HETEROGENEOUS – CATALYTIC PROCESS FOR OBTAINING PYRIDINES FROM THE CROTON FRACTION: CATALYST SELECTION AND REACTION PARAMETERS

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Annotation. This article describes the technology of synthesizing pyridine and alkylpyridines by a heterogeneous-catalytic method based on acetylene and its processing products. In the study, new types of multifunctional catalysts were developed using local raw materials, and their composition, structure, and physicochemical properties were investigated. The heterocyclization reaction of the croton fraction with ammonia and amines under flow conditions was examined, and the effects of temperature, space velocity, molar ratio of reagents, and catalyst composition on the reaction yield were determined. Optimal conditions for obtaining pyridine and 3-methylpyridine from the acetaldehyde–formaldehyde–ammonia system were established, and the structures of the synthesized compounds were confirmed by NMR, IR, and chromatographic-mass spectrometry. The obtained pyridine derivatives were tested as effective inhibitors of metal corrosion, demonstrating high protective efficiency (92–94%). The research results contribute to the development of technology for producing pyridine and its derivatives from local raw materials and their implementation in the chemical, pharmaceutical, and anticorrosion protection industries.

Keywords. Pyridine; alkylpyridines; heterogeneous catalysis; acetylene; carbonyl compounds; croton fraction; ammonia; heterocyclization; polyfunctional catalyst; 3-methylpyridine; β-picoline; corrosion inhibitors; reaction selectivity.

Аннотация. В статье описана технология синтеза пиридина и алкилпиридинов гетерогенно-каталитическим методом на основе ацетилена и продуктов его переработки. В ходе исследования были разработаны новые типы многофункциональных катализаторов с использованием местного сырья, а также изучены их состав, структура и физико-химические свойства. Исследована реакция гетероциклизации кротоновой фракции с аммиаком и аминами в проточном режиме, определено влияние температуры, объемной скорости, мольного соотношения реагентов и состава катализатора на выход целевых продуктов. Установлены оптимальные условия получения пиридина и 3-метилпиридина из системы ацетальдегид–формальдегид–аммиак. Структура синтезированных соединений подтверждена методами ЯМР, ИК-спектроскопии и хромато-масс-спектрометрии. Полученные производные пиридина были испытаны в качестве эффективных ингибиторов коррозии металлов и показали высокую защитную эффективность (92–94%). Результаты исследования способствуют развитию технологий получения

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пиридина и его производных из местного сырья и их внедрению в химической, фармацевтической и антикоррозионной промышленности.

Ключевые слова. Пиридин; алкилпиридины; гетерогенный катализ; ацетилен; карбонильные соединения; кротоновая фракция; аммиак; гетероциклизация; полифункциональный катализатор; 3-метилпиридин; β-пиколин; ингибиторы коррозии; селективность реакции.

Annotatsiya. Maqolada asetilen va uni qayta ishlash mahsulotlari asosida piridin va alkilpiridinlarni geterogen-katalitik usulda sintez qilish texnologiyasi bayon etilgan. Tadqiqot davomida mahalliy xomashyolardan foydalangan holda yangi turdagi ko‘p funksiyali katalizatorlar ishlab chiqildi hamda ularning tarkibi, tuzilishi va fizik-kimyoviy xossalari o‘rganildi. Oqimli sharoitda kroton fraksiyasining ammiak va aminlar bilan geterotsikllanish reaksiyasi tadqiq qilinib, harorat, fazoviy tezlik, reagentlarning molyar nisbati va katalizator tarkibining mahsulot chiqishiga ta’siri aniqlandi. Asetaldegid–formaldegid–ammiak tizimidan piridin va 3-metilpiridin olishning optimal sharoitlari belgilandi. Sintez qilingan birikmalarning tuzilishi YAMR, IQ-spektroskopiya va xromato-mass-spektrometriya usullari yordamida tasdiqlandi. Olingan piridin hosilalari metallarning korroziyasiga qarshi samarali ingibitorlar sifatida sinovdan o‘tkazilib, yuqori himoya samaradorligini (92–94 %) namoyon etdi. Tadqiqot natijalari piridin va uning hosilalarini mahalliy xomashyolardan olish texnologiyalarini rivojlantirish hamda ularni kimyo, farmatsevtika va korroziyadan himoyalash sohalarida joriy etishga xizmat qiladi.

Kalit so‘zlar. Piridin; alkilpiridinlar; geterogen kataliz; asetilen; karbonil birikmalar; kroton fraksiyasi; ammiak; geterotsikllanish; ko‘p funksiyali katalizator; 3-metilpiridin; β-pikolin; korroziya ingibitorlari; reaksiya selektivligi.

Introduction.

Heterocyclic compounds, especially pyridine and its alkyl derivatives, are among the most important directions of modern organic synthesis. The pyridine ring is a structural component of many natural substances and is widely used in the synthesis of biologically active pharmaceuticals, agricultural chemicals, polymers, dyes, photographic materials, and ion-exchange resins. Therefore, the development of economically efficient, selective, and continuous technologies for obtaining pyridine and alkylpyridines is considered highly relevant.

In the global chemical industry, scientific research aimed at creating polyfunctional, highly selective heterogeneous catalysts for synthesizing pyridine derivatives is consistently advancing. In this context, the heterocyclization reaction of carbonyl compounds, acetylene derivatives, and ammonia is regarded as one of the main directions. Since these processes consist of complex sequential steps, optimizing catalyst composition, identifying the nature of active centers, and

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explaining their reaction mechanisms constitute essential scientific and practical tasks.

In Uzbekistan's chemical industry, large-scale reforms are being implemented to develop high value-added products based on local raw materials, introduce environmentally safe and energy-efficient technologies, and increase the processing of oil and gas resources. The Development Strategy of "New Uzbekistan" designates the creation of energy-saving and environmentally friendly technologies, localization of chemical industry products, and the introduction of innovative developments into industrial production as priority tasks. Establishing domestic production of pyridine and its derivatives aligns with these priorities, creating significant opportunities for enhancing economic efficiency, producing import-substituting products, and developing new chemical technologies. The synthesis of pyridine and alkylpyridines by a heterogeneous-catalytic method based on available raw materials such as croton fraction, acetaldehyde, formaldehyde, and ammonia is considered a promising direction. Such processes offer advantages including high selectivity, inexpensive raw materials, reusable catalysts, and environmental cleanliness.

Therefore, the main objectives of this study were to investigate the heterocyclization of the croton fraction with ammonia and amines, examine the influence of various catalyst compositions on the reaction, determine the optimal conditions, and identify the physicochemical properties of the synthesized pyridine derivatives. In addition, to increase the practical significance of the obtained pyridine derivatives, their corrosion-inhibiting properties for metals were investigated. This makes the results of the research relevant for the chemical, oil-gas, metallurgical, and pharmaceutical industries.

Thus, 2- and 4-methylpyridines and 2-methyl-5-ethylpyridines are used in industry as raw materials for the production of 2- and 4-vinylpyridines and 2-methyl-5-vinylpyridine, which serve as the basis for manufacturing latexes for impregnating fine cord, ion-exchange resins, photographic films, and other materials. Many physiologically active drugs used in agriculture and healthcare are produced on the basis of pyridine and methylpyridines.

Derivatives of 3- and 4-methylpyridines are effective agents for the treatment of tuberculosis. Due to the steadily increasing demand for alkylpyridines and their limited production in the coke industry, the synthesis of synthetic alkylpyridines has been developed and implemented in many industrially developed countries. The resources of alkylpyridines extracted from coal tar are highly limited. Moreover, coal tar contains more than 70 pyridine isomers, and isolating individual bases in their pure form is a very time-consuming process. In addition, coal tar mainly contains pyridine and 2-methylpyridine.

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To date, methods for the technical synthesis of alkylpyridines from various organic compounds have been developed. All alkylpyridine production plants in the world use only carbonyl compounds and ammonia as raw materials.

A review of the literature shows the industrial methods for producing synthetic alkylpyridines and the main directions of their application.

The synthesis of a mixture of pyridine and 3-methylpyridine from carbonyl compounds and ammonia belongs to well-studied processes. JSC "Navoiyazot" has established production of 20 thousand tons of acetaldehyde and 7 thousand tons of formaldehyde per year. Accordingly, the study of the joint production process of pyridine and 3-methylpyridine from acetaldehyde, formaldehyde, and ammonia has attracted considerable interest.

The heterocyclization reaction of carbonyl compounds with ammonia (and amines) involves complex parallel–sequential reactions, including nucleophilic addition of ammonia, isomerization, dehydrocyclization, and others. All these processes can be combined in the vapor phase in the presence of multifunctional catalysts. Based on this, in selecting the catalyst composition, the role of each component in the formation reactions of pyridine and methylpyridines was taken into account.

Elements with strongly filled d10 orbitals (Cu^{+1}, Ag^{+1}, Au^{+2}, Hg^{+2}, Zn^{+2}, Cd^{+2}, Pt^{+2}, Ni^{0}, etc.) have the ability to form π-complexes with acetylene compounds. That is, if these elements are present in the catalyst composition, the activation of the acetylene component is characterized, on the one hand, by the deformation of acetylene due to the partial shift of its electron pair into the free s-orbitals of the ion, and on the other hand, by the formation of dative or donor π-bonds resulting from the transfer of electrons from the ion's d-orbitals to the antibonding orbital of acetylene.

The transfer of electrons from π-ligands to the metal and from the metal back to the π-ligand can lead to significant polarization of the unsaturated molecule. The formation of donor–acceptor bonding in the metal–carbonyl group results in a decrease in electron density on the carbon atoms of the –C=O bonds. Consequently, the electrophilicity of the double bonds and their ability to interact with nucleophilic reagents increase.

Indeed, elements and molecules possessing d10 orbitals have been shown to be effective catalysts in acetylene conversion reactions. The use of zinc oxide and chromium is associated with their widespread application in the synthesis and dehydrogenation processes of methanol and dehydrocyclization.

Since iron oxides exhibit affinity toward ammonia and are used as contact materials in ammonia synthesis, we assumed that their presence in the catalyst

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composition should contribute to the adsorption and activation of ammonia during the synthesis of pyridine bases.

In addition, we investigated the heterocyclization reaction of the croton fraction with aniline and o-aminophenol in the presence of mixed multifunctional catalysts with the following composition, mass %:

Cd – 3,0-5,0; ZnO – 5,0-10,0; Cr_2O_3 – 3,0-5,0; Fe_2O_3 – 3,0-5,0; γ-Al_2O_3 – 75,0-86,0

The catalysts were prepared by suspension, molding, washing, drying, and calcination. Aluminum oxide hydrate was used as the carrier (PPP–33%). A 3–5% solution of hydrofluoric and acetic acids was used as the peptizing agent. The textural properties of the developed catalysts were determined (Table 1).

Table 1

Physical-Chemical and Operational Properties of the Developed Catalysts

№	Composition, % mass	Specific Surface Area, m^2/g	Mechanical Strength, MPa	Service Life before Regeneration, h	Total, g/kg·cat·h
1.	CdF_2 – 3,0 ZnO – 5,0 Cr_2O_3 – 5,0 Al_2O_3 – 87,0	225	6,8	68,0	81,0
2.	CdF_2 – 3,0 ZnO – 7,0 Fe_2O_3 – 5,0 Al_2O_3 – 83,0	168	7,1	76,0	92,0
3.	CdF_2 – 5,0 ZnO – 5,0 Cr_2O_3 – 3,0 Fe_2O_3 – 3,0 Al_2O_3 – 84,0	240	7,8	96,0	101,0
4.	CdF_2 – 5,0 ZnO – 5,0 Cr_2O_3 – 5,0 Fe_2O_3 – 3,0 Al_2O_3 – 82,0	225	7,3	72,0	98,0
5.	CdF_2 – 5,0 ZnO – 10,0 Cr_2O_3 – 3,0 Fe_2O_3 – 5,0	196	8,0	120	122

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6.	CdF_2 – 5,0 ZnO – 5,0 Cr_2O_3 – 5,0 Fe_2O_3 – 5,0 Al_2O_3 – 80,0	184	8,2	184	130

The condensation reaction of the croton fraction with ammonia and amines was carried out under flow conditions in a stainless steel reactor with dimensions d × l = 25 × 1000 mm, using external electric heating and a catalyst volume of 100 cm^3.

The analysis of the liquid products was performed using gas chromatography (GC) (LXM-8MD chromatograph, I-modification, with thermal conductivity detector, detection, and mobile phase – Selit 545, column temperature – 120 °C, absolute calibration).

The reaction of the croton fraction with ammonia was conducted at 360–420 °C in the presence of catalyst No. 6. The main reaction products were identified as 2- and 4-methylpyridines (up to 50%) and a mixture of 2-methyl-5-ethylpyridine (up to 26%) at 360–420 °C. Side products included acetonitrile, di- and trimethylpyridine mixtures, resin, and water.

We studied the effects of temperature, space velocity, initial reagent ratios, and catalyst bed height on the yield of target products and the conversion of the croton fraction.

The effect of temperature was investigated in the range of 360–420 °C (Table 2).

The table data show that at temperatures below 360 °C, the reaction does not proceed. Increasing the temperature from 360 to 400 °C leads to a smooth rise in the yield of target products, reaching a maximum at 400 °C. Further temperature increase causes a decrease in the yield of target products due to side reactions such as coking, polymerization, decomposition, and others.

Table 2

Effect of Temperature on the Yield of Target Products

Croton fraction : ammonia = 1:2; Space velocity = 200 h^{-1}, Catalyst = No. 6

№	Temperature, °C	Amount in Catalyst, %			Σ Side Products	Croton Fraction Conversion
		2-metil-piridin	4-metil-piridin	2-metil-5-etilpiridin		
1.	350	5,0	3,0	3,0	8,0	35,0
2.	360	14,0	8,0	8,0	12,0	45,0
3.	370	18,0	12,0	11,0	14,0	56,0
4.	380	22,0	16,0	14,0	18,0	64,0

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5.	390	32,0	22,0	20,0	26,0	85,0
6.	400	38,0	25,0	25,0	12,0	95,0
7.	410	36,0	24,0	26,0	14,0	98,0
8.	420	37,0	23,0	25,0	15,0	98,0
9.	430	33,0	22,0	20,0	25,0	99,0

The study of the effect of space velocity on the yield of target products, croton fraction conversion, and process selectivity showed that when the space velocity of ammonia increases from 150 to 300 h^{-1} and that of the croton fraction from 0.1 to 0.7 h^{-1}, the yield of pyridines gradually decreases. This indicates that the process occurs within the region of internal diffusion limitations.

To expand the raw material base for the production of pyridine and pyridine derivatives, the heterocyclization reaction of carbonyl compounds with ammonia was investigated. The heterocyclization reaction of acetaldehyde, formaldehyde, and ammonia was carried out under flow conditions in a stainless steel reactor with dimensions d × l = 25 × 1000 mm, using a catalyst volume of 10 cm^3.

The reaction was conducted under the following conditions:

Temperature: 400–425 °C

Molar ratio: $CH_3CHO : CH_2O : NH_3 = 1 : 1.25 : 2$

Catalyst: No. 5

During the reaction of the acetaldehyde–formaldehyde mixture with ammonia, a complex mixture of nitrogen-containing compounds is formed in water. Due to the high water content in formaldehyde (up to 70%) and the water produced during the reaction, a highly dilute aqueous mixture of nitrogen-containing compounds is obtained. The nitrogen-containing compounds are separated from the aqueous solution by distillation. When driving off the aqueous solution of nitrogen-containing compounds, azeotropes are formed and distilled in the range of 91–94 °C.

The composition of the organic layer of the catalyst (according to chromatographic analysis) is, mass %:

Pyridine composition, %:

Pyridine – 35.7

2-methylpyridine – 0.26

3-methylpyridine – 25.2

4-methylpyridine – 0.07

2,3-dimethylpyridine – 0.65

2,5-dimethylpyridine – 0.15

3-ethylpyridine – 0.5

3,5-dimethylpyridine – 3.29

High-boiling alkylpyridines and resins – 9.0%

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To separate them, the organic layer of the catalyst is dried with solid KOH and the β-picoline fraction is distilled off by rectification at a boiling range of 138–146 °C. Boiling temperature:

3- methylpyridine - 144,143°c

4- methylpyridine - 145,356°c

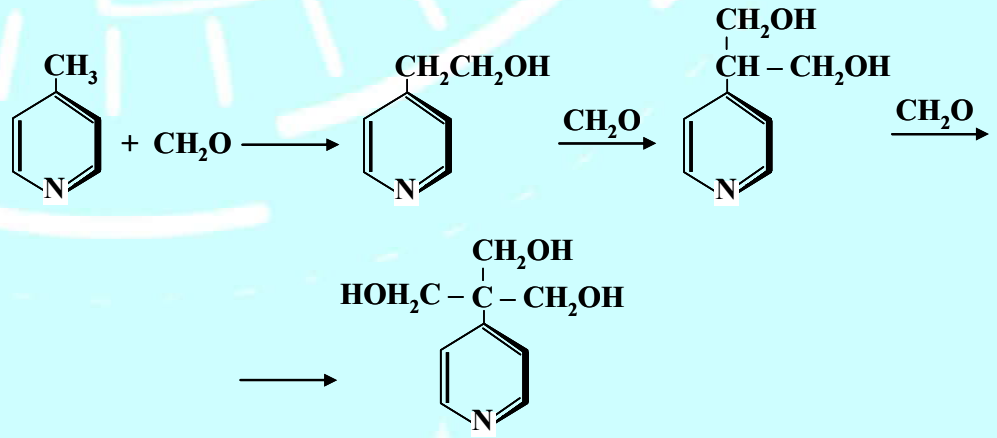
2,6- dimethylpyridine - 144,045°c

Since the boiling points of 3-methylpyridine, 4-methylpyridine, and 2,6-dimethylpyridine are nearly the same, they cannot be separated in pure form by physical methods.

3-methylpyridine is separated from the mixture by steam distillation. In this process, 3-methylpyridine is distilled with water. The remaining methyl derivatives in the residue cube are used for the production of isonicotinic acid.

3-methylpyridine is obtained from the aqueous solution with benzene and then separated by rectification. The isolated 3-methylpyridine has the following physical properties (literature data are given in parentheses).

We used a chemical method to obtain 3-methylpyridine in pure form. For this purpose, at 90 °C, 4-methylpyridine and 2,6-dimethylpyridine react with formaldehyde, producing the methyl derivatives of the latter according to the scheme.



Boiling temperature - 144 - 144,5 °C (144-143)

Melting temperature - 3,60 °C (3,65)

0,910 °C (0,9658)

1,5 67 °C (1,50682)

Purity of 3-methylpyridine 99,2 %.

Conclusion. In this study, the efficiency of synthesizing pyridine and alkylpyridines from croton fraction, acetylene, and carbonyl compounds by a heterogeneous-catalytic method was investigated. New polyfunctional catalysts based on local raw materials were developed, and it was found that they enable the production of pyridine derivatives with high yield at around 400 °C. The effects of

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process parameters (temperature, space velocity, reagent ratios) were evaluated, and the optimal conditions were determined. The structures of the synthesized pyridine derivatives were confirmed using spectroscopic methods. The obtained compounds demonstrated effective metal corrosion inhibition (92–94%), indicating their potential practical application, particularly in the chemical and metallurgical industries. The results of this study provide an important scientific and practical foundation for improving pyridine production technology using local raw materials.

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