylation proceeds via a consecutive-parallel mechanism. O-alkylation and C-isopropylation reactions are parallel, while the formation of diisopropyl derivatives of m-cresol proceeds through a consecutive mechanism. The product of O-alkylation - 3MFIPE, is obtained with 10.5% selectivity at 310°C. When the temperature increases to 370°C, a small amount of it (1.5-2.0% selectivity) is observed in some experiments.

As with propylation, the isomer obtained with higher yield and selectivity from the alkylation of m-cresol with 2-propanol is 2IP5MF. At 310°C, the yield calculated based on the converted cresol is 70.5%. As the temperature increases, the yield of this compound decreases, reaching 61.5% at 370°C and 56.5% at 400°C.

Table 3

The results of alkylation reaction of 3-methylphenol with 1-propanol in the presence of Pd-HSVM catalyst

Reaction condition			Conversion of 3-methylphenol, %	The yields of the reaction products calculated based on the converted 3-methylphenol, %					The yields calculated based on the 3-methylphenol in the feedstock, %			
T ^{0}C	υ, st^{-1}	ν, mol/mol		3MFPE	2P5MF	2P3MF	4P3MF	2,6DP3MF	2P5MF	2P3MF	4P3MF	2,6DP3MF
310	1.0	1:1	38.5	9.0	70.0	12.0	6.0	1.5	27.0	4.6	2.3	0.6
340	1.0	1:1	49.0	3.0	61.5	18.0	13.5	2.5	30.1	8.8	6.6	1.2
370	1.0	1:1	59.5	-	58.0	20.0	17.5	2.0	34.5	11.9	10.4	1.2
400	1.0	1:1	66.0	-	54.5	15.5	17.0	11.0	36.0	10.2	11.2	7.3
370	0.7	1:1	62.5	-	56.0	19.0	19.5	4.0	35.0	11.9	12.2	2.5
370	1.3	1:1	53.0	1.5	60.0	18.5	16.0	1.5	31.8	9.8	8.5	0.8
370	1.0	1:0.75	48.5	-	70.0	17.5	10.0	1.5	34.0	8.5	4.9	0.7
370	1.0	1:2	80.5	1.0	51.0	16.0	16.0	14.5	41.1	12.9	12.9	11.7

Table 4

The results of the alkylation reaction of 3-methylphenol with 2-propanol in the presence of Pd-HSVM catalyst

Reaction condition			Conversion of 3-methylphenol,%	The yields of the reaction products calculated based on the converted 3-methylphenol, %					The yields calculated based on the 3-methylphenol in the feedstock, %			
T ^{0}C	υ, st^{-1}	ν, mol/mol		3MFIPE	2IP5MF	3M4IPF	3IP5MF	2,4DIP5MF	2IP5MF	3M4IPF	3IP5MF	2,4DİP5MF
310	1.0	1:1	40.0	10.5	70.5	13.0	2.5	2.0	28.2	5.2	1.0	0.8
340	1.0	1:1	51.0	4.0	65.0	17.0	5.0	6.0	33.2	8.7	2.6	3.1
370	1.0	1:1	63.5	-	61.5	20.0	8.5	7.5	39.0	12.7	5.4	4.8
400	1.0	1:1	70.0	-	56.5	16.5	11.0	13.0	39.6	11.6	7.7	9.1
370	0.7	1:1	69.5	-	60.0	18.0	9.5	10.5	41.7	12.5	6.6	7.3
370	1.3	1:1	55.0	2.0	66.0	16.0	7.0	6.0	36.3	8.8	3.9	3.3
370	1.0	1:0.75	54.0	-	69.5	16.0	6.0	6.5	37.5	8.6	3.2	3.5
370	1.0	1:2	82.5	1.5	50.0	14.0	14.5	16.5	41.3	11.6	12.0	13.6

Among other mono-isopropyl isomers of cresol, 3M4IPF forms with 13.0-20.0% selectivity. The lowest result is obtained at 310°C, while the highest selectivity is observed at 370°C. With the increase in temperature, the selectivity of the third mono-isopropyl cresol (3IP5MF) rises to 11.0%. Raising the temperature from 310°C to 400°C also increases the selectivity of another product - 2,4DIP5MF, obtained by consecutive alkylation, from 2.0% to 13.0%.

In the alkylation reaction of 3-methylphenol with 2-propanol, the total yield of mono-isopropyl isomers (2IP5MF, 3M4IPF, and 3IP5MF) calculated based on the converted cresol (91.5%) was obtained under the following reaction conditions: T-370°C, υ-1.0 st-1, ν=1:0.75 mol/mol. The high yield of these isomers (64.9%) calculated based on the 3-methylphenol in the feedstock was achieved under the following conditions: T-370°C, υ-1.0 st-1, ν=1:2 mol/mol.

One of the interesting aspects of the study is the significant amount of the 5-isopropyl derivative of 3-methylphenol, which is used in the production of pesticides. As seen in Tab. 4, due to the unique properties of the Pd-HSVM catalyst, 3IP5MF phenol can be obtained with 2.5-14.5% selectivity and 1.0-12.0% yield in alkylates. The difference in boiling points of mono-isopropyl derivatives of m-cresol (6.0-15.0°C) is sufficient to allow for their precise separation by rectification, ensuring that the purity levels (≥ 99.0%) are high.

Palladium-containing zeolites (Y, mordenite, ZSM-5) exhibit sufficient catalytic activity in the alkylation reactions of phenol and cresols with methanol, ethanol, and propanols. However, the properties of these catalysts have been practically unexplored in the alkylation reactions of phenol with propanol homologs.

Based on this, the alkylation reaction of 3,4-isomer of dimethylphenols with 1- and 2-propanols was studied in the presence of PdCaY, Pd, H-mordenite, Pd-ZSM-5, and Pd-HSVM catalytic systems, and the results were compared with cases involving cresols.

The nature of the main and side transformations occurring in the alkylation process of cresols with 1- and 2-propanols differs depending on the reaction conditions and the composition of the catalyst used. In a mild process, the O-alkylation share in the interaction of monomethylphenols with propanols is quite significant.

With increasing temperature and contact time, the share of C-alkylation in the aromatic core increases, while the rate of O-substitution decreases sharply. The reaction conditions also affect the main and side transformations of the propanols. Special studies were carried out for determining the nature of these transformations, and based on the results, kinetic pathways were identified. An important result of these studies is the emergence of a new method for obtaining propyl and isopropyl derivatives of cresols.

The alkylation reaction of a mixture of 2-, 3-, and 4-methylphenols with 1-propanol (molar ratio 1:1) resulted in the formation of primarily propyl ethers of the cresol isomers in the presence of NaX zeolite, at a temperature of 280°C and a volumetric flow rate of 1.0 st^{-1} and the purity was 98.0-99.0% after the appropriate treatment.

The catalytic conversion of the resulting ethers was studied in the presence of Pd-HSVM zeolite and OMNIKAT-210P catalysts. The results obtained are shown in Tab. 5.

The first noteworthy point is that the composition of the catalyzates differs from that of the alkylates obtained from the 1-propanol alkylation of the respective cresol. For example, selectivity for 2-propyl-6-methylphenol formed by the isomerization of 2-methylphenol propyl ether is several times lower in comparison to the analogous selectivity of the isomer obtained from the alkylation reaction. Selectivity for this isomer is temperature-dependent with 22.0% at 320°C and 10.0% at 360°C in the case of using Pd-HSVM. These values are higher at 35.0% and 30.0%, respectively, in the presence of the OMNIKAT-210P catalyst.

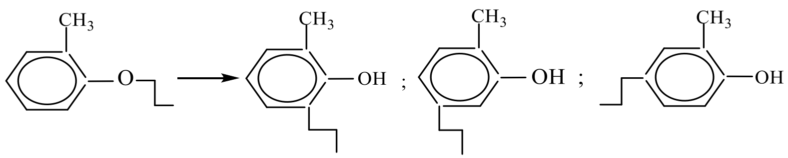
Regarding other propyl derivatives of 2-methylphenol, the intra-molecular conversion of the ether results in the formation of 2-methyl-5-propylphenol with 45-50.0% selectivity and 2-methyl-4-propylphenol with 28.0-30.0% selectivity. In comparison to OMNIKAT-210P, these values are 8-15.0% higher in the first case and 7.5% higher at 360°C in the second case.

Schematic representation of the main transformations of 2-methylphenol propyl ether can be shown as follows.

Table 5

The results of the catalytic conversion of 2-methylphenol propyl ether

Properties	Catalyst			
	Pd-HSVM		OMNIKAT-210P	
Temperature, °C	320	360	320	360
Volumetric flow rate, st^{-1}	0.8	0.8	0.8	0.8
Conversion of 2-methylphenol propyl ether, %	86.0	100	77.0	99.0
The yields of the products calculated based on the converted 2-methylphenol propyl ether, % Including	-	-	-	-
2-propyl-6-methylphenol	22.0	10.0	35.0	30.0
2-methyl-5-propylphenol	45.0	50.0	30.0	42.0
2-methyl-4-propylphenol	30.0	28.0	30.5	20.5
2-methyl-3-propylphenol	-	3.0	1.0	1.5
Dipropyl derivatives of 2-methylphenol	1.0	4.0	1.5	2.5
Cresols	1.5	3.0	0.5	1.5



The yields of 2-methyl-3-propylphenol and 2-methylphenol dipropyl derivatives in the obtained catalyzates vary depending on the catalyst and temperature. Specifically, the yield is 1.0% at 320°C and 3.0% at 360°C in the presence of Pd-HSVM. The respective yields at these temperatures are 1.0% and 4.0% in the presence of OMNIKAT-210P. As the temperature increases, the rate of dealkylation in the catalytic process slightly increases. This transformation, primarily accompanied by depropylation, results in cresols with a formation selectivity of 1.5% and 3.0% in the presence of Pd-HSVM, and 0.5% and 1.5% when a catalytic cracking catalyst is used.

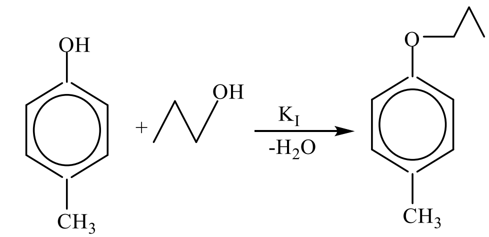
The ether is practically fully converted in the presence of both catalysts at 360°C.

It's interesting, that intramolecular isomerization predominates in the conversion process of 2-methylphenol propyl ether. Specifically, the total selectivity for the monopropyl derivatives of the cresol formed by the isomerization of the ether is 91.0% at 360°C and 97.0% at 320°C in the presence of Pd-HSVM. In the case of using industrial catalyst, the selectivities are 94.0% and 96.5%, respectively. As shown, an increase in temperature results in a decrease in selectivity for both catalysts.

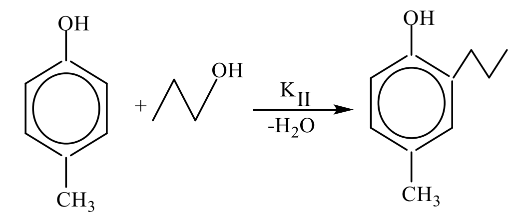
Kinetic Studies of the Alkylation Reaction of 4-Methylphenol wth 1-Propanol

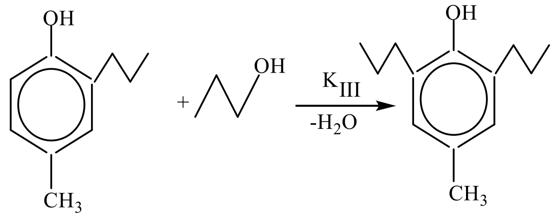
Based on previously conducted studies, the main pathways in the alkylation process of 4-methylphenol with 1-propanol have been determined.

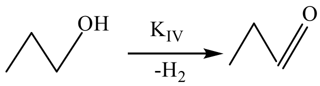
I



II



III 

IV 

The four participants of the reaction are selected as key substances (3): 4-methylphenol (1), 1-propanol (2), 2-propyl-4-methylphenol (3), and 2,6-dipropyl-4-methylphenol (4).

The number of the selected key substance corresponds to the number of its partial pressure. The given stoichiometric basis is derived from the graphical mechanism of catalytic alkylation (Fig.3).

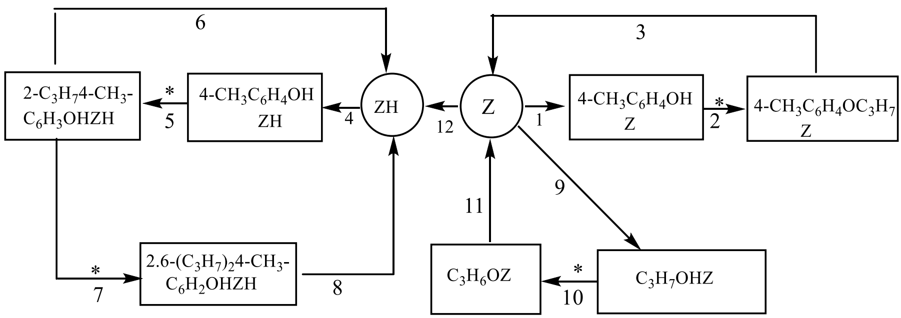


Figure 3. Graphical mechanism of the catalytic alkylation reaction of 4-methylphenol with 1-propanol

Steps 2, 5, 7, and 10 are limiting, but the other steps are chosen as rapidly occurring equilibrium steps. Step 12 is given to express the two types of centers at equilibrium on the surface.

Based on the obtained experimental results and the proposed model, the kinetic constants were calculated. Their values were initially determined graphically and then refined using the method of minimizing ortho-quadratic errors for the rates calculated through the system of equations (1-4) based on the MATLAB program.

$$r_1 = K_1 P_1 P_2 \quad (1)$$
$$r_{11} = K_{11} P_1 P_2 \quad (2)$$
$$r_{111} = K_{111} P_3 P_2 \quad (3)$$
$$r_{1V} = K_{1V} P_2 \quad (4)$$

As a result, the following Arrhenius expressions were obtained:

$$K_1 = 7.4 \cdot 10^2 \cdot \frac{exp\left(-\frac{33261}{RT}\right) mol}{sm^3(kat) \cdot st} \cdot MPa^2; \quad (5)$$

$$K_{II} = 5.05 \cdot 10^9 \cdot \frac{exp\left(-\frac{105807}{RT}\right) mol}{sm^3(kat) \cdot st} \cdot MPa^2; \quad (6)$$

$$K_{III} = 3.583 \cdot 10^7 \cdot \frac{exp\left(-\frac{78560}{RT}\right) mol}{sm^3(kat) \cdot st} \cdot MPa^2; \quad (7)$$

$$K_{IV} = 2.05 \cdot 10^3 \cdot \frac{exp\left(-\frac{30265}{RT}\right) mol}{sm^3(kat) \cdot st} \cdot MPa; \quad (8)$$

For the purpose of obtaining a more favorable basis, modifying the kinetic arrangements in equations (1-4) led to more erroneous results.

The obtained kinetic model adequately describes both the qualitative and quantitative aspects of chemical conversions occurring on the catalytic surface and can be used in the future for mathematical modeling, optimization, and the selection and calculation of the reactor.

CONCLUSIONS

1. The more active and selective modified H-mordenite catalyst (SiO_2/Al_2O_3=24) was determined by the alkylation process of 2-methylphenol with propanols and its catalytic and performance properties were enhanced by modification with palladium and nickel. The most favorable compositions in H-mordenites containing 0.5-2.0 wt.% of modifiers were found to be H-mordenites with 1.0 wt.% nickel or palladium [6, 9].
2. The selectivity of the obtained monopropyl derivatives decreased in the following order in the alkylation reaction of cresols with 1-propanol in the presence of Pd, H-mordenite catalyst: 2-methylphenol (96.5%) > 3-methylphenol (93.5%) > 4-methylphenol (84.0%). The corresponding selectivity decreased in the order when alkylation was carried out with 2-propanol: 3-methylphenol (90.5%) > 2-methylphenol (89.0%) > 4-methylphenol (82.5%). In the interaction of cresols with 2-propanol over Ni, H-mordenite, the selectivity of the mono-isopropyl derivatives decreased in the order: 2-methylphenol (91.0%) > 3-methylphenol (89.5%) > 4-methylphenol (80.0%). When alkylation was performed with 1-propanol, the sequence changed to: 2-methylphenol (93.0%) > 3-methylphenol (91.0%) > 4-methylphenol (84.5%). Sequential propylation (isopropylation) occurs more with 4-methylphenol [3, 12, 13].
3. The activity and selectivity of various modular palladium-containing (HSVM, ZSM-5, and CaY) zeolites in the alkylation reactions of 2-, 3-, and 4-methylphenols with 1- and 2-propanols were determined, and Pd-HSVM was selected. Its properties were compared with Pd, H-mordenite, revealing that it’s an effective catalytic system for the production of propyl and isopropyl derivatives of cresols [6, 11, 12].
4. It was determined that Pd-HSVM catalyst reveals high activity and selectivity in the alkylation reactions of cresols with propanols. This catalyst was primarily an *ortho*-alkylating catalyst for 2-methylphenol, and when isopropyl alcohol was used as the alkylating agent, it also exhibited significant *para*-alkylating

properties [15].

5. The yields calculated on the basis of converted and collected cresol for the monopropyl derivatives (2P5MF, 2P3MF, and 4P3MF) obtained by the alkylation reaction of 3-methylphenol with 1-propanol in the presence of Pd-HSVM, ranged from 83.0% to 97.5% and 33.9% to 66.9%, respectively. The total selectivity for mono-isopropyl isomers (2IP5MF, 4IP3MF, and 3IP5MF) obtained by the alkylation of 3-methylphenol with 2-propanol, was 91.5% (T=370°C, υ=1.0 st^{-1}, ν=1:0.75 mol/mol), and the total yield calculated based on the initial cresol was 64.9%, obtained under the following conditions: T=370°C, υ=1.0 st^{-1}, ν=1:2 mol/mol [2, 5, 11].
6. The effective method for obtaining 2,6-diisopropyl-4-methylphenol in one- and two-step processes using Pd-HSVM zeolite was studied in the alkylation reaction of 4-methylphenol with 2-propanol. The mixture of 2-isopropyl-4-methylphenol and 2,6-diisopropyl-4-methylphenol in various molar ratios (1:0.13-0.40) showed total selectivity of 90.2-94.5%, and the diisomer was obtained with a selectivity of 91.5-97.5% and yields of 38.2-46.5% from the interaction of 2-isopropyl-4-methylphenol with 2-propanol [1, 4, 7, 10].
7. As the number of methyl groups in phenol molecule increases during propylation and isopropylation reactions in the presence of Pd-HSVM, a decrease was observed in selectivity for the desired products and an increase in yields (compared to cresols). For example, selectivity for 2-propyl-4,5-dimethylphenol obtained from propylation of 3,4-dimethylphenol was 90.0%, and for 2-isopropyl-4,5-dimethylphenol obtained from isopropylation - 82.5%. The yields for these products were 47.0% and 54.0%, respectively. Catalytic conversion of cresol propyl ethers resulted in the formation of thermodynamically more stable isomers [14].
8. Alkylation process of cresols with propanols, in addition to the main conversion, the nature of side reactions was clarified. The reaction pathways for the alkylation of 4-methylphenol with 1-propanol, reflecting both the main and side conversions, were determined, kinetic constants were calculated, and a low-error

kinetic model was developed. A method for selective and high-yield synthesis of 2,6-diisopropyl-4-methylphenol from the alkylation of 4-methylphenol with 2-propanol in the presence of Pd-HSVM was also developed [7, 8, 14].

The main results of the dissertation were expressed in the following publications:

1.Aghayev, A.A. Alkilation of 4-methylphenol with 1-and 2-propanols over palladium-contaning zeolite / Akbar Aghayev, Khayala Gadjieva, Ziyafet Abushova, Penah Shirinov // European Science Review Scientific Journal, – Vienna: -2018. November-December, vol.1, №11-12, - p.133-135.

2.Hajiyeva, Kh.A., Aghayeva, N.A., Garayeva, I.E., Mutallimova, K.M. Study of the alkylation reaction of 3-methylphenol with 1-propanol // International scientific-practical conference "Innovative prospects for the development of oil refining and petrochemistry," dedicated to the 110th anniversary of Academician V.S. Aliyev, - Baku: - November 9-10, 2018. - p.51.

3.Hajiyeva, Kh.A., Mutəllimova, K.M., Ramazanov, G.A., Aghayev, A.A. Alkylation of 4-methylphenol with isopropyl alcohol in the presence of mordenites // Proceedings of the scientific conference "Nağıyev Readings" dedicated to the 110th anniversary of Academic Murtuza Nağıyev, - Baku: October 30-31, 2018. - p.162.

4.Aghayev, A.A. Study of the catalytic synthesis process of 2,6-diisopropylphenol / A.A. Aghayev, Kh.A. Hajiyeva, P.T. Shahtakhtinskaya, K.M. Mutallimova // News of Sumgayit State University. Natural and Technical Sciences Section, - Sumgayit: -2019. Volume 19, No.4, - p.19-22.

5.Aghayev, A.A., Hajiyeva, Kh.A., Garayeva, I.E., Aghayeva, N.A. Catalytic alkylation of 3-methylphenol with 2-propanol // Abstracts of the International Scientific Conference on "Current Issues of Modern Chemistry" dedicated to the 90th anniversary of the academician Y.H. Mammadaliyev, - Baku: - October 2-4, 2019. -p.241.

6.Hajiyeva, Kh.A. Catalytic alkylation of 2-methylphenol with

2-propanol // Materials of the XXIII Republican Scientific Conference for PhD Students and Young Researchers, - Baku: - December 3-4, 2019. Volume I, - p.75-76.

7.Hajiyeva, Kh.A. Study of the synthesis process of 2,6-diisopropyl-4-methylphenol // Sumgayit: Sumgayit State University, Scientific News. Natural and Technical Sciences Section, - 2020. Volume 20, No.3, - p.38-40.

8. Aghayev, A.A., Muradov, M.M., Hajiyeva, Kh.A. Kinetic model of the alkylation process of 4-methylphenol with 1-propanol. Mathematical Methods in Engineering and Technologies // Proceedings of the International Scientific Conference, Publishing House of Polytechnic University, - St. Petersburg: - 2020. Volume 12, Part 15, - p.13-17.

9. Hajiyeva, Kh.A. Catalytic alkylation of 2-methylphenol with propanols / Kh.A. Hajiyeva, M.M. Muradov, M.K. Nazarova, A.A. Aghayev // Annali d'Italia Scientific Journal of Italy, - Italy: - 2020. Vol.1, No.11, - p.9-11.

10. Aghayev, A.A. Method for the synthesis of a mixture of 2-isopropyl-4-methylphenol and 2,6-diisopropyl-4-methylphenol, Patent i2021 0045, Republic of Azerbaijan / A.A. Aghayev, M.M. Muradov, P.T. Shahtakhtinskaya, Kh.A. Hajiyeva – 2021.

11. Aghayev, A.A. Study of the alkylation reaction of 3-methylphenol with 1-propanol in the presence of different catalysts / A.A. Aghayev, M.M. Muradov, Kh.A. Hajiyeva, K.M. Mutallimova // News of Sumgayit State University. Natural and Technical Sciences Section, - Sumgayit: - 2022. Volume 22, No.2, - p.17-20.

12. Aghayev, A.A., Muradov, M.M., Hajiyeva, Kh.A., Mutallimova, K.M. Study of the catalytic alkylation of cresols with 1-propanol // Proceedings of the Republican Scientific Conference dedicated to the 90th anniversary of Academic Nadir Mir-Ibrahim oglu Seyidov on the topic "Catalysts, Olefin-based Oils", - Baku: - May 19-20, 2022. - p.79.

13. Hajiyeva, Kh.A. Study of the alkylation reaction of cresols with 1-propanol in the presence of Ni, H-mordenite, and Pd, H-mordenite catalysts // - Sumgayit: Sumgayit State University, News of Sumgayit State University. Natural and Technical Sciences Section, -

2022. Volume 22, No.3, - p.46-48.

14. Aghayev, A.A. Alkylation of 3,4-dimethylphenol with propanols in the presence of palladium-containing zeolites / A.A. Aghayev, M.M. Muradov, Kh.A. Hajiyeva, N.A. Murshudlu // Neftepererabotka i Neftekhimiya. Scientific-technical achievements and advanced experience, - Moscow: - 2022. - p.11-13.

15. Aghayev, A.A. Alkylation of 2-methylphenol with normal alcohols C_1-C_3 over Pd-HSVM / A.A. Aghayev, M.M. Muradov, Kh.A. Hajiyeva // Bashkir Chemical Journal, - Ufa: - 2023. Volume 30, No.3, - p.7-9.

The defense will be held on 14 May 2025 at 10:00 at the meeting of the Dissertation council ED 1.16 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at academician Y.H. Mammadaliyev Institute of Petrochemical Processes of the Ministry of Science and Education of the Republic of Azerbaijan.

Address: AZ 1025, Baku, 30 Khojaly ave.

Dissertation is accessible at the Library of academician Y.H. Mammadaliyev Institute of Petrochemical Processes of the Ministry of Science and Education of the Republic of Azerbaijan.

Electronic version of the abstract is available on the official website of academician Y.H. Mammadaliyev Institute of Petrochemical Processes of the Ministry of Science and Education of the Republic of Azerbaijan: www.nkpi.az

Abstract was sent to the required addresses on 14 Aprel 2025.

Signed for print: 09.04.2025

Paper format: A5

Volume: 36120

Number of copies: 20