JOURNAL OF FUTURE

MILLIY SOHALARARO ILMIY-INNOVATSION JURNAL

VOL. 2 | ISSUE 2 | 2026
ISSN 3093-8899

TECHNOLOGY & INNOVATION
SUSTAINABLE DEVELOPMENT
GREEN CHEMISTRY
BIOTECHNOLOGY

TEXNOLOGIYA & INNOVATSIYA
BARQAROR RIVOJLANISH
YASHIL KIMYO
BIOTEXNOLOGIYA

future-journal.uz

JOURNAL OF FUTURE

Journal of Future – ilmiy, elektron, fanlararo innovatsion jurnali O‘zbekiston Respublikasi Oliy attestatsiya komissiyasining dissertatsiyalar asosiy ilmiy natijalarini chop etish tavsiya etilgan ilmiy nashrlar ro‘yxatida e’tirof etilgan 14-ResearchBib va 40-ResearchGate bazalarida indekslangan.
Jurnal bir yilda o‘n ikki marta chop etiladi

O‘zbekiston Respublikasi Prezidenti huzuridagi Davlat xizmatini rivojlantirish agentligida 2025-yil 25-martda 682701 raqam bilan ro'yxatga olingan.

Muassis: “Uranium Publishing” MChJ
Elektron manzil: future.journal.official@gmail.com

TAHRIRIYAT

Bosh muharrir:
Egamberdiyev Elmurod Abduqodirovich, Islom Karimov nomidagi Toshkent davlat texnika universiteti professori, texnika fanlari doktori

Tahririyat kengashi raisi:
Maxsumov Abduxamid Gafurovich, Toshkent kimyo-texnologiya instituti professori, kimyo fanlari doktori

Tahririyat kengashi a’zolari:
José R. Simões Moreira, Braziliyaning San-Paulu universiteti qoshidagi Politécnica universitetining professori
Parmanov Askar Basimovich, O‘zbekiston Milliy universiteti, kimyo fanlari doktori, dotsent
Abdullayev Toxir Xasanbayevich, Tojikiston Milliy Fanlar akademiyasining V.I. Nikitin nomidagi Kimyo instituti, kimyo fanlari doktori, dotsent
Seyedeh Samira Mohammadi Nezamobadi, Eron davlatining Azad universiteti, texnika fanlari bo‘yicha falsafa doktori, dotsent
Vorobyev Stepan Vladimirovich Rossiya Federatsiyasining Gubkin nomidagi Rossiya davlat neft va gaz universiteti (Milliy tadqiqot universiteti) kimyo fanlari nomzodi, dotsent
Abdirahimov Mirzohid Ibrohimjon o‘g‘li, Polsha Fanlar akademiyasi Kimyo muhandisligi instituti, texnika fanlari bo‘yicha falsafa doktori, dotsent
Mengliyev Sherzod Shoimovich, Toshkent kimyo-texnologiya instituti, kimyo fanlari bo‘yicha falsafa doktori, dotsent
Ziyadullayev Anvar Egamberdiyevich, Toshkent kimyo-texnologiya instituti, kimyo fanlari doktori, dotsent
Jumayev Shahobiddin Shamsidinovich, Tojikiston Konchilik va metallurgiya instituti, kimyo fanlari nomzodi, dotsent
Ismailov Boburbek Maxmudjanovich, Toshkent kimyo-texnologiya instituti, texnika fanlari bo‘yicha falsafa doktori, dotsent
Ergashev Yorqinjon To‘lqin o‘g‘li, Islom Karimov nomidagi Toshkent davlat texnika universiteti, texnika fanlari bo‘yicha falsafa doktori, dotsent
Mashayev Eldor Ergashvoy o'g'li, Toshkent kimyo-texnologiya instituti, kimyo fanlari bo'yicha falsafa doktori
Raximov Xusniddin Nurboboyevich, Toshkent kimyo-texnologiya instituti, texnika fanlari bo‘yicha falsafa doktori, dotsent
Abdukarimova Saida Abdujalilovna, Islom Karimov nomidagi Toshkent davlat texnika universiteti, texnika fanlari bo‘yicha falsafa doktori, dotsent
Xakimov Farrux Shokirjonovich, Farg‘ona politexnika instituti, texnika fanlari bo‘yicha falsafa doktori, dotsent
Obidov Shoyunus Botir o‘g‘li, Toshkent kimyo-texnologiya instituti, texnika fanlari bo‘yicha falsafa doktori, dotsent
Mardonov Asror Hasanovich, O‘zbekiston Respublikasi Fanlar akademiyasining akademik S.Yu.Yunusov nomidagi O‘simlik moddalari kimyosi instituti, texnika fanlari bo‘yicha falsafa doktori
Meyliyeva Laziza Qahramonovna, Toshkent kimyo-texnologiya instituti, kimyo fanlari bo‘yicha falsafa doktori

MUNDARIJA

MUNDARIJA * СОДЕРЖАНИЕ * CONTENTS

DIFFERENCE BETWEEN ZEOLITE AND HYDROGEN-PERMUTITE WITH MAIN INDICATORS

Sanalar
Qabul qilindi: 24.04.2026
Nashrga qabul qilindi: 28.04.2026
Nashr qilindi: 04.05.2026

Sherzodbek Ikram o'g'li Berdiev
Doctor of Philosophy in Technical Sciences,PhD, Office of the Registrar, Tashkent Chemical-Technological Institute, Tashkent, Uzbekistan.
E-mail:ions2602@gmail.com
ORCID:0009-0005-4146-5685

Mirolim Mirazim o'g'li Aripov
Doctor of Philosophy in Technical Sciences,PhD, Office of the Registrar, Tashkent Chemical-Technological Institute, Tashkent, Uzbekistan.
ORCID: 0009-0007-8012-8985

Jamshid Sayfullaevich Kayumov
Doctor of Philosophy in Technical Sciences,PhD, Office of the Registrar, Tashkent Chemical-Technological Institute, Tashkent, Uzbekistan.
ORCID: 0000-0002-6493-1192

Furqat Ilyasovich Erkabaev
Doctor of Philosophy in Technical Sciences,PhD, Head of the laboratory of the Research Institute for Environment and Nature Conservation Technologies, Tashkent, Uzbekistan.
ORCID: 0000-0001-9610-1727

Abstract. Scientific research is being conducted worldwide to purify process and wastewater generated by industrial enterprises to meet established requirements for reuse as circulating process water, to develop low-waste or waste-free technologies, and to comprehensively recycle solid and liquid waste generated during enterprise activities. In this regard, special attention is paid to purifying domestic, process, and industrial wastewater contaminated with various additives to meet established requirements and to use them as circulating water in the process or for watering trees and plants on the enterprise's territory. The scientific significance of the research results is that the effective course of the synthesis process for obtaining H-permutite depends on the type and ratio of components, and the efficiency of wastewater treatment is closely related to the degree of contamination and the environmental pH. The article presents general information on theoretical and practical research regarding methods and technologies for treating industrial, technical, and wastewater, based on published articles and patent literature. Based on the issues raised and a critical analysis of the data obtained, the article defines the research goals and objectives. Currently, there are

Berdiev Sh.I., Aripov M.M., Kayumov J.S., Erkabaev F.I. Difference between zeolite and hydrogen-permutite with main indicators // Journal of future. 2026. Vol. 2. Iss. 2. pp. 1–12. https://doi.org/10.66960/jof.3093-8899.00021

both natural and artificial zeolites. In this scientific work, an alternative to zeolite, H-permutite, was synthesized from natural raw materials. In this article, the study of the structural properties of the molecular compounds of the samples was conducted on a Nicolet iS50 (Thermo Fisher Scientific, USA) FT-IR spectrometer. Measurements were carried out in the spectral range of 4000–400 cm⁻¹, with a spectral resolution of no more than 0.1 cm⁻¹. The test sample was pressed onto the surface of the mounted assembly with a flat-tip probe.

Keywords: *H-permutite, Adsorption, Specific Surface, Calcium Permutite, Sodium Permutite, Adsorbent, Hydrogen Permutite*

Annotatsiya. Sanoat korxonalari tomonidan ishlab chiqarilgan texnologik va oqova suvlarni aylanma texnologik suv sifatida qayta ishlatish uchun belgilangan talablarga javob berish maqsadida tozalash, kam chiqindili yoki chiqindisiz texnologiyalarni ishlab chiqish va korxona faoliyati davomida hosil boʻlgan qattiq va suyuq chiqindilarni kompleks qayta ishlash boʻyicha butun dunyo boʻylab ilmiy tadqiqotlar olib borilmoqda. Shu munosabat bilan, belgilangan talablarga javob berish va ulardan jarayonda aylanma suv sifatida yoki korxona hududida daraxtlar va oʻsimliklarni sugʻorish uchun foydalanish maqsadida turli qoʻshimchalar bilan ifloslangan maishiy, texnologik va sanoat oqova suvlarini tozalashga alohida eʻtibor qaratilmoqda. Tadqiqot natijalarining ilmiy ahamiyati shundaki, H-permutit olish uchun sintez jarayonining samarali jarayoni komponentlarning turi va nisbatiga bogʻliq boʻlib, oqova suvlarni tozalash samaradorligi ifloslanish darajasi va atrof-muhitning pH qiymati bilan chambarchas bogʻliq. Maqolada nashr etilgan maqolalar va patent adabiyotlariga asoslangan holda sanoat, texnik va oqova suvlarni tozalash usullari va texnologiyalari boʻyicha nazariy va amaliy tadqiqotlar haqida umumiy maʼlumotlar keltirilgan. Koʻtarilgan masalalar va olingan maʼlumotlarning tanqidiy tahlili asosida maqolada tadqiqot maqsadlari va vazifalari belgilangan. Hozirgi vaqtda tabiiy va sun'iy seolitlar mavjud. Ushbu ilmiy ishda seolitga alternativ boʻlgan H-permutit tabiiy xom ashyolardan sintez qilindi. Ushbu maqolada namunalarning molekulyar birikmalarining strukturaviy xususiyatlarini oʻrganish Nicolet iS50 (Thermo Fisher Scientific, AQSh) FT-IR spektrometrida oʻtkazildi. Oʻlchovlar 4000–400 sm⁻¹ spektral diapazonida, spektral oʻlchamlari 0,1 sm⁻¹ dan oshmagan holda amalga oshirildi. Sinov namunasi oʻrnatilgan yigʻma yuzasiga yassi uchli zond bilan bosildi.

Kalit so'zlar: *H-permutit, Adsorbsiya, Maxsus sirt, Kaltsiy permutit, Natriy permutit, Adsorbent, Vodorod permutit*

Аннотация. Во всем мире проводятся научные исследования по очистке технологических и сточных вод, образующихся на промышленных предприятиях, для соответствия установленным требованиям по их повторному использованию в качестве циркуляционной технологической воды, разработке малоотходных или безотходных технологий, а также по комплексной переработке твердых и жидких отходов, образующихся в процессе деятельности предприятий. В этой связи особое внимание уделяется очистке бытовых, технологических и промышленных сточных вод, загрязненных различными добавками, для соответствия установленным требованиям и их использованию в качестве циркуляционной воды в технологических процессах или для полива деревьев и растений на территории предприятия. Научная значимость результатов исследований заключается в том, что эффективный ход процесса синтеза Н-пермутита зависит от типа и соотношения компонентов, а эффективность очистки сточных вод тесно связана со степенью загрязнения и pH окружающей среды. В статье представлена общая информация о теоретических и практических исследованиях методов и технологий очистки промышленных, технических и сточных вод на основе опубликованных статей и патентной литературы. На основе поднятых вопросов и критического анализа полученных данных в статье определены цели и задачи исследований. В настоящее время существуют как природные, так и искусственные цеолиты. В данной научной работе из природного сырья был синтезирован альтернативный цеолиту Н-пермутит. В статье исследование структурных свойств молекулярных соединений образцов проводилось на ИК-спектрометре с преобразованием Фурье Nicolet iS50 (Thermo Fisher Scientific, США). Измерения проводились в спектральном диапазоне 4000–400 см$^{-1}$ с разрешением не более 0,1 см$^{-1}$. Образец прижимался к поверхности установленной конструкции с помощью зонда с плоским наконечником.

Ключевые слова: *Н-пермутит, адсорбция, удельная поверхность, пермутит кальция, пермутит натрия, адсорбент, пермутит водорода*

INTRODUCTION

Beginning in the early 1940s, scientists at Union Carbide began research on the synthesis of zeolites, and they succeeded in synthesizing pure zeolites A and X in 1950 [1]. The discovery of zeolites in the world began in 1756 with the discovery of stilbite by a scientist named A.F. Constedt. Constedt described the peculiarity of this mineral: when heated, it seems to boil because the molecules lose water very quickly. According to these properties, this mineral was given the name zeolite, which comes from two Greek words, zeo, meaning boiling, and lithos, meaning stone (Kirk-Othmer, 1981) [2]. It is called a zeolite because it boils and emits steam when heated (Dyer, 1994). Zeolite is used in the separation and purification of petroleum hydrocarbons, as a catalyst, and in gas purification, drying, and separation of gases (including air), drying of freons, extraction of radioactive elements, and the creation of strong vacuums. Zeolite deposits exist in the Russian Federation, Armenia, and Georgia. In Uzbekistan, it is found among silts and opaque clays [3,4].

Table 1. Sodium silicate Liquid index M2.2Be50

Sodium silicate standard	Sodium silicate standard 51 °C	Test result
Relative density (20 °C)%	50.0 ~ 51.0	50.7
Composition (Na_2O) %	12.8	13.95
Composition (SiO_2) %	29.2	31.05
Module (M)	2.2 ~ 2.4	2.3

Table 2. Sodium silicate Liquid index M3.3Be38

Sodium silicate standard	Sodium silicate standard 38 °C	Test result
Relative density (20 °C)%	36.0 ~ 38.0	38
Composition (Na_2O) %	≥ 8.2	8.4
Composition (SiO_2) %	≥ 26.0	26.64
Module (M)	3.1 ~ 3.40	3.27

Table 3. Sodium silicate Liquid index M2.2Be40

Sodium silicate standard	Sodium silicate standard 40 °C	Test result
Relative density (20 °C)%	38.0 ~ 40.0	38.9
Composition (Na_2O) %	≥ 9.5	39.1 ~ 40.0
Composition (SiO_2) %	≥ 22.1	≥ 22.1
Module (M)	2.2 ~ 2.5	2.2 ~ 2.5

Table 4. Molecular mass ratio of zeolite

Element	Symbol	Atomic mass	atomic num.	Mass percentage
Sodium	Na	22.9898 g/m	1	100%
Silicon	Si	28.0855 g/m	1	100%
Oxygen	O	31.9988 g/m	2	100%

MATERIALS AND METHODS

In the research on sorbents, the authors [5] used different materials and researched their sorption properties. Peat and sawdust-based sorbents have been proposed for softening technical waters in oil processing. Additionally, wood shavings containing cellulose have been recommended as a chemical reductant for the treatment of industrial wastewater containing certain heavy metals produced in galvanic plants due to the presence of cellulose-containing functional groups [6].

Bentonite, kaolinite, biotite, vermiculite, and glauconite recycled sorbents in various ways are effective and promising in softening industrial technical water and removing heavy metals because their natural resources are sufficient in our republic [7]. In addition, these minerals are relatively cheap, their deposits are widely distributed throughout the territory of our republic, their reserves have been studied, and their operational characteristics are high.

Adsorption properties of natural minerals are explained by their chemical and mineralogical structure, crystal structure, and dispersion of particles. The main components of natural minerals are SiO_2 (30-70%), Al_2O_3 (10-40%), and H_2O (5-10%); their relative surfaces are up to 500 m^2/g.

Zeolites are used more often than permutates from mineral substances and synthetically obtained adsorbents because they have selective absorption properties. Permutites and zeolites consist of layered aluminosilicates $[SiO_4]_4$ and $[AlO_4]_5$, crystal lattices are tetrahedral. The microstructure of these adsorbents consists of layered channels, and the free movement of water molecules and cations improves their adsorption and ion exchange properties.

Zeolites exchange their cation (Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}, etc.) with pollutant cations in wastewater or waste solutions, while they can selectively absorb.

To increase the sorption properties of zeolites, they are chemically modified with 3% chitosan solution or ferro ferricyanide complexes. In the process of obtaining the proposed H-permutite, this step is not performed. Despite the great demand for natural zeolites, the process of their application is not free from shortcomings, because the cracks in their crystal structure have certain sizes, and only small-sized ions can enter the space. In some processes, the sorption pores are not filled, which is caused by the relatively large size of absorbed ions. In addition, the ion exchange process is directly dependent on temperature, which limits the use of ultra-in-water treatment technologies.

Synthetic zeolites are free of these defects and are widely used in industry, but their use in water purification processes is not justified due to their relatively high cost

Table 5. Obtained proportions of aluminum chloride and sodium silicates for the synthesis of H-permutite

No	Aggregate status	Components, g/l		Efficiency,%
	Water solution	$Na_2SiO_3 \cdot 9H_2O$	$AlCl_3$	
1	1:1	25.0	5.0	47
2	1:1	25.0	4.5	48
3	1:1	25.0	4.0	50
4	1:1	25.0	3.5	51
5	1:1	25.0	3.0	49
6	1:1	25.0	2.5	45
7	1:1	24.0	5.0	46
8	1:1	24.0	4.5	48
9	1:1	24.0	4.0	50
10	1:1	24.0	3.5	52
11	1:1	24.0	3.0	51
12	1:1	24.0	2.5	48
13	1:1	23.0	5.0	49
14	1:1	23.0	4.5	51
15	1:1	23.0	4.0	53
16	1:1	23.0	3.5	54
17	1:1	23.0	3.0	52
18	1:1	23.0	2.5	50
19	1:1	22.0	5.0	44
20	1:1	22.0	4.5	46
21	1:1	22.0	4.0	48
22	1:1	22.0	3.5	51
23	1:1	22.0	3.0	49
24	1:1	22.0	2.5	45

and the complexity of regeneration processes. Therefore, it is urgent to use new types of adsorbents for cleaning technical or industrial wastewater, preparing them for use in boiler houses [8].

As mentioned above, the treatment of industrial wastewater contaminated with various organic and inorganic substances, and the softening of technical water for reuse, are relatively expensive processes. The reason for this is that most of the adsorbents used in the cleaning process are imported, and the regeneration processes are complicated [9]. Taking this into account, research was conducted on obtaining aluminosilicate adsorbent with a layered structure, that is, H-permutite. H-permutite softens technical water up to the established requirements and is very effective in obtaining circulating water for boilers, where the softened water is not contaminated with Na^+ ions, as in the case of Na-permutite application.

Various mineral and artificial adsorbents, including Na-permutite, are used in industry for wastewater treatment and softening of technical waters. When Na-permutite is used for water softening, the calcium and magnesium ions in the water are softened due to the exchange of equivalent amounts of sodium ions. In this case, the water is cooled, free of calcium and magnesium ions, which give hardness, but its mineralization remains unchanged due to sodium ions, which do not give hardness properties [10,11]. If H-permutite is applied to this process, the mineralization of water decreases, the efficiency of steam boilers increases dramatically, and especially the efficiency of high-pressure steam boilers improves, and the useful work coefficient increases dramatically.

It is known that permutates can be synthesized in an aqueous environment with the presence of aluminum sulfate or aluminum chloride and sodium silicates, where the ratio of components plays a major role in the product yield. For the synthesis of H-permutite, experiments were conducted using aluminum chloride and sodium silicates in different proportions (Table 5).

From the results of the conducted experiments, it became clear that the efficiency was the highest when the amount of $Na_2SiO_3 \cdot 9H_2O$ was 23 g, and the amount of $AlCl_3$ was 3.5 g in the synthesis process, and it was 54%. To synthesize H-permutite in optimal proportions, 23.0 grams of $Na_2SiO_3 \cdot 9H_2O$ were dissolved in 1 L of distilled water at room temperature (1), and 3.5 g of $AlCl_3$ were also dissolved in 1 L of distilled water and mixed for 10 minutes. In this case, the process proceeds according to the following equation in aqueous medium at room temperature:

$$2AlCl_3 + 3Na_2SiO_3 \cdot 9H_2O + H_2O = Na_2Al_2Si_2O_8\downarrow \cdot nH_2O + 6NaCl + SiO_2 \qquad (1)$$

The formed $Na_2Al_2Si_2O_8$ reacts with added $CaHCO_3$ to form $Ca_2Al_2Si_2O_8$. After treatment with 5% HCl, $H_2Al_2Si_2O_8$ (H-permutite) is formed and precipitates, while NaCl and SiO_2 ions remain in solution. The precipitate was filtered and dried to constant weight at 1200 °C, and the efficiency was determined. The weight of our obtained product was 19.6 g, and the efficiency of the process was 74%. A sample of 2.2 kg of H-permutite was taken under optimal conditions determined by this technology. Navbakhor mine bentonite was added to the obtained sample in the amount of 5% as a plasticizer and granulated. To determine the amount of water needed for granulation, samples with different amounts of water added to the mixture were prepared and tested (Table 6).

Table 6. Required for the granulation of H-permutite, determine the amount of water

No	Sample	Moisture,%	Water content,%	Result
1	$H_2Al_2Si_2O_8$	4	19	The granules are broken, emulsifying
2	$H_2Al_2Si_2O_8$	4	20	The bulk of the granules is whole, emulsifiable
3	$H_2Al_2Si_2O_8$	4	21	The granules are whole, and the consistency is sufficient
4	$H_2Al_2Si_2O_8$	4	22	The granules are whole, slightly sticky due to moisture
5	$H_2Al_2Si_2O_8$	4	23	Granules are partially deformed, sticky
6	$H_2Al_2Si_2O_8$	4	24	The shape of the granules is distorted, and the shape is variable

Table 6 shows that when we added 5% bentonite and 21% water to a sample with a moisture content of 4%, a mixture with optimal moisture content for granulation was obtained. The prepared mixture was granulated in an FSH-0.004M laboratory granulator with a 3.0 mm diameter. The prepared granules were dried for 1 hour at a temperature of 180°C with periodic mixing. The dried granules were sieved through laboratory sieves, and the fraction between 1 and 3 mm was separated. This fraction was 92%.

The obtained product was placed in a sorption column with a diameter of 50 mm and a height of 200 mm. To check the absorption of Fe^{2+} ions, a model solution with a concentration of 22 mg/l (the wastewater of METFURSERVIS LLC contains 22 mg/l Fe^{2+} ions) was prepared. The results of the experiment to determine the adsorption kinetics of the obtained sorbent on Fe^{2+} ions are presented in Figure 1.

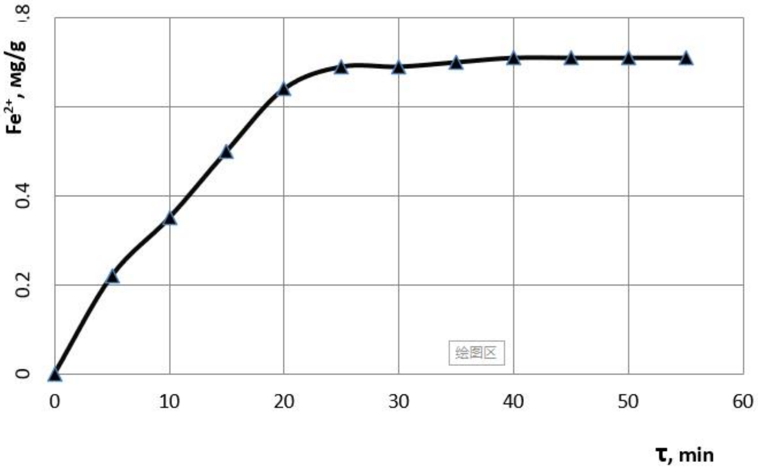


Figure 1. Adsorption kinetics of Fe^{2+} ions from a model solution with a concentration of Fe^{2+} ions of 22 mg/l

As can be seen from Figure 1, the sorption process of Fe^{2+} ions is fast in the first 20 minutes, the adsorbent is approaching saturation, and the process is relatively slow in the next 30 minutes. The obtained results showed that the absorption capacity of the obtained adsorbent was 0.65 mg/g in terms of Fe^{2+} ions.

Based on the data obtained as a result of the conducted research, the optimal proportions of raw materials for obtaining H-permutite were determined, the possibilities of separating the product from the water part, choosing a plasticizer for granulation, and determining the optimal amount of water added for granulation were created. The obtained granules were dried in the established order, granulated and dried, and placed in a sorption column, and their sorption properties were studied. Based on the test results, it can be concluded that the obtained product is a good adsorbent material, has a good effect on water purification and softening, and reduces mineralization.

H-permutite can be used in the preparation of electrolytes for various electrochemical processes and the preparation of water for high-pressure steam boilers. Doing so ensures their effective operation and leads to a sharp increase in the useful work coefficient due to the reduction of the processes of cleaning the formed clots.

Review the planning stage

Measurement of the phase characteristics of the studied samples by an X-ray diffractometer was carried out on a Panalytical Empyrean powder X-ray diffractometer. All monitoring of equipment performance was performed by computer using Data Collector software and X-ray diffraction pattern analysis software [12]. Measurements were taken at room temperature in a 2-angle range, 5° to 90° stepwise scan mode with 0.013 (2-Main Graphics, Analyze View: 2-Sample X-ray Analysis) degree step, and the signal at 5 s point was collected with the collection time and IK. To study the characteristics of the structure of the molecular compounds of the studied samples, the Nicolet iS50 (Thermo Fisher Scientific, AQS H) IR-Fourier spectrometer was used. Measurements were made in the 4000-400 cm^{-1} spectral range, with spectral resolution not exceeding 0.1 cm. The test specimen was pressed against the mounting surface with a flat-tip probe. The following analysis values were determined using a pinhole and diamond crystal to measure near, mid, and far IR attenuated total internal reflection (ATR) at IS50.

If the water is hard (the total amount of calcium and magnesium salts in its content is higher than normal), it is softened. Groundwater is often de-ironed (enriched with oxygen) by aeration. Lime, sodium aluminate $NaAlO_2$, and sometimes burnt

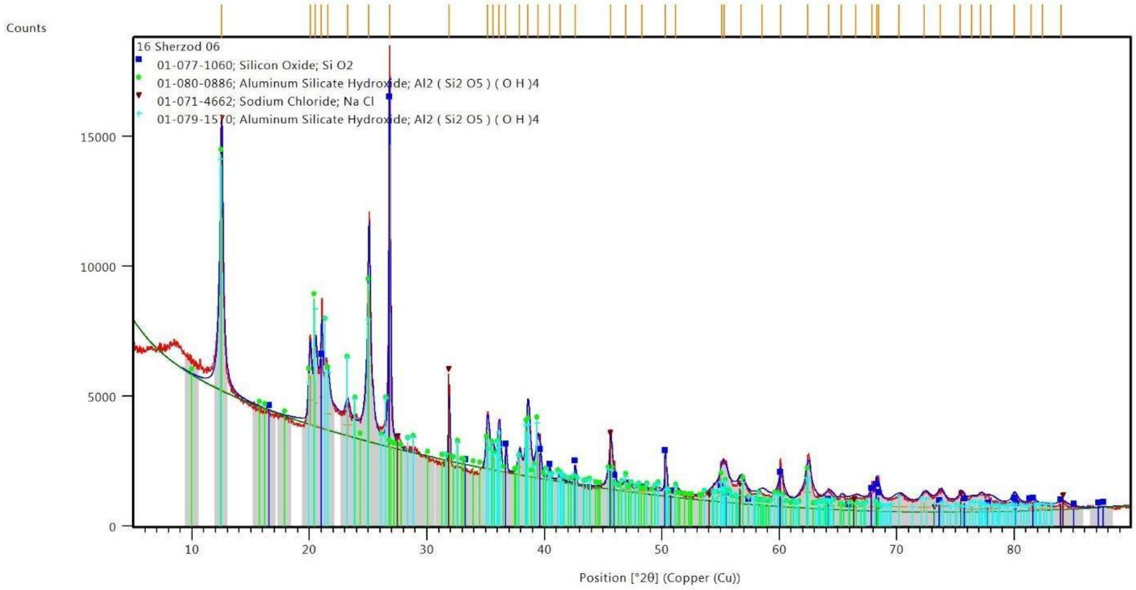


Figure 2. (A) X-ray phase analysis results of the labeled zeolite.

dolomite are used for water desilicification (reducing the amount of metasilicic acid H_2SiO_3 and its salts). To remove other dissolved salts in the water, it is sweetened or desalinated with ions. Water is degassed to remove hydrogen sulfide, methane, radon, carbon dioxide, and other dissolved gases. The water is filtered through activated alumina to reduce excess fluoride in the water. If the water is found to contain radioactive substances, it will be deactivated. If the water has a strong smell, it is treated with activated carbon, ozone, potassium permanganate, or chlorine dioxide.

In Uzbekistan, it is found among silts and opaque clays. Gilmoya is one of the types of clay. Consists of montmorillonite. In Uzbekistan, gilmoya is also called gilvata, mountain oil, and stone soap. Gilmoya is mainly formed from the physical and chemical transformation of volcanic ash and clay in the alkaline environment at the bottom of the sea and ocean. Color is white, green, gray, brown, etc. Soap-like and soft, it dries quickly in the heat and turns into stone. In water, its volume increases 2-15 times. Gilmoya can also absorb (adsorb) various substances and radioactive elements. When heated to 1110-1125°C, it expands and turns into a porous stone - expanded clay. Clay soil is widely used in rubber, paper, metallurgy, the food industry, medicine, and agriculture. Gilmoya is widespread in the Cretaceous and Paleogene strata. It has been determined that there are about 200 clay soil deposits in Uzbekistan.

Aluminum trichloride was used for the synthesis of permutite hydrogen, for which 23.5 grams of $Na_2SiO_3{\cdot}9H_2O$ were dissolved in a volume of 2 L of distilled water and 3.4 grams of $AlCl_3$ in a volume of 1 L of distilled water, and stirred for 10 minutes. at room temperature (2). The reaction chemistry of this process can be described as follows:

$$2AlCl_3 + 3Na_2SiO_3 \cdot 9H_2O + H_2O = H_2Al_2Si_2O_8 \cdot nH_2O\downarrow + 6NaCl + SiO_2 \qquad (2)$$

After that, the resulting product, namely hydrogen permutite precipitates, NaCl, and SiO_2, remains in solution. The product is filtered, washed, dried at a temperature of 110 °C to a constant weight, and the yield of the product is determined. In our case,

Table 7. Chemical composition of permutite (%)

Si	Al	Fe	Ti	No	O	Cl	K	C
22.39	14.89	1.08	0.39	11.36	42.73	0.77	0.27	6.13

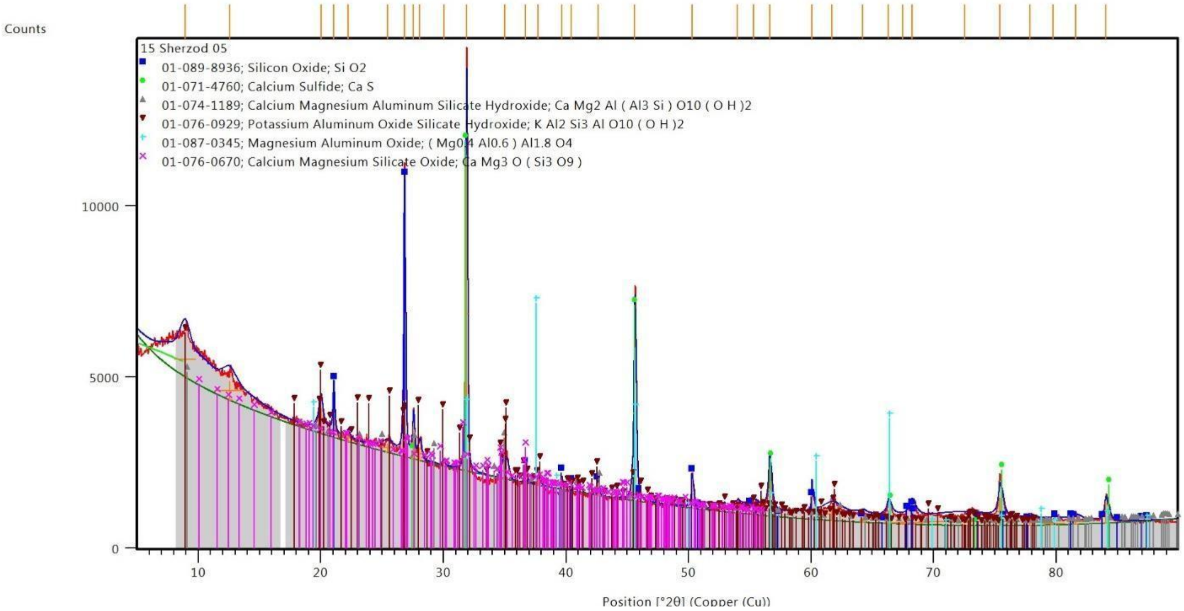


Figure 3. Results of X-ray phase analysis of hydrogen peroxide

the dried product was 14.3 grams, and its yield was 53%. Using this technology, a sample of 1.1 kg of hydrogen peroxide was obtained. The resulting product is granulated, for which 8% enriched bentonite from the Navbahor mine is added as a plasticizer. Water was added to the pre-determined optimal amount of granulation, which was 21%, and water was added in an FSH-004 laboratory granulator with a screw hole diameter of 1.0 mm. The finished granules were dried at a temperature of 175° C, stirring from time to time. The dried granules were sieved, 1-3 mm fractions were sorted to study the sorption properties. We saw that the x-ray analysis of the obtained sorbent (Fig. 3) is proportional to the x-ray analysis of zeolite.

The obtained data made it possible to determine the optimal ratio of components for the production of hydrogen peroxide, the resulting product was separated from the aqueous medium, the plasticizer and the optimal amount of water were selected, and granules of a certain fraction were obtained. The obtained granules are dried and placed in a sorption column, and their sorption properties are checked. As a result, the obtained product is a good adsorbent, it does not pollute the water environment in the process of softening and cleaning water, and reduces mineralization. The resulting product can be successfully used in the production of electrolytes containing high-pressure steam and can be successfully used in cleaning water from boilers. Meanwhile, effective softening and a decrease in the general mineralization of water have a positive effect.

Source discovery stage

Zeolite, as an ion exchanger, can exchange cations with other ions in the surrounding solution. With this property, zeolite-A with Na^+ ions can be used as a water softener, where Na^+ ions replace Ca^{2+} ions from hard water. Zeolite saturated with Ca^{2+} can be renewed by dissolving it in a pure Na^+ or K^+ salt solution. Zeolite-A is now added to detergents as a water softener to replace polyphosphates, which can cause environmental damage. Production of potable water from seawater using a mixture of Ag and Ba zeolite is a good desalination process, although the process is relatively expensive [13].

Aluminum chloride is hygroscopic, which means it can absorb moisture from the air. Normally, this chemical compound evaporates in air containing moisture. Makes a hissing sound when it comes into contact with water. During the reaction, Cl^- ions are replaced by H_2O molecules (3), forming the hexahydrate $[Al(H_2O)_6]Cl_3$. The anhydrous state of $AlCl_3$ is lost, and when heat is applied, HCl is also released, and the final product obtained is aluminum hydroxide.

$$Al(H_2O)_6Cl_3 \rightarrow Al(OH)_3 + 3HCl + 3H_2O \quad (3)$$

When the temperature rises to about 400°C, aluminum oxide is formed from the hydroxide (4).

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O \quad (4)$$

A characteristic feature of aqueous solutions of $AlCl_3$ is that they are ionic. Therefore, they conduct electricity well (5). They are also acidic, and this can lead to partial hydrolysis in the Al^{3+} ion. The reaction can be written as:

$$[Al(H_2O)_6]^3+(aq) \rightleftharpoons [Al(OH)(H_2O)_5]_2+(aq) + H^+(aq) \quad (5)$$

Aluminum salts containing the hydrated Al^{3+} ion are similar to aqueous solutions of aluminum chloride. They do the same (6). For example, when reacting with dilute sodium hydroxide, a thick precipitate of $Al(OH)_3$ is formed.

$$AlCl_3 + 3NaOH \rightarrow Al(OH)_3 + 3NaCl \quad (6)$$

Aluminum chloride is often regarded as a versatile chemical compound and is therefore used in many fields, especially in chemical reactions and synthesis. We will learn about the use of aluminum chloride below.

1. $AlCl_3$ is mainly used as a catalyst for various chemical reactions. It is widely used in Friedel-Crafts reactions, including acylations and alkylations. It is used in the preparation of anthraquinone from phosgene and benzene.

2. Aluminum chloride can be used to introduce or attach aldehyde groups to aromatic series or rings. For example, we can consider the Gattermann-Koch reaction, in which a Lewis acid (aluminum chloride) is used to remove a chloride ion from a species.

3. It is also used in polymerization and isomerization reactions of light molecular hydrocarbons. Some common examples include the production of dodecylbenzene for detergents.

4. To synthesize bis(arene) metal complexes, aluminum chloride can be mixed with aluminum, along with arene.

5. Aluminum chloride has a variety of other applications, particularly in organic chemistry. For example, it is used to catalyze the "ene reaction". We can take the example of the addition of 3-buten-2-one to carvone (methyl vinyl ketone).

6. Aluminum chloride is used to induce various hydrocarbon compounds and rearrangements.

- Industrial Uses of Aluminum Chloride ($AlCl_3$)
- Aluminum chloride is widely used in the production of rubber, lubricants, wood preservatives, and paints.
- Used in pesticides and pharmaceuticals.
- As flux in aluminum smelting.
- Used as an antiperspirant.
- It is also used in the production of petrochemicals such as ethylbenzene and alkylbenzene

Know-how stage

For comparison, the industrial test experiments showed that the modified glauconite sorbent could soften the technical water of the enterprise with a hardness of 15 mg-eq/l to 7.0 mg-eq/l, while the H-permutite sorbent proposed by the researcher had a hardness of 15 showed that technical water with mg-eq/l can be softened up to 3.5 mg-eq/l, which in turn allows to recycle technical water at the enterprise and use it in high-pressure boilers (table). After saturation, the proposed sorbent can be regenerated and reused up to 9-11 times. The volume of washing water produced during the regeneration process is relatively small. The used sorbent is rich in microelements and recommended to be added to mineral or local fertilizers.

Comparison of Si and Al from zeolites describes the function of their cation exchange capacity. Data from XRF analysis shows that the percentage comparison between SiO_2 and Al_2O_3 is relatively smaller, namely 5.56. This comparison theoretically shows that the capacity of the cations is relatively large. These results were obtained in Natural zeolite that has been processed using acid.

HCl reacts with zeolite to extract Al from the zeolite. This resulted in decreasing the Al content in the zeolite so that the ratio of Si/Al moles increases. Metal content, such as Ca and Mg in zeolite, decreased after treatment due to ion exchange between cations from zeolite with protons from HCl. Analysis results using XRF show that the acid treatment process (HCl5 M) on the catalyst causes a decrease in Ca and Mg metal content in zeolites and an increase in zeolite acidity. Chemical activation carried out by acidification with the aim of agar dealumination occurs. The purpose of dealumination is to optimize aluminum content in zeolite, so that the zeolite becomes more stable at high temperatures, controlling acidity and zeolite selectivity. Dealumination is a process of destruction of the zeolite framework structure that occurs as the disconnection of Al in the framework (Al framework) becomes Al outside the framework (Al non-framework). As a result, the Si/Al ratio will increase [14].

Results and discussion

Currently, many ion-exchange materials are found of natural origin: humus and brown coal, peat, wood, starch, glauconite, volkonskoite, bentonite, and other aluminosilicates created according to the type of naturally or artificially created zeolite. (zeolites), - permutite, etc. However, all these materials are characterized by a small ion exchange capacity, different designs of ion filters have been proposed and put into use, and they all have a parallel flow (purified water and regeneration solution flow in the filter in the same direction - from top to bottom). The results of our studies showed that we can achieve economic efficiency if we clean technical water and boiler water using H-permutite. It was found that the cost of generating H-permutite is much lower compared to other adsorbents. We can achieve economic efficiency by producing mineral-rich plant fertilizer from spent H-permutite.

Conclusion

The maximum adsorption of the dye solution occurred at pH 3. Here, an equilibrium was reached between the dye and the hydroxyl ions in the solution. so that the dye could capture the added hydroxyl ions, and the dye solution experienced a decrease in adsorption capacity at higher levels. If analyzed in the neutral pH range, the reactive dye could cause oxidation on its surface, as a result of which it imparted a positive charge to the zeolite surface. A sharp decrease in adsorption capacity was observed at alkaline pH. This is because alkaline pH was observed to inhibit the increase in protonation in the dye solution. This is because too many OH^- ions in the solution could not be captured by the dye, so there were still many free OH^- ions in the solution, which caused competition between the dye and the free OH- ions for occupying the zeolite surface, which reduced the adsorption capacity of the substance. OH- neutralizes the methylene blue solution so that the negative charge tendency on the adsorbent does not attract the adsorbate. At high pH, the surface of the reactive dyes increased positively charged cations through attractive electrostatic forces. Increasing alkalinity was observed to change the adsorbent layer from positive to negative. Therefore, it reduced the adsorption capacity. Scientific research and scientific news of the following consists of:

1) H-permutite synthesis in the process, the raw items ratio plays a big role in this component. The ratio of Na_2SiO_3 : $AlCl_3$ is 6: 1 when processing the product most efficiently, and the output is 74% organize did.

2) Synthesis Na-permutite when $AlCl_3$ is used in the process harvest to be processed, in which Na^+ ions are the main part, and Cl^- ions bind to the solution passed, and in the sediment, H-permutite is left.

3) Technician the water H-permuted with the help of when cleaned of water ion replacement to account for mineralization, sharp decrease, and high-pressure working warm up their stomachs pre-vention cleaning of the process, decrease to account for useful work coefficient, sharp brought.

4) H-permutite studies as a result determined component proportions and another optimal parameter based on high exit with synthesis to create technology.

REFERENCES

1. Bambang Setiaji, Utilization of Zeolite for Adsorption of Benzopyrene as a Toxic Compound in Liquid Smoke. Science and Technology Magazine Vol. 11, No. 4, November (2000).

2. Wustoni, Shofarul, Rino Rahmata Mukti, Agus Wahyudi, Ismunandar, Synthesis of Zeolite Mordenite with the Help of Indonesian Natural Minerals, Journal of Mathematics and Science, Vol. 16, No.3, (2011).

3. Djaeni, M., Laeli Kurniasari, Setia Budi Sasongko, Preparation of Natural Zeolite for Air Dehumidification in Food Drying, International Journal of Science and Engineering, Vol. 8, No. 2, (2015).

4. Solikah, Siti, Budi Utami, Differences in the Use of Adsorbents from Activated Natural Zeolite and Dithizone Mobilized Zeolite for Absorption of Cu2+ Copper Metal Ions, National Seminar on Chemistry and Chemical Education VI, Surakarta, (2014).

5. VS Galakhov, EP Aghasyan. VA Komarov. VA Uslikov and BB Blinov. A method of wastewater treatment for chromium compounds. Avt.sv. No 882951. MKI SSSR S02F1/70, (2015).

6. Sh. I. Berdiev, F.I.Erkabaev, D.A. Muxammadieva. Method for Obtaining H-permutite //Texas Journal of Multidisciplinary Studies. -Vol 12. -p 37-40, (2022).

7. Igbokwe P.K, Okolomike RO., and Nwokolo SO. (2008). Zeolite for Drying of Ethanol-Water and Methanol-Water Systems from Nigerian Clay Resource, Journal of The University of Chemical Technology and Metallurgy, 43: 109-112.

8. Ackley M.W, Rege S.U., and Saxena H. (2003), Application of Natural Zeolites in The Purification and Separation. Journal of Microporous and Mesoporous Materials. 61, 25- 42.

9. Kamarudin KSN, Mat H, dan Hamdan H (2003). Structural Synthesis and Modification of Zeolite as Methane Adsorbent. Paper of University Teknologi Malaysia submitted at Annual Fundamental Science Seminar. 13 (2): 272-278.

10. Asilbek Mamatkulov and Furkat Erkabaev. Factors affecting electrolytic level maintenance in acid batteries. E3S Web of Conf. Volume 401, 2023 V International Scientific Conference “Construction Mechanics, Hydraulics and Water Resources Engineering” (CONMECHYDRO - 2023). https://doi.org/10.1051/e3sconf/202340103067

11. Erkabaev F.I, Madrimov R.M., Nurmatova V.B. Status quo analysis of the Aidar-Arnasay Lake System. 5th International Conference on Energetics, Civil and Agricultural Engineering (ICECAE 2024), E3S Web Conf. Volume 497, 2024, 07 March 2024, https://doi.org/10.1051/e3sconf/202449702025.

12. Pattahov N.A., Erkabaev F.I. Climatic conditions, composition and type of soil Jizzakh steppe // 5th International Conference on Energetics, Civil and Agricultural Engineering (ICECAE 2024), E3S Web Conf. Volume 497, 2024, 07 March 2024, https://doi.org/10.1051/e3sconf/202449702025.

13. Erkabayev Furkat, Pattakhov Nasibulla Jizzakh Steppe: climatic conditions, composition and type of soil // E3S Web of Conferences 563, 03045 (2024) ICESTE 2024 https://doi.org/10.1051/e3sconf/202456303045

14. Erkabayev Furkat, Sherzodbek Berdiyev, Tuychi Pirimov, Dilshod Rakhimov Comparison of zeolite adsorbent with N permutite adsorbent // BIO Web of Conferences 116, 03.08 (2024) EBWFF 2024 https://doi.org/10.1051/bioconf/20241160300

CHARACTERIZATION OF HYDROCARBON LIQUID BY-PRODUCT FROM POLYETHYLENE WAX PRODUCTION: GC–MS COMPOSITION AND FUEL PROPERTY EVALUATION

Sanalar
Qabul qilindi: 21.04.2026
Nashrga qabul qilindi: 29.04.2026
Nashr qilindi: 04.05.2026

Eldor Ergashvoy ugli Mashaev
Acting Associate Professor, PhD of the Department of Chemical Technology of Oil and Gas Refining at the Tashkent Institute of Chemical Technology.
E-mail:eldor275@gmail.com
Orcid:0000-0003-4594-3670

Akhmadali Itolmas ugli Khudoyberdiyev
Assistant of the Department of High Molecular Compounds and Plastics, Tashkent Institute of Chemical Technology.
E-mail: axmadxudoyberdiyev@gmail.com
Orcid: 0000-0001-9495-5251

Iroda Ermakhamatovna Talipova
Chief Forensic Expert, Laboratory of Forensic Analysis of Materials, Substances, and Products, Kh.S. Suleimanova Republican Forensic Center, 1st Class Lawyer

Dianna Enverovna Lukasheva
Leading Forensic Expert, Laboratory of Forensic Analysis of Materials, Substances, and Products, Kh.S. Suleimanova Republican Forensic Center, 2nd Class Lawyer.
E-mail: ledydial@mail.ru

Elena Yuryevna Mezentseva
Senior Forensic Expert, Laboratory of Forensic Analysis of Materials, Substances, and Products, Kh.S. Suleimanova Republican Forensic Center, 2nd Class Justice Advisor
E-mail: lenokinna@mail.ru

Khusain Borat ugli Urakov
PhD student, Department of Cellulose and Wood Technologies, Tashkent Institute of Chemical Technology
E-mail: sayn9427@gmail.com

Mohinur Sirojiddin qizi Pardaeva
Student of the Department of High Molecular Compounds and Plastics, Tashkent Institute of Chemical Technology.

Mashaev E.E., Xudoyberdiyev A.I., Talipova I.E., Lukasheva D.E., Mezentseva Y.Y., Urakov X.B., Pardayeva M.S. Characterization of hydrocarbon liquid by-product from polyethylene wax production: GC–MS composition and fuel property evaluation // Journal of future. 2026. Vol. 2. Iss. 2. pp. 13–26. https://doi.org/10.66960/jof.3093-8899.00022

Annotatsiya. Yuqori molekulyar ogʻirlikdagi polietilenning termik parchalanishi orqali polietilen mumining ishlab chiqarilishining ortishi qoʻshimcha mahsulot sifatida suyuq uglevodorod fraksiyasini hosil qiladi, uning tarkibi va foydalanish potensiali yetarlicha oʻrganilmagan. Ushbu ishda ushbu suyuq fraksiyaning kimyoviy tarkibi va fizik-kimyoviy xususiyatlari uning sanoatda qoʻllanilishini baholash uchun har tomonlama oʻrganildi. Namuna polietilenni termik krekinglash jarayonida olingan va keyinchalik 220 °C gacha atmosfera bosimida haydash orqali fraksiyalangan. Molekulyar tarkib gaz xromatografiyasi-massa spektrometriyasi (GX-MS) yordamida aniqlangan, yonilgʻi bilan bogʻliq xususiyatlar esa tegishli ASTM usullariga muvofiq oktan soni, setan soni va past harorat xususiyatlarini oʻlchash orqali baholangan. GX-MS tahlili shuni koʻrsatdiki, suyuq fraksiya asosan C_8-C_{26} uglerod soni oraligʻidagi parafinli uglevodorodlardan iborat boʻlib, asosiy hissasi C_{10}-C_{16} birikmalaridan kelib chiqadi. Chiziqli alkanlar dominant komponentlar sifatida aniqlandi, ularga oz miqdordagi tarmoqlangan alkanlar va polietilen zanjirining uzilishi paytida hosil boʻlgan oz miqdordagi olefinlar hamroh boʻldi. Olingan uglevodorod taqsimoti oʻrganilayotgan mahsulot odatda kerosin-dizel turidagi yonilgʻilar bilan bogʻliq boʻlgan oʻrta distillyat diapazoniga tegishli ekanligini koʻrsatadi. Yonilgʻi xususiyatlarini tahlil qilish shuni koʻrsatdiki, suyuqlik taxminan 42 setan sonini koʻrsatadi, bu uning siqishli yonuv dvigatellari uchun qulay yonish xususiyatlarini tasdiqlaydi. Past haroratli oʻlchovlar −16 °C hiralanish haroratini va −27 °C qotish haroratlarini koʻrsatdi, bu parafinga boy uglevodorod aralashmalari uchun odatiy holdir.

Natijalar shuni koʻrsatadiki, oʻrganilgan suyuq fraksiyani toʻgʻridan-toʻgʻri standart tijorat yonilgʻisi sifatida tasniflash mumkin emas, lekin tegishli yangilash va tozalashdan soʻng kerosin va dizel yonilgʻilari uchun istiqbolli aralashtirish komponenti boʻlib xizmat qilishi mumkin. Yonilgʻi qoʻllanilishidan tashqari, sanoat erituvchisi sifatida foydalanish, keyingi krekinglash yoki piroliz jarayonlari uchun xom ashyo, parafin ishlab chiqarish uchun xom ashyo, sirt faol moddalar va sintetik moylash materiallari uchun prekursor va sanoat reaktorlari uchun potentsial issiqlik uzatish suyuqligi kabi bir qancha muqobil foydalanish yoʻllari aniqlandi. Topilmalar polietilen krekingi suyuqliklarining qimmatli ikkilamchi uglevodorod resurslari sifatidagi salohiyatini ta’kidlaydi va polimerdan olingan uglevodorod oqimlari uchun yanada samarali va aylanma foydalanish strategiyalarini ishlab chiqishga hissa qoʻshadi.

Kalit soʻzlar: *Polietilen krekingi, GX-MS tahlili, uglevodorod tarkibi, yonilgʻi xususiyatlari, setan soni, past haroratli xususiyatlar, polimer chiqindilari utilizatsiyasi, neft-kimyo xom ashyosi*

Abstract. The increasing production of polyethylene wax through thermal degradation of high-molecular-weight polyethylene generates a liquid hydrocarbon fraction as a by-product, the composition and potential utilization of which remain insufficiently studied. In the present work, the chemical composition and physicochemical properties of this liquid fraction were comprehensively investigated in order to evaluate its potential industrial applications. The sample was obtained during the thermal cracking of polyethylene and subsequently fractionated by atmospheric distillation up to 220 °C. Molecular composition was determined using gas chromatography–mass spectrometry (GC–MS), while fuel-related properties were evaluated through measurements of octane number, cetane number, and low-temperature characteristics according to relevant ASTM methods. GC–MS analysis revealed that the liquid fraction is predominantly composed of paraffinic hydrocarbons in the carbon number range C_8–C_{26}, with the major contribution originating from C_{10}–C_{16} compounds. Linear alkanes were identified as the dominant components, accompanied by smaller amounts of branched alkanes and minor quantities of olefins formed during polyethylene chain scission. The obtained hydrocarbon distribution indicates that the investigated product belongs to the middle-distillate range typically associated with kerosene–diesel type fuels. Fuel property analysis showed that the liquid exhibits a cetane number of approximately 42, confirming its favorable ignition characteristics for compression ignition engines. Low-temperature measurements indicated a cloud point of −16 °C and a pour point of −27 °C, which are typical for paraffin-rich hydrocarbon mixtures.

The results suggest that the investigated liquid fraction cannot be directly classified as a standard commercial fuel but may serve as a promising blending component for kerosene and diesel fuels after appropriate upgrading and purification. In addition to fuel applications, several alternative utilization pathways were identified, including use as an industrial solvent, feedstock for further cracking or pyrolysis processes, raw material for paraffin production, precursor for surfactants and synthetic lubricants, and potential heat-transfer fluid for industrial reactors. The findings highlight the potential of polyethylene cracking liquids as valuable secondary hydrocarbon resources and contribute to the development of more efficient and circular utilization strategies for polymer-derived hydrocarbon streams.

Keywords: *Polyethylene cracking, GC–MS analysis, hydrocarbon composition, fuel properties, cetane number, low-temperature properties, polymer waste valorization, petrochemical feedstock*

Аннотация. Увеличение производства полиэтиленового воска путем термической деградации высокомолекулярного полиэтилена приводит к образованию жидкой углеводородной фракции в качестве побочного продукта, состав и потенциальное использование которой остаются недостаточно изученными. В данной работе был проведен всесторонний анализ химического состава и физико-химических свойств данной жидкой фракции с целью оценки ее потенциального промышленного применения. Образец был получен в процессе термического крекинга полиэтилена и впоследствии фракционирован атмосферной дистилляцией до 220 °C. Молекулярный состав определяли с помощью газовой хроматографии-масс-спектрометрии (ГХ-МС), а свойства, связанные с топливом, оценивали путем измерения октанового числа, цетанового числа и низкотемпературных характеристик в соответствии с соответствующими методами ASTM. Анализ ГХ-МС показал, что жидкая фракция преимущественно состоит из парафиновых углеводородов в диапазоне числа атомов углерода C_8–C_{26}, причем основной вклад вносят соединения C_{10}–C_{16}. В качестве доминирующих компонентов были идентифицированы линейные алканы, сопровождаемые меньшим количеством разветвленных алканов и незначительным количеством олефинов, образующихся в процессе разрыва полиэтиленовой цепи. Полученное распределение углеводородов указывает на то, что исследуемый продукт относится к диапазону средних дистиллятов, обычно ассоциируемых с керосиново-дизельным топливом. Анализ свойств топлива показал, что жидкость имеет цетановое число приблизительно 42, что подтверждает ее благоприятные характеристики воспламенения для двигателей внутреннего сгорания. Низкотемпературные измерения показали температуру помутнения −16 °C и температуру застывания −27 °C, что типично для смесей углеводородов, богатых парафинами.

Результаты показывают, что исследованная жидкая фракция не может быть напрямую классифицирована как стандартное коммерческое топливо, но может служить перспективным компонентом для смешивания керосина и дизельного топлива после соответствующей модернизации и очистки. В дополнение к применению в качестве топлива были выявлены несколько альтернативных путей использования, включая использование в качестве промышленного растворителя, сырья для дальнейших процессов крекинга или пиролиза, сырья для производства парафина, прекурсора для поверхностно-активных веществ и синтетических смазочных материалов, а также потенциального теплоносителя для промышленных реакторов. Полученные результаты подчеркивают потенциал жидкостей, образующихся при крекинге полиэтилена, как ценных вторичных углеводородных ресурсов и способствуют разработке более эффективных и циклических стратегий использования углеводородных потоков, полученных из полимеров.

Ключевые слова: *Крекинг полиэтилена, анализ ГХ-МС, состав углеводородов, свойства топлива, цетановое число, низкотемпературные свойства, утилизация полимерных отходов, нефтехимическое сырье.*

INTRODUCTION

The global growth of polymer production has significantly increased the volume of polymer waste and industrial by-products generated during manufacturing processes. Among synthetic polymers, polyethylene (PE) represents the most widely produced thermoplastic due to its low cost, chemical resistance, and versatility in industrial and consumer applications [1]. However, the high chemical stability of polyethylene makes it resistant to natural degradation, creating environmental challenges associated with both post-consumer plastic waste and process-related by-products [2,16]. Thermochemical conversion technologies such as pyrolysis and thermal cracking have emerged as promising routes for the valorization of polyolefin materials. During these processes, long polymer chains undergo random chain scission and β-scission reactions that generate lower molecular weight hydrocarbons including n-alkanes, iso-alkanes, and α-olefins [3,4]. These reactions transform polymeric feedstocks into liquid hydrocarbon fractions that can resemble petroleum-derived fuels and petrochemical intermediates [5]. As a result, thermal conversion of polyethylene has gained increasing attention as a pathway for producing alternative hydrocarbon resources and circular carbon feedstocks [20]. In industrial practice, controlled thermal degradation of polyethylene is widely used in the production of polyethylene waxes. This process involves the reduction of polymer molecular weight through thermal cracking, producing wax fractions with defined chain length distributions. During this process, a liquid hydrocarbon fraction is formed as a secondary product [6]. Previous studies have shown that such liquids often contain hydrocarbons in the range of C8–C30, primarily composed of linear paraffins and olefins formed through random chain cleavage reactions [8,15]. The composition of these products strongly depends on the cracking conditions such as temperature, residence time, and reactor configuration [14,18]. Compared with conventional plastic pyrolysis oils obtained from mixed polymer wastes, by-product liquids generated during controlled polyethylene processing may exhibit a more uniform composition and lower contamination by heteroatom-containing compounds. This makes them potentially attractive as feedstocks for fuel production or petrochemical applications [7]. Several studies have reported that polyolefin pyrolysis oils can contain significant fractions of linear paraffins and α-olefins that resemble components present in petroleum-derived fuels such as kerosene or diesel [10]. The physicochemical properties of these hydrocarbon mixtures play a critical role in determining their possible industrial utilization. In particular, parameters such as octane number, cetane number, boiling range, and cold-flow properties are essential indicators for evaluating fuel performance [11]. Paraffinic hydrocarbons generally exhibit high cetane numbers but relatively poor low-temperature properties due to the crystallization of long-chain n-alkanes [10]. As the temperature decreases, wax crystals can form in the fuel, leading to turbidity and eventually loss of fluidity. These phenomena are typically characterized by parameters such as cloud point and pour point, which are widely used to evaluate the cold-flow behavior of hydrocarbon fuels [17].

Modern analytical techniques provide powerful tools for investigating the composition and properties of complex hydrocarbon mixtures. Gas chromatography coupled with mass spectrometry (GC–MS) is one of the most widely used analytical techniques for detailed molecular characterization of petroleum fractions and pyrolysis oils [9,12,13]. GC–MS analysis enables identification of individual hydrocarbon compounds and determination of carbon number distribution, which is crucial for understanding fuel properties and potential processing routes. Despite the growing body of research on plastic pyrolysis oils, relatively limited attention has been paid to the characterization of liquid hydrocarbon fractions produced as by-products during polyethylene wax production. Such materials represent a potentially valuable hydrocarbon resource that could be utilized as blending components for fuels or as feedstocks for further catalytic upgrading. In addition, pyrolysis-derived hydrocarbon mixtures may contain unsaturated compounds and light hydrocarbons that influence odor, volatility, and combustion characteristics [19]. Therefore, comprehensive characterization of these by-product liquids is required in order to evaluate their chemical composition and fuel-related properties. In this context, combined analytical approaches integrating chromatographic composition analysis and physicochemical testing are particularly important for assessing their potential industrial applications.

The aim of the present study is to investigate the chemical composition and physicochemical properties of a liquid hydrocarbon fraction obtained as a by-product during polyethylene wax production through thermal cracking of high-molecular-weight polyethylene. The research combines GC–MS analysis with measurements of octane number, cetane number, and low-temperature fuel properties according to ASTM methods. The results provide new insights into the molecular composition and potential applications of polyethylene cracking liquids as alternative hydrocarbon resources. The present study provides a comprehensive characterization of a liquid hydrocarbon fraction formed as a by-product during polyethylene wax production through thermal cracking of high-molecular-weight polyethylene. While most previous studies have focused on pyrolysis oils obtained from mixed plastic waste streams, limited information is available regarding the composition and fuel-related properties of liquid fractions generated under controlled industrial polyethylene degradation processes.

The novelty of this work lies in the integrated analysis of the molecular composition and physicochemical properties of this by-product liquid using gas chromatography–mass spectrometry (GC–MS) combined with fuel property evaluation, including octane number, cetane number, and low-temperature characteristics determined according to ASTM standards. The obtained results reveal the predominance of C_8–C_{26} paraffinic hydrocarbons and demonstrate that the investigated liquid fraction exhibits physicochemical properties comparable to kerosene–diesel range hydrocarbon mixtures. Furthermore, the study provides new insights into the potential utilization pathways of polyethylene cracking liquids as alternative hydrocarbon resources for fuel blending or petrochemical feedstock applications.

METHODS

The investigated liquid hydrocarbon fraction was obtained as a by-product during the industrial production of polyethylene wax. In this process, high-molecular-weight polyethylene undergoes controlled thermal degradation, resulting in the cleavage of polymer chains and formation of lower molecular weight hydrocarbons. The resulting liquid product represents a complex mixture of paraffinic hydrocarbons formed during the cracking process. Prior to analysis, the liquid product was subjected to atmospheric distillation, and the fraction boiling below 220 °C was collected and used for further physicochemical and compositional analysis. The obtained fraction was a transparent, colorless liquid with a characteristic hydrocarbon odor. The chemical composition of the liquid fraction was determined using gas chromatography coupled with mass spectrometry (GC–MS). The analysis was performed on an Agilent gas chromatograph equipped with a mass selective detector and an automatic injection system. Separation of the components was carried out on a capillary column coated with a non-polar stationary phase (5% phenyl–95% dimethylpolysiloxane). Helium was used as the carrier gas. The injection was performed in split mode, and the sample volume was 1 μL. The oven temperature program was designed to ensure effective separation of hydrocarbons over a wide boiling range. The temperature was initially held at a low value and then gradually increased to allow elution of heavier components. Mass spectra were recorded in electron ionization (EI) mode. Identification of individual compounds was performed by comparing the obtained mass spectra with reference spectra from the NIST mass spectral library. Only compounds with high similarity indices were considered for qualitative identification.

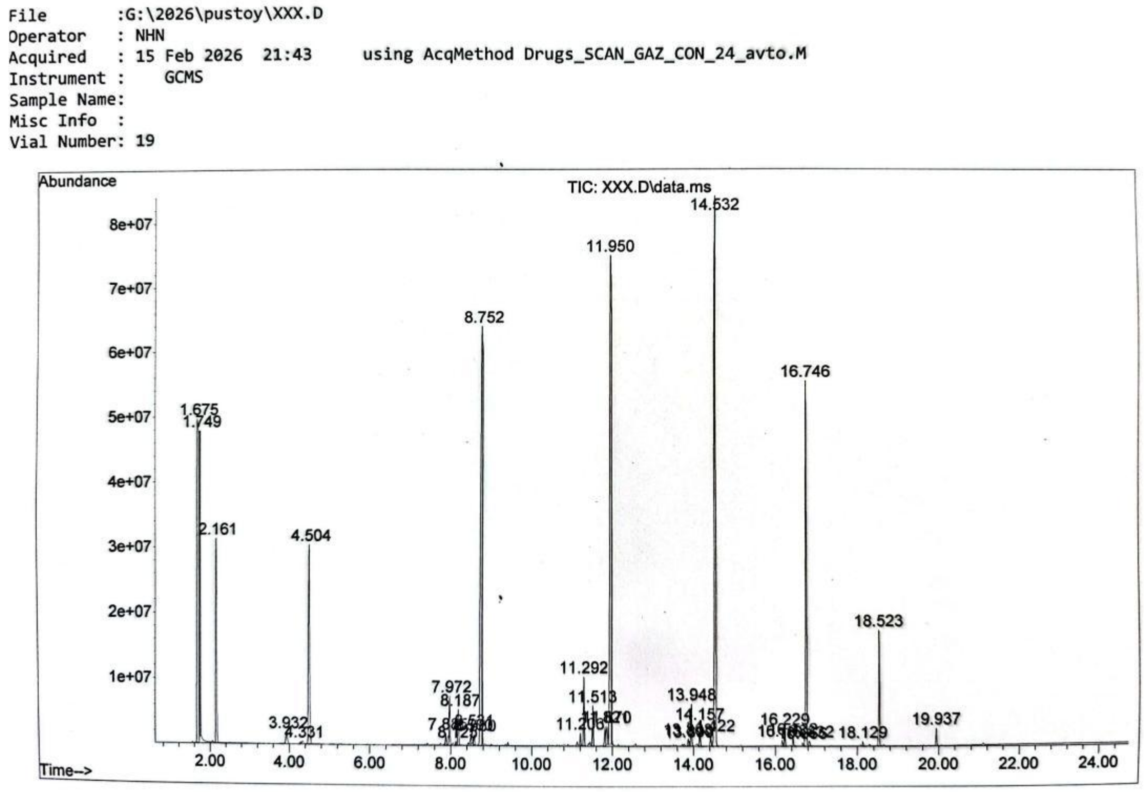
The octane number of the investigated liquid fraction was measured using a portable fuel analyzer Shatox SX-300. This instrument determines octane number based on the measurement of dielectric properties of the fuel and comparison with calibration models developed for hydrocarbon fuels. Measurements were performed using several operational modes of the analyzer, including Octane, Octane1, and Oct+Oct modes. The instrument provides calculated values of Research Octane Number (RON), Motor Octane Number (MON), and Anti-Knock Index (AKI). Each measurement was repeated several times to ensure reproducibility, and the average values were reported. The cetane number of the liquid fraction was evaluated using the same Shatox SX-300 analyzer operating in Cetane mode. The instrument estimates the cetane number (CN) of diesel-type fuels based on dielectric properties and internal calibration algorithms. The measurements were performed at ambient laboratory conditions. The instrument also provides additional parameters such as estimated flash point and fuel type classification.

Low-temperature fuel properties were determined using the TPZ-LAB-12 automated analyzer, which is designed for evaluating cold-flow characteristics of petroleum fuels. The cloud point and pour point of the investigated liquid fraction were determined according to the standardized test methods: ASTM D6749 – Standard test method for determination of cloud point of petroleum products using automatic optical detection; ASTM D7683 – Standard test method for determination of pour point using automated instruments. During the experiment, the sample was gradually cooled under controlled conditions. The cloud point was determined as the temperature at which the first wax crystals became visible, causing turbidity in the sample. The pour point was defined as the lowest temperature at which the liquid remained capable of flowing under the test conditions. All measurements were performed in accordance with the operational procedures of the instrument and the requirements of the respective ASTM standards.

RESULTS AND DISCUSSION

The molecular composition of the liquid hydrocarbon fraction obtained during polyethylene wax production was investigated using gas chromatography–mass spectrometry (GC–MS). The chromatographic profile revealed a complex mixture of hydrocarbons dominated by linear and slightly branched alkanes within the carbon number range C_8–C_{26}, accompanied by minor quantities of unsaturated hydrocarbons Figure 1.

The chromatogram exhibits a characteristic distribution pattern typical for products generated during thermal degradation of polyolefins. The identified compounds include a homologous series of n-alkanes such as octane (C_8), nonane (C_9), decane (C_{10}), undecane (C_{11}), dodecane (C_{12}), tridecane (C_{13}), tetradecane (C_{14}), pentadecane (C_{15}), and higher paraffins extending up to C_{26} Table 1. In addition to the linear hydrocarbons, several branched alkanes and olefinic compounds were detected in smaller quantities, including methyl-substituted alkanes and α-olefins such as 1-decene and 1-dodecene. The presence of this homologous distribution



```
File       :G:\2026\pustoy\XXX.D
Operator   : NHN
Acquired   : 15 Feb 2026  21:43      using AcqMethod Drugs_SCAN_GAZ_CON_24_avto.M
Instrument :     GCMS
Sample Name:
Misc Info  :
Vial Number: 19
```

Fig. 1. The molecular composition of the liquid hydrocarbon fraction obtained during polyethylene wax production using gas chromatography–mass spectrometry (GC–MS)

of n-alkanes is consistent with the well-established mechanism of polyethylene thermal cracking. During thermal degradation, polymer chains undergo random scission followed by β-scission reactions, generating shorter hydrocarbon fragments that subsequently stabilize to form saturated and unsaturated hydrocarbons. The predominance of n-alkanes indicates that hydrogen transfer reactions play an important role in the stabilization of primary radical fragments formed during the cracking process. The carbon number distribution observed in the chromatogram suggests that the main fraction of the liquid product is concentrated in the C_{10}–C_{16} region, which corresponds to the boiling range typical of kerosene and diesel fuels. This distribution explains the relatively moderate boiling range observed during distillation of the liquid fraction. The presence of heavier hydrocarbons up to C_{20}–C_{26} indicates that partial secondary reactions and incomplete chain scission occur during the degradation process, resulting in the formation of heavier paraffinic species. Another notable feature of the chromatographic profile is the relatively low abundance of aromatic hydrocarbons and oxygen-containing compounds. The absence of significant aromatic fractions can be attributed to the chemical structure of polyethylene, which consists exclusively of saturated carbon chains. As a result, thermal degradation primarily produces aliphatic hydrocarbons rather than aromatic species. This observation distinguishes polyethylene-derived liquids from pyrolysis oils obtained from mixed plastic wastes, where aromatic hydrocarbons are often present in higher concentrations. The detected olefinic compounds, including several α-olefins, are typical intermediates formed during polyolefin degradation. These compounds originate from β-scission reactions of polymer radicals and can subsequently undergo hydrogenation, isomerization, or secondary cracking reactions. Although their concentration in the investigated liquid fraction is relatively low, the presence of olefins contributes to the characteristic odor of the product and may influence its chemical reactivity during further processing.

The overall chromatographic pattern indicates that the investigated liquid fraction can be classified as a paraffin-rich hydrocarbon mixture, predominantly composed of linear alkanes. Such compositions are commonly observed in hydrocarbon liquids obtained from the pyrolysis or thermal cracking of polyethylene. Compared with conventional petroleum fractions, polyethylene-derived liquids often contain a higher proportion of straight-chain hydrocarbons due to the linear structure of the original polymer. From the perspective of potential applications, the observed composition is particularly favorable for processes where paraffinic hydrocarbons are desired. The predominance of linear alkanes may contribute to relatively high cetane numbers and favorable ignition characteristics if the material is used as a diesel blending component. At the same time, the presence of α-olefins may provide opportunities for further catalytic upgrading or petrochemical processing.

Overall, the GC–MS analysis demonstrates that the liquid fraction generated during polyethylene wax production consists primarily of middle-range paraffinic hydrocarbons with a broad carbon number distribution and limited contamination by

Table 1. Relative peak area distribution of hydrocarbons in the sample according to GC–MS analysis

Hydrocarbon class	Relative content (peak area, %)
n-alkanes C_8–C_{12}	25–30%
n-alkanes C_{13}–C_{18}	40–45%
Heavy hydrocarbons C_{20+}	10–15%
Branched alkanes	15–20%
Oxygen-containing compounds	<2%

heteroatomic compounds. These characteristics highlight the potential value of this by-product as a hydrocarbon resource for fuel or petrochemical applications.

Prior to analytical characterization, the liquid product was subjected to atmospheric distillation and the fraction boiling below 220 °C was collected for analysis Table 2. This boiling range corresponds approximately to hydrocarbons from C_8 to C_{12}–C_{13}, which is consistent with the compounds detected by GC–MS. The relatively narrow boiling range indicates that the obtained liquid fraction represents a middle distillate-type hydrocarbon mixture rather than heavy wax fractions. Similar boiling ranges have been reported for hydrocarbon fractions obtained during plastic pyrolysis and polyethylene cracking processes [5]. The transparency and low color of the obtained liquid further indicate the absence of heavy aromatic compounds and polymeric residues, which are commonly found in pyrolysis oils derived from mixed plastic wastes. This observation suggests that the controlled degradation of polyethylene during wax production results in a relatively clean paraffinic hydrocarbon fraction.

Estimated distillation curve of the hydrocarbon liquid fraction obtained during polyethylene wax production Figure 2. The curve was constructed based on GC–MS carbon number distribution of hydrocarbons (C_8–C_{26}) and corresponding boiling point correlations for n-alkanes.

The estimated distillation curve of the investigated hydrocarbon liquid fraction is presented in Figure 2. The curve was constructed based on the carbon number distribution obtained from GC–MS analysis and the corresponding boiling points of n-alkanes. The results indicate that the majority of the fraction is concentrated within the 150–210 °C boiling range, which corresponds to hydrocarbons in the C_{10}–C_{13} region. Approximately 50 % of the distilled volume boils at around 180 °C, confirming that the investigated liquid fraction belongs to the middle distillate range typical for kerosene–diesel type hydrocarbon mixtures. The relatively smooth distillation profile suggests a homogeneous hydrocarbon distribution and the absence of heavy aromatic or polymeric residues. Such distillation characteristics are typical for paraffinic liquids obtained from thermal degradation of polyethylene and indicate potential applicability of this fraction as a blending component in middle distillate fuels.

Table 2. Estimated distillation characteristics

Distilled volume (%)	Temperature (°C)	Main hydrocarbons
IBP	125	C_8-C_9
10%	140	C_9-C_{10}
20%	150	C_{10}
30%	160	C_{10}-C_{11}
40%	170	C_{11}
50%	180	C_{11}-C_{12}
60%	190	C_{12}
70%	200	C_{12}-C_{13}
80%	210	C_{13}
90%	215	C_{13}-C_{14}
FBP	220	C_{14+}

The anti-knock characteristics of the obtained liquid fraction were evaluated using a portable fuel analyzer. Measurements performed in different operational modes produced varying results, with the Research Octane Number (RON) ranging

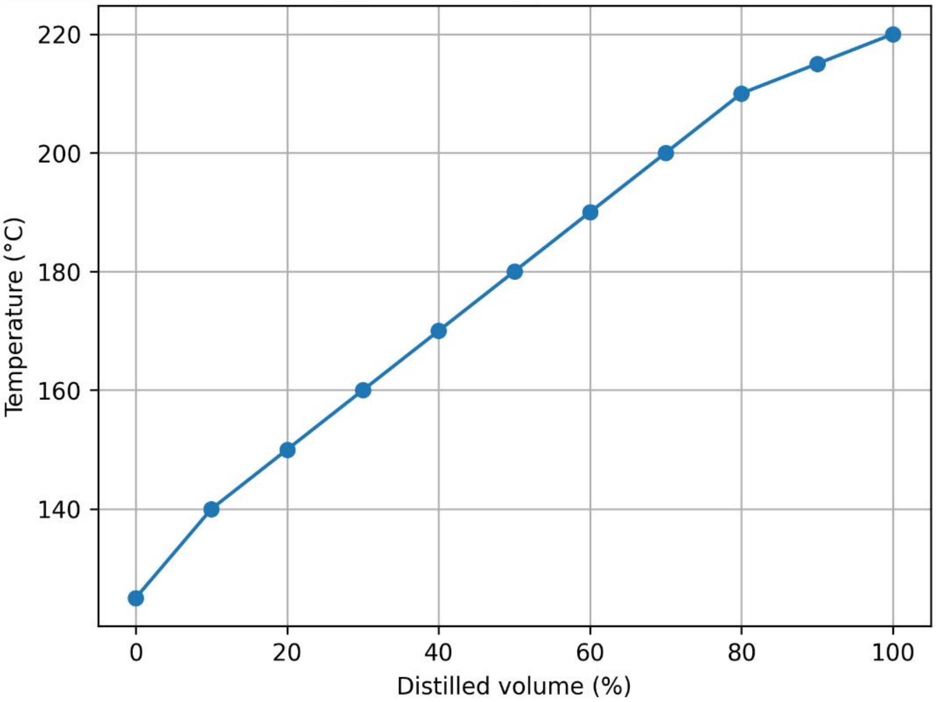
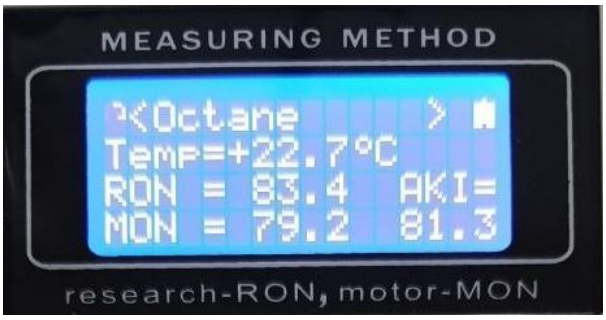


Fig. 2. Estimated distillation curve of the hydrocarbon liquid fraction obtained during polyethylene wax production

between approximately 83 and 105 depending on the selected calibration model Figure 3. The variation in the measured values can be explained by the composition of the investigated liquid. Portable octane analyzers estimate octane number based on dielectric properties of fuels and calibration models developed primarily for conventional gasoline blends. However, the investigated liquid fraction contains a high concentration of linear paraffins, which typically exhibit low octane numbers but high cetane numbers. Therefore, the obtained octane values should be interpreted cautiously, as the measurement technique is optimized for gasoline-type fuels rather than paraffinic hydrocarbon mixtures.

The results nevertheless indicate that the investigated liquid does not possess the chemical characteristics of conventional gasoline.

The ignition quality of the investigated liquid fraction was evaluated through determination of the cetane number (CN). The obtained value of approximately 42 indicates that the investigated hydrocarbon mixture exhibits ignition characteristics similar to those of conventional diesel fuels Table 3. The relatively high cetane number can be attributed to the dominance of linear paraffins in the hydrocarbon composition. It is well known that n-alkanes exhibit high cetane numbers because they ignite readily under compression conditions. In contrast, aromatic



```
<Octane       >
Temp=+22.7°C
RON = 83.4   AKI=
MON = 79.2   81.3
```

Fig. 3. The octane number of the investigated liquid fraction was measured using a portable fuel analyzer Shatox SX-300

Table 3. Fuel quality parameters of the polyethylene cracking liquid measured using the Shatox SX-300 analyzer

Measurement mode	RON	MON	AKI	Additional parameters
Octane	83.4	79.2	81.3	–
Octane1	91.5	82.7	87.1	–
Oct+Oct	104.9	105.4	105.1	–
Oct+Bd.time	–	–	–	A80 / Normal; Tbd = 162.9 °C
Cetane	–	–	–	Cetane number = 42.0; Fuel type = A; Estimated flash point (Tfl) = −45.5 °C

hydrocarbons and branched compounds generally exhibit lower cetane values [10]. The measured cetane number suggests that the liquid fraction obtained from polyethylene cracking could potentially be used as a blending component in diesel fuels or as a feedstock for further upgrading processes.

The low-temperature behavior of the investigated liquid fraction was evaluated by determining the cloud point and pour point using an automated cold-flow analyzer according to ASTM standards Table 4. The measured cloud point was −16 °C, while the pour point was −27 °C. These values indicate that the fuel begins to form wax crystals at approximately −16 °C, and the flow properties become significantly restricted at lower temperatures Figure 4.

These results are consistent with the paraffinic composition revealed by GC–MS analysis. Linear paraffins tend to crystallize at relatively high temperatures compared to aromatic hydrocarbons or branched compounds. The formation of wax crystals leads to turbidity in the liquid, followed by progressive loss of fluidity as the crystal network develops. The difference between the cloud point and pour point (approximately 11 °C) is typical for paraffin-rich hydrocarbon mixtures. Similar cold-flow characteristics have been reported for paraffinic diesel fuels and synthetic fuels derived from Fischer–Tropsch processes.

The combined results of compositional and physicochemical analyses suggest that the investigated liquid fraction obtained during polyethylene wax production represents a paraffinic hydrocarbon mixture with properties comparable to middle

ТП: -16.0°C
ТПТ:-27°C
01:32:54 27.02.2026 11:53:16

Поиск Ттекучести/Тзастывания

```
-25   ->   5 мм.в.ст.
-26   ->   5 мм.в.ст.
-27   ->   1 мм.в.ст.
-28   ->   30 мм.в.ст.
```

Поиск Тпомутнения

```
-15.8   <=>   1173
-15.9   <=>   1172
-16.0   <=>   1171
-16.1   <=>   1167
```

Fig. 4. Low-temperature fuel properties were determined using the TPZ-LAB-12

Table 4. Comparison with typical diesel fuels

Fuel	Cloud Point	Pour Point
Summer diesel	–5…–10 °C	–15…–20 °C
Winter diesel	–15…–20 °C	–25…–35 °C
Arctic diesel	–30…–40 °C	–45…–60 °C

distillate fuels. The dominance of C_{10}–C_{16} hydrocarbons, relatively high cetane number, and moderate cold-flow properties indicate that this liquid could potentially be utilized as: a blending component for diesel fuels; a feedstock for hydroprocessing or catalytic upgrading; a raw material for petrochemical applications involving paraffinic hydrocarbons. Compared with conventional plastic pyrolysis oils, the investigated product appears to have a relatively clean hydrocarbon composition with limited contamination by heteroatom-containing compounds. This characteristic may facilitate its integration into existing refining and fuel production processes. Further research should focus on detailed distillation analysis, determination of density and viscosity, and evaluation of catalytic upgrading pathways to improve the fuel quality and broaden the potential applications of this material.

The comparative analysis indicates that the investigated liquid hydrocarbon fraction obtained during polyethylene wax production exhibits physicochemical properties close to those of middle distillate petroleum fractions Table 4. The boiling range and hydrocarbon distribution correspond to kerosene–diesel type hydrocarbons, while the measured cetane number (42) approaches the lower limit of conventional diesel fuels. The cold-flow properties of the investigated liquid (cloud point −16 °C and pour point −27 °C) fall within the range typical for winter-grade diesel fuels but do not meet the stricter requirements of aviation kerosene. Therefore, the obtained hydrocarbon fraction cannot be directly classified as a standard commercial fuel but may be considered a potential blending component for diesel fuels or a petrochemical feedstock after further upgrading.

CONCLUSION

This study investigated the chemical composition and physicochemical properties of a liquid hydrocarbon fraction obtained as a by-product during polyethylene wax

Table 4. Comparison of physicochemical properties of polyethylene cracking liquid with standard specifications for kerosene and diesel fuels

Parameter	Polyethylene cracking liquid	Kerosene (GOST 10227-2013)	Diesel fuel (GOST 32511-2013 / GOST 305-2013)
Hydrocarbon range	C_8–C_{26}	C_8–C_{16}	C_{10}–C_{22}
Boiling range (°C)	up to 220	150–300	180–360
Research octane number (RON)	83	not regulated	not regulated
Cetane number	42	not regulated	≥ 45–51
Cloud point (°C)	−16	≤ −50 (aviation fuels)	−5 to −35 (depending on grade)
Pour point (°C)	−27	≤ −60	−10 to −35
Appearance	transparent	transparent	transparent

production via thermal cracking of high-molecular-weight polyethylene. The combined analytical approach, including GC–MS analysis, fuel property measurements, and low-temperature characterization, provided comprehensive insight into the nature and potential applications of the investigated liquid fraction. GC–MS analysis revealed that the liquid product consists predominantly of paraffinic hydrocarbons within the carbon number range C_8–C_{26}, with the main fraction concentrated in the C_{10}–C_{16} region. Linear alkanes were identified as the dominant components, accompanied by smaller amounts of branched alkanes and minor quantities of olefinic compounds. This hydrocarbon distribution is typical for polyethylene thermal degradation and reflects the random chain scission mechanism characteristic of polyolefin cracking processes. Distillation characteristics indicated that the majority of the liquid fraction falls within the middle distillate boiling range, corresponding to kerosene–diesel type hydrocarbons. The transparency and relatively uniform composition of the product suggest the absence of significant aromatic compounds and heavy polymeric impurities, which distinguishes this material from conventional mixed plastic pyrolysis oils. Fuel property measurements demonstrated that the investigated liquid exhibits a cetane number of approximately 42, indicating ignition characteristics comparable to conventional diesel fuels. At the same time, the measured cloud point (−16 °C) and pour point (−27 °C) confirm the paraffinic nature of the mixture and indicate moderate low-temperature flow properties typical of paraffin-rich middle distillates. Based on the obtained results, the investigated liquid fraction may be considered a potential blending component for petroleum fuels after appropriate upgrading and detailed characterization. In particular, the lighter fraction could potentially be used as an additive to kerosene-type fuels, while the heavier fraction may be suitable as a blending component for diesel fuels. However, before practical application, comprehensive physicochemical and environmental analyses are required, including evaluation of combustion properties, stability, and removal of the characteristic hydrocarbon odor associated with the presence of light olefinic compounds.

In addition to fuel applications, several alternative utilization pathways can be considered. Due to its hydrocarbon composition, the liquid fraction may potentially be used as an industrial solvent, particularly in processes where slow evaporation is acceptable. Another promising direction is its use as a feedstock for further thermal or catalytic cracking and pyrolysis processes, enabling the production of lighter hydrocarbons and petrochemical intermediates. The heavier fractions of the product may also serve as a raw material for paraffin production, which is widely used in chemical, cosmetic, and industrial applications. Furthermore, the presence of linear hydrocarbons suggests potential applicability as a feedstock for the synthesis of surfactants and surface-active compounds, which are important components of detergents and industrial formulations. Due to the relatively high viscosity and paraffinic nature of the heavier fraction, it may also be considered as a candidate for the production of lubricating oils or synthetic base oils, including precursors for polyalphaolefins (PAO). In addition, the liquid fraction may potentially be utilized as a heat-transfer fluid in reactor jackets and industrial heating systems, where stable hydrocarbon heat carriers are required.

Overall, the results of this study demonstrate that the liquid by-product formed during polyethylene wax production represents a promising secondary hydrocarbon resource with multiple potential industrial applications. Further research will focus on more detailed compositional analysis, fractional separation, catalytic upgrading, and evaluation of its applicability in the fuel, petrochemical, solvent, lubricant, and heat-transfer fluid sectors.

Funding. This study was conducted "additionally" in accordance with the work

program of the Republican Center for Forensic Expertise named after Kh.S. Suleimanova and the Tashkent Institute of Chemical Technology.

Acknowledgments. The authors would like to thank Rakiya Karimovna Akhmedova, Head of the Laboratory of Forensic Analysis of Materials, Substances, and Products and Sherzod Shoimovich Mengliev, Head of the Department of Chemical Technology of Oil and Gas Processing.

References

1. Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics ever made. Science advances, 3(7), e1700782. https://doi.org/10.1126/sciadv.1700782

2. Al-Salem, S.M., Lettieri, P. and Baeyens, J. (2009) Recycling and Recovery Routes of Plastic Solid Waste (PSW): A Review. Waste Management, 29, pp. 2625-2643. https://doi.org/10.1016/j.wasman.2009.06.004

3. Aguado, J., Serrano, D.P., Miguel, G.S., Escola, J.M. and Rodriguez, J.M. (2007) Catalytic activity of zeolitic and mesostructured catalysts in the cracking of pure and waste polyolefins. Journal of Analytical and Applied Pyrolysis, 78, pp. 153-161. doi:10.1016/j.jaap.2006.06.004

4. Achyut K. Panda, R.K. Singh, D.K. Mishra, Thermolysis of waste plastics to liquid fuel: A suitable method for plastic waste management and manufacture of value added products—A world prospective, Renewable and Sustainable Energy Reviews, Volume 14, Issue 1, 2010, pp. 233-248, https://doi.org/10.1016/j.rser.2009.07.005.

5. Lopez, G., Artetxe, M., Amutio, M., Bilbao, J. and Olazar, M. (2017) Thermochemical Routes for the Valorization of Waste Polyolefinic Plastics to Produce Fuels and Chemicals: A Review. Renewable and Sustainable Energy Reviews, 73, 346-368. https://doi.org/10.1016/j.rser.2017.01.142

6. Walter Kaminsky, Ignacio-Javier Nuñez Zorriqueta, Catalytical and thermal pyrolysis of polyolefins, Journal of Analytical and Applied Pyrolysis, Volume 79, Issues 1–2, 2007, pp. 368-374, https://doi.org/10.1016/j.jaap.2006.11.005.

7. Scheirs, J., & Kaminsky, W. (2006). Feedstock Recycling and Pyrolysis of Waste Plastics. Wiley. https://doi.org/10.1002/0470021543

8. P. T. Williams and E. A. Williams, “Fluidised Bed Pyrolysis of Low Density Polyethylene to Produce Petrochemical Feedstock,” Journal of Analytical and Applied Pyrolysis, Vol. 51, No. 1-2, 1999, pp. 107-126.

9. A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass and Bioenergy, Volume 38, 2012, pp. 68-94, https://doi.org/10.1016/j.biombioe.2011.01.048.

10. Speight, J. G. (2014). The Chemistry and Technology of Petroleum (5th ed.). CRC Press. https://doi.org/10.1201/b16559

11. Knothe, G., Krahl, J., & Van Gerpen, J. (2015). The Biodiesel Handbook. AOCS Press. https://doi.org/10.1016/C2012-0-06784-0

12. Jan Beens, Udo A.Th Brinkman, The role of gas chromatography in compositional analyses in the petroleum industry, TrAC Trends in Analytical Chemistry, Volume 19, Issue 4, 2000, pp. 260-275, https://doi.org/10.1016/S0165-9936(99)00205-8.

13. Poole, C. F. (2012). Gas Chromatography. Elsevier. https://doi.org/10.1016/C2010-0-66028-8

14. Miandad, R., Barakat, M.A., Aburiazaiza, A.S., Rehan, M. and Nizami, A.S. (2016) Catalytic Pyrolysis of Plastic Waste: A Review. Process Safety and Environmental Protection, 102, pp. 822-838. https://doi.org/10.1016/j.psep.2016.06.022

15. D.P Serrano, J Aguado, J.M Escola, E Garagorri, Conversion of low density polyethylene into petrochemical feedstocks using a continuous screw kiln reactor, Journal of Analytical and Applied Pyrolysis, Volumes 58–59, 2001, pp. 789-801, https://doi.org/10.1016/S0165-2370(00)00153-4.

16. Achilias, D. S., Roupakias, C., Megalokonomos, P., Lappas, A. A., & Antonakou, E. V. (2007). Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP). Journal of hazardous materials, 149(3), pp. 536–542. https://doi.org/10.1016/j.jhazmat.2007.06.076

17. Nicholas A. Rorrer, Scott Nicholson, Alberta Carpenter, Mary J. Biddy, Nicholas J. Grundl, Gregg T. Beckham, Combining Reclaimed PET with Bio-based Monomers Enables Plastics Upcycling, Joule, Volume 3, Issue 4, 2019, pp. 1006-1027. https://doi.org/10.1016/j.joule.2019.01.018.

18. Al-Salem, S.M. (2019) Thermal Pyrolysis of High Density Polyethylene (HDPE) in a Novel Fixed Bed Reactor System for the Production of High Value Gasoline Range Hydrocarbons (HC). Process Safety and Environmental Protection, 127, pp. 171-179. https://doi.org/10.1016/j.psep.2019.05.008

19. Arena, U. and Mastellone, M.L., (2006) Fluidized bed pyrolysis of plastic wastes. In: Scheirs, J. and Kaminsky, W., Eds., Feedstock Recycling and Pyrolysis of Plastic Wastes: Converting Waste Plastics into Diesel and Other Fuels, John Wiley & Sons, Chichester. doi:10.1002/0470021543.ch16

20. Dogu, O., Pelucchi, M., Van de Vijver, R., et al. (2021). "The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: State-of-the-art, challenges, and future directions. Progress in Energy and Combustion Science, 84, 100901, DOI: 10.1016/j.pecs.2020.100901.

KREKING DISTILLYATLARINI GIDRIRLASH JARAYONIDA Co–Mo/Al_2O_3 va Ni–Mo/Al_2O_3 KATALIZATORLARINING GIDRODESULFIRLASH SAMARADORLIGI VA SUYUQ FRAKSIYA UNUMIGA TA’SIRI

Shuxratqodir Toshmatovich G‘ulomov
PhD, dotsent, Toshkent kimyo-texnologiya instituti, katta ilmiy xodim
ORCID:0000-0002-5793-3018
shuhratrich@gmail.com

Go‘zal Xusan qizi Yusupova
PhD, dotsent, Olmaliq davlat texnika instituti,
ORCID: 0000-0003-2810-4592
gozalyusupova056@gmail.com

Shaxnoza Isakulovna Shonazarova
Olmaliq davlat texnika instituti, katta o'qituvchi

Diyora Akimboy qizi Djulanova
Olmaliq davlat texnika instituti, magistr talabasi

Ra’no Sirojiddin qizi Sultonqulova
Olmaliq davlat texnika instituti, bakalavr talabasi

Sanalar
Qabul qilindi: 28.04.2026
Nashrga qabul qilindi: 02.05.2026
Nashr qilindi: 04.05.2026

Annotatsiya. Maqolada kreking distillyatlarini gidrirlash jarayonida Co-Mo/Al_2O_3 va Ni-Mo/Al_2O_3 tipidagi sanoat gidrotozalash katalizatorlarining gidrodesulfirlash samaradorligi, mahsulotning suyuq fraksiyasi unumi va optimal harorat oralig‘iga ta’siri tahlil qilindi. Kreking distillyatlari, xususan suyuq katalitik kreking jarayonidan olingan yengil sikl moyi, yuqori aromatiklik hamda oltingugurtli va azotli geterosiklik birikmalar miqdori bilan tavsiflanadi. Bunday xomashyolarni chuqur gidrotozalashda katalizatorning faol sulfid fazasi, vodorod bosimi, harorat, xomashyoning hajmiy tezligi va H_2/xomashyo nisbati hal qiluvchi omillar hisoblanadi.

Tahlil natijalariga ko‘ra, harorat 280 °C dan 400 °C gacha oshirilganda gidrodesulfirlash darajasi 45,2 % dan 99,5 % gacha ortadi. Shu bilan birga, mahsulotning suyuq fraksiyasi unumi 98,5 % dan 91,2 % gacha kamayadi. Jarayonni faqat gidrodesulfirlash darajasi bilan baholash yetarli emasligi sababli $K_{eff} = \eta_S \times Y_{liq}/100$ ko‘rinishidagi texnologik samaradorlik koeffitsiyenti taklif qilindi.

G‘ulomov Sh.T, Yusupova G.X., Shonazarova Sh.I., Djulanova D.A., Sultonqulova R.S. Kreking distillyatlarini gidrirlashda Co-Mo/Al_2O_3 va Ni-Mo/Al_2O_3 katalizatorlarining desulfurizatsiya samaradorligi va suyuq fraksiya unumiga ta’siri // Journal of future. 2026. Vol. 2. Iss. 2. pp. 27–39. https://doi.org/10.66960/jof.3093-8899.00023

Hisob-kitoblarga ko‘ra, 360-370 °C oralig‘i yuqori gidrodesulfirlash darajasi, suyuq fraksiya unumining saqlanishi va gidrokreking reaksiyalarini cheklash nuqtayi nazaridan maqbul sanoat harorat sohasi sifatida asoslandi.

Kalit so'zlar: *kreking distillyat, gidrirlash, gidrotozalash, gidrodesulfirlash, Co-Mo/*Al_2O_3*, Ni-Mo/*Al_2O_3*, CoMoS, NiMoS, suyuq fraksiya unumi, gidrokreking, texnologik samaradorlik koeffitsiyenti.*

Аннотация. В статье проанализировано влияние промышленных гидроочистных катализаторов типа Co–Mo/Al_2O_3 и Ni–Mo/Al_2O_3 на эффективность гидродесульфуризации, выход жидкой фракции и оптимальный температурный диапазон в процессе гидрирования крекинг-дистиллятов. Крекинг-дистилляты, в частности лёгкий циклойл, получаемый в процессе каталитического крекинга, характеризуются высокой ароматичностью, а также повышенным содержанием серо- и азотсодержащих гетероциклических соединений. При глубокой гидроочистке такого сырья решающую роль играют активная сульфидная фаза катализатора, давление водорода, температура, объемная скорость подачи сырья и соотношение H_2/сырьё.

По результатам анализа установлено, что при повышении температуры от 280 °C до 400 °C степень гидродесульфуризации возрастает с 45,2 % до 99,5 %. Одновременно выход жидкой фракции снижается с 98,5 % до 91,2 %. Поскольку оценка процесса только по степени гидродесульфуризации является недостаточной, предложен коэффициент технологической эффективности в виде $K_{eff}=\eta_S \times Y_{liq}/100$. Расчёты показали, что температурный диапазон 360–370 °C является оптимальным с точки зрения достижения высокой степени гидродесульфуризации, сохранения выхода жидкой фракции и ограничения реакций гидрокрекинга.

Ключевые слова: *крекинг-дистиллят, гидрирование, гидроочистка, гидродесульфуризация, Co–Mo/*Al_2O_3*, Ni–Mo/*Al_2O_3*, CoMoS, NiMoS, выход жидкой фракции, гидрокрекинг, коэффициент технологической эффективности.*

Abstract. The article analyzes the effect of i ndustrial hydrotreating catalysts of Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 types on hydrodesulfurization efficiency, liquid fraction yield, and the optimal temperature range during the hydrotreating of cracking distillates. Cracking distillates, particularly light cycle oil obtained from the fluid catalytic cracking process, are characterized by high aromaticity and elevated contents of sulfur- and nitrogen-containing heterocyclic compounds. In deep hydrotreating of such feedstocks, the catalyst active sulfide phase, hydrogen pressure, temperature, liquid hourly space velocity, and H_2/feed ratio play a decisive role.

The analysis shows that increasing the temperature from 280 °C to 400 °C raises the hydrodesulfurization level from 45.2 % to 99.5 %, while the liquid fraction yield decreases from 98.5 % to 91.2 %. Since evaluating the process solely based on hydrodesulfurization is insufficient, a technological efficiency coefficient expressed as $K_{eff}=\eta_S \times Y_{liq}/100$ is proposed. The calculations indicate that the temperature range of 360–370 °C is optimal in terms of achieving high hydrodesulfurization, maintaining liquid fraction yield, and limiting hydrocracking reactions.

Keywords: *cracking distillate, hydrotreating, hydrodesulfurization, Co–Mo/Al_2O_3, Ni–Mo/Al_2O_3, CoMoS, NiMoS, liquid fraction yield, gidrogenlashrocracking, technological efficiency coefficient.*

Kirish

Zamonaviy neftni qayta ishlash sanoatida ekologik toza motor yoqilg‘ilari ishlab chiqarish talabi gidrogenizatsion jarayonlarning ilmiy va amaliy ahamiyatini keskin oshirmoqda. Dizel, gazoyl va kreking distillyatlari tarkibidagi oltingugurtli, azotli hamda to‘yinmagan uglevodorodlarning kamaytirilishi yoqilg‘i sifati, dvigatel ishlashi, chiqindi gazlarni neytrallash tizimlari barqarorligi hamda atmosfera chiqindilarini pasaytirish bilan bevosita bog‘liq [1–3]. Ultra chuqur gidrodesulfirlash bo‘yicha zamonaviy tadqiqotlar dizel yoqilg‘ilarini ekologik standartlarga moslashtirishda murakkab aromatik oltingugurtli birikmalar, xususan dibenzotiofen va uning alkil hosilalarining reaktivligini chuqur hisobga olish zarurligini ko‘rsatadi [3,11].

Kreking distillyatlari, xususan suyuq katalitik kreking jarayonidan olingan yengil sikl moyi (FCC-LCO), to‘g‘ri haydalgan o‘rta distillyatlarga nisbatan murakkabroq tarkibga ega. Kim va Lee tomonidan FCC-LCO ni gidrotozalashga bag‘ishlangan tadqiqotda ushbu xomashyo tarkibidagi oltingugurtli va azotli birikmalar reaktivligi kobalt–molibden sulfidi (CoMoS) hamda nikel–molibden sulfidi (NiMoS) katalizatorlari ishtirokida alohida guruhlarga ajratilib o‘rganilgan [1]. Mualliflar NiMoS katalizatori gidrogenlash yo‘nalishini kuchaytirgani sababli murakkab birikmalar konversiyasida yuqori samaradorlik ko‘rsatishini aniqlagan.

LCO tipidagi xomashyolar yuqori aromatiklikka ega bo‘lgani sababli ularni gidrirlash jarayonida vodorod sarfi va issiqlik effekti ortadi. Azizi va boshqalar tomonidan o‘rganilgan tizimlarda yuqori aromatiklik va oltingugurt miqdori gidrodesulfirlash va gidrogenlash jarayonlarining o‘zaro bog‘liqligini kuchaytirishi ko‘rsatilgan [5]. Shu sababli gidrotozalash jarayonini faqat oltingugurtni kamaytirish emas, balki xomashyo tarkibi, vodorod balansi va mahsulot sifatini kompleks boshqarish tizimi sifatida qarash zarur.

Co–Mo/Al_2O_3 va Ni–Mo/Al_2O_3 katalizatorlari sanoat gidrotozalashining asosiy katalitik sistemalari hisoblanadi. Ularning faol holati sulfidlangan CoMoS va NiMoS fazalari bilan bog‘liq bo‘lib, MoS_2 qatlamlarining chekka markazlari va promotor atomlari reaksiya yo‘nalishini belgilaydi [4,6]. Tadqiqotlar shuni ko‘rsatadiki, Ni promotori MoS_2 chekkalarida faol markazlar hosil bo‘lishini kuchaytiradi va bu murakkab aromatik oltingugurtli birikmalarni gidrogenlash orqali konversiyalashda muhim rol o‘ynaydi [4,11,12].

Gidrodesulfirlash jarayonida ikki asosiy reaksion yo‘nalish ajratiladi: to‘g‘ridan-to‘g‘ri desulfirlash (DDS) va gidrogenlash orqali desulfirlash (HYD). DDS yo‘nalishida C–S bog‘i bevosita uzilsa, HYD yo‘nalishida avval aromatik halqa gidrogenlanadi, so‘ngra oltingugurt H_2S shaklida ajraladi [1,3]. Co–Mo katalizatorlari DDS yo‘nalishida samarali bo‘lsa, Ni–Mo katalizatorlari HYD yo‘nalishini kuchaytiradi. Bu farq ayniqsa 4,6-dimetildibenzotiofen kabi sterik to‘silgan birikmalar uchun muhimdir [3,7].

So‘nggi yillarda gidrotozalash katalizatorlarini takomillashtirish faqat faol metall miqdorini oshirish bilan cheklanmayapti. Tashuvchining pora tuzilishi, metall–tashuvchi o‘zaro ta’siri, promotorlarning taqsimlanishi va yangi konstruktiv shakllar yaratish muhim yo‘nalishlarga aylangan [6–9]. Xususan, Ni–Mo/Al_2O_3 asosidagi monolit va kompozit katalizatorlar yuqori barqarorlik va selektivlik ko‘rsatgani qayd etilgan [9,13].

Gidrotozalash jarayonining sanoat samaradorligi harorat bilan chambarchas bogʻliq. Haroratning oshishi reaksiyalar kinetikasini tezlashtiradi, biroq haddan tashqari yuqori harorat gidrokreking, gaz hosil boʻlishi va vodorod sarfining ortishiga olib keladi [2,3]. Aleksandrov va boshqalar tomonidan oʻtkazilgan tadqiqotlar turli oltingugurtli komponentlar reaktivligini hisobga olish zarurligini koʻrsatadi [2]. Shu bilan birga, zamonaviy tadqiqotlar gidrotozalash jarayonini optimallashtirishda koʻp parametrli yondashuv zarurligini tasdiqlaydi [11,14].

Mahalliy xomashyo asosida katalizatorlar olish ham dolzarb yoʻnalish hisoblanadi. Yunusov va hammualliflar tomonidan ishlab chiqilgan texnologiyalar mineral xomashyolar asosida samarali katalizatorlar olish va energiya tejamkor jarayonlar yaratish imkoniyatini koʻrsatadi [8,13,15]. Bu yondashuv resurs tejash va import oʻrnini bosish nuqtayi nazaridan muhim ahamiyatga ega.

Shu bilan birga, gidrotozalash samaradorligini faqat desulfirlash darajasi bilan baholash yetarli emas. Mahsulot unumi, vodorod sarfi, katalizatorning xizmat muddati va issiqlik rejimi kabi omillar ham kompleks hisobga olinishi lozim [2,4,10]. Shu sababli ushbu ishda jarayon samaradorligi desulfirlash darajasi va suyuq fraksiya unumi bilan birgalikda tahlil qilindi.

Ushbu ishning maqsadi kreking distillyatlarini Co–Mo/Al_2O_3 va Ni–Mo/Al_2O_3 katalizatorlari ishtirokida gidrirlash jarayonida haroratning desulfirlash darajasi hamda mahsulotning suyuq fraksiyasi unumiga taʼsirini aniqlash, katalizatorlarning texnologik farqlarini asoslash va 360–370 °C oraligʻini sanoat uchun maqbul ishchi zona sifatida ilmiy jihatdan izohlashdan iborat.

Ushbu yondashuv kreking distillyatlarini gidrirlash jarayonida katalizator tanlovi, harorat rejimi va mahsulot unumini oʻzaro bogʻliq holda baholash imkonini beradi.

1-jadval. Kreking distillyati / FCC-LCO tipidagi xomashyoning adabiyotlarda keltirilgan muhim xossalari

Koʻrsatkich	Adabiyotlarda keltirilgan qiymat yoki tavsif	Texnologik ahamiyati	Manba
Xomashyo turi	Suyuq katalitik kreking jarayonidan olingan yengil sikl moyi (FCC-LCO) / kreking distillyati	Yuqori aromatiklik va geteroatomli birikmalar mavjudligi sababli gidrotozalash uchun murakkab xomashyo hisoblanadi	[1,5]
Aromatik birikmalar	50–80 massa %; ayrim FCC-LCO namunalarida 72,5 massa % va undan yuqor	Vodorod sarfini oshiradi, setan xossalarini pasaytiradi va gidrogenlash reaksiyalariga talabni kuchaytiradi	[1,5]
Oltingugurt miqdori	4700 mg/kg dan bir necha massa % gacha	Gidrodesulfirlash (HDS) jarayonining asosiy yuklamasini belgilaydi	[1,5]
Azotli birikmalar	Taxminan 600 mg/kg atrofida boʻlishi mumkin	Katalizatorning faol markazlarini inhibitsiyalashi va gidrotozalash samaradorligini pasaytirishi mumkin	[1]
Asosiy oltingugurtli birikmalar	Benzotiofen (BT), dibenzotiofen (DBT), alkil-dibenzotiofenlar va 4,6-dimetildibenzotiofen (4,6-DMDBT)	Toʻgʻridan-toʻgʻri desulfirlash (DDS) va gidrogenlash (HYD) yoʻnalishlari boʻyicha reaktivlik farqini belgilaydi	[1,3]
Qiyin konversiya-lanadigan guruh	Sterik toʻsilgan alkil-dibenzotiofenlar	Ni–Mo katalizatorlari va gidrogenlash (HYD) yoʻnalishining ustunligini asoslaydi	[1,3,9]

Tadqiqot obyekti, manbalar va hisoblash usullari

Tadqiqot obyekti sifatida kreking distillyatlarini gidrirlash jarayonida qo‘llaniladigan Co–Mo/Al_2O_3 va Ni–Mo/Al_2O_3 tipidagi gidrotozalash katalizatorlari tanlandi. Maqolada ikki turdagi ma’lumotlar bloki birlashtirildi: birinchisi — dastlabki maqola variantida keltirilgan harorat, desulfirlash darajasi va mahsulotning suyuq fraksiyasi unumi bo‘yicha qiymatlar; ikkinchisi — 2020–2026-yillarda chop etilgan zamonaviy ilmiy adabiyotlarda FCC-LCO, gazoyl hamda Ni–Mo/Co–Mo katalizatorlari bo‘yicha berilgan ma’lumotlar. Dastlabki maqoladagi 280–400 °C harorat oralig‘iga oid natijalar ushbu ishda qayta hisoblandi va texnologik samaradorlik koeffitsiyenti bilan boyitildi.

Oltingugurtdan tozalash darajasi quyidagi formula orqali baholandi: $\eta_S = ((S_0 - S_1)/S_0) \times 100$. Bu yerda η_S - oltingugurtdan tozalash darajasi, %; S_0 - xomashyodagi boshlang‘ich oltingugurt miqdori, mg/kg yoki mass. %; S_1 - gidrotozalangan mahsulotdagi qoldiq oltingugurt miqdori. Mahsulotning suyuq fraksiya unumi $Y_{liq} = (m_{liq}/m_{feed}) \times 100$ formula orqali aniqlandi. Jarayonni kompleks baholash uchun $K_{eff} = \eta_S \times Y_{liq}/100$ koeffitsiyenti kiritildi. Ushbu koeffitsiyent yuqori desulfurizatsiya darajasi va suyuq mahsulot unumini bir vaqtning o‘zida hisobga oladi.

1-jadvaldan ko‘rinib turibdiki, kreking distillyat oddiy dizel fraksiyasidan ancha murakkab xomashyo hisoblanadi. Yuqori aromatiklik vodorod sarfini oshiradi, azotli birikmalar esa katalizatorning kislota va metall-sulfid faol markazlarida raqobatli adsorbsiyalanib, HDS tezligini pasaytirishi mumkin. Shuning uchun bunday xomashyo uchun katalizator tanlashda Co-Mo va Ni-Mo sistemalarining mexanistik farqlarini hisobga olish zarur.

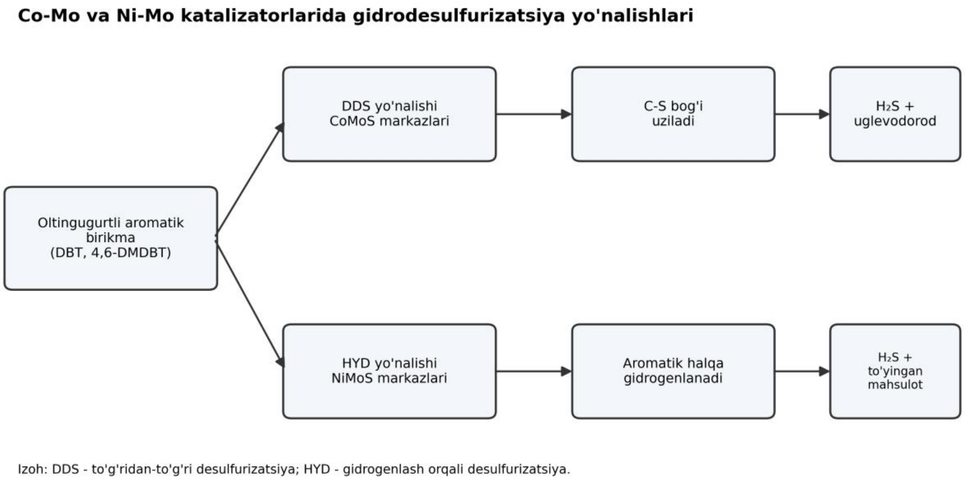
2-jadval. Co–Mo/Al_2O_3 va Ni–Mo/Al_2O_3 katalizatorlarining solishtirma tavsifi

Mezon	Co–Mo/Al_2O_3	Ni–Mo/Al_2O_3	Izoh
Faol sulfid faza	CoMoS	NiMoS	MoS_2 qatlamlarining chekka markazlari va promotor atomlari katalitik faollikda asosiy rol o‘ynaydi.
Asosiy reaksion yo‘nalish	To‘g‘ridan-to‘g‘ri desulfirlash (DDS): C–S bog‘ining bevosita uzilishi	Gidrogenlash (HYD) + to‘g‘ridan-to‘g‘ri desulfirlash (DDS): avval aromatik halqa gidrogenlanadi, so‘ng C–S bog‘i uziladi	Murakkab va sterik to‘silgan oltingugurtli birikmalarni qayta ishlashda muhim.
Aromatik birikmalarni gidrogenlash	O‘rtacha	Yuqoriroq	Ni–Mo/Al_2O_3 katalizatori LCO tipidagi aromatik xomashyo uchun afzalroq bo‘lishi mumkin.
Vodorod sarfi	Nisbatan pastroq	Nisbatan yuqoriroq	Energiya sarfi va H_2 balansi texnologik-iqtisodiy jihatdan baholanishi kerak.
4,6-DMDBT konversiyasi	Sterik to‘siq sababli qiyinroq	Gidrogenlash yo‘nalishi kuchliroq bo‘lgani sababli qulayroq	Ultra chuqur gidrodesulfirlash talablarida muhim mezon hisoblanadi.
Amaliy qo‘llanish sohasi	Oddiy oltingugurtli birikmalar ko‘p bo‘lgan xomashyolar uchun qulay	Aromatik, azotli va sterik to‘silgan birikmalarga boy xomashyolar uchun qulay	Katalizator tanlovi xomashyo tarkibi va tozalash chuqurligi asosida belgilanadi.

Ayniqsa sterik to‘silgan dibenzotiofen hosilalari mavjud bo‘lganda gidrogenlash yo‘nalishining kuchayishi gidrodesulfirlash samaradorligini oshiradi. Shu sababli Ni–Mo asosidagi katalizatorlar yuqori aromatik va murakkab oltingugurtli birikmalarga boy kreking distillyatlari uchun istiqbolli katalitik sistema sifatida baholanishi mumkin.

2-jadval katalizator tanlashning asosiy texnologik va mexanistik mantiqini ochib beradi. Co–Mo/Al_2O_3 katalizatori nisbatan oddiy oltingugurtli birikmalarni to‘g‘ridan-to‘g‘ri gidrodesulfirlash yo‘nalishida samarali bo‘lib, C–S bog‘ining bevosita uzilishi orqali oltingugurtning H S shaklida ajralishini ta’minlaydi. Bunday katalitik sistema vodorod sarfi nisbatan past bo‘lgan sharoitlarda ham yetarli samaradorlik ko‘rsatishi mumkin.

Ni–Mo/Al_2O_3 katalizatori esa gidrogenlash yo‘nalishini kuchaytiradi. Bu holat ayniqsa aromatik halqali, sterik to‘silgan va azotli geterosiklik birikmalarga boy xomashyolarni qayta ishlashda muhim ahamiyatga ega. Ni–Mo katalizatori aromatik halqani qisman gidrogenlash orqali C–S bog‘ining uzilishini osonlashtiradi va murakkab oltingugurtli birikmalarning chuqurroq konversiyasiga yordam beradi.


Co-Mo va Ni-Mo katalizatorlarida gidrodesulfurizatsiya yo'nalishlari

Izoh: DDS - to'g'ridan-to'g'ri desulfurizatsiya; HYD - gidrogenlash orqali desulfurizatsiya.

1-rasm. Co-Mo/Al_2O_3 va Ni-Mo/Al_2O_3 katalizatorlarida gidrodesulfirlashning DDS va GIDROGENLASH yo‘nalishlari.

Shu sababli katalizator tanlashda faqat umumiy gidrodesulfirlash faolligini emas, balki xomashyo tarkibi, oltingugurtli birikmalarning molekulyar tuzilishi, aromatiklik darajasi, vodorod resursi va mahsulot sifatiga qo‘yiladigan talablarni ham hisobga olish zarur. Ushbu mexanistik farq maqolaning keyingi qismidagi 1-rasmda sxematik tarzda ko‘rsatilgan.

1-rasmda CoMoS faol markazlari orqali C-S bog‘ining to‘g‘ridan-to‘g‘ri uzilishi va NiMoS faol markazlarida aromatik halqaning dastlab gidrogenlanishi, so‘ng oltingugurtning H_2S shaklida ajralishi tasvirlangan. Ushbu sxema 2-jadvalda berilgan katalizatorlar farqini vizual tarzda tushuntiradi: Ni-Mo sistemasi chuqur gidrotozalashda ayniqsa murakkab aromatik oltingugurtli birikmalar uchun afzallik beradi.

Natijalar va muhokama

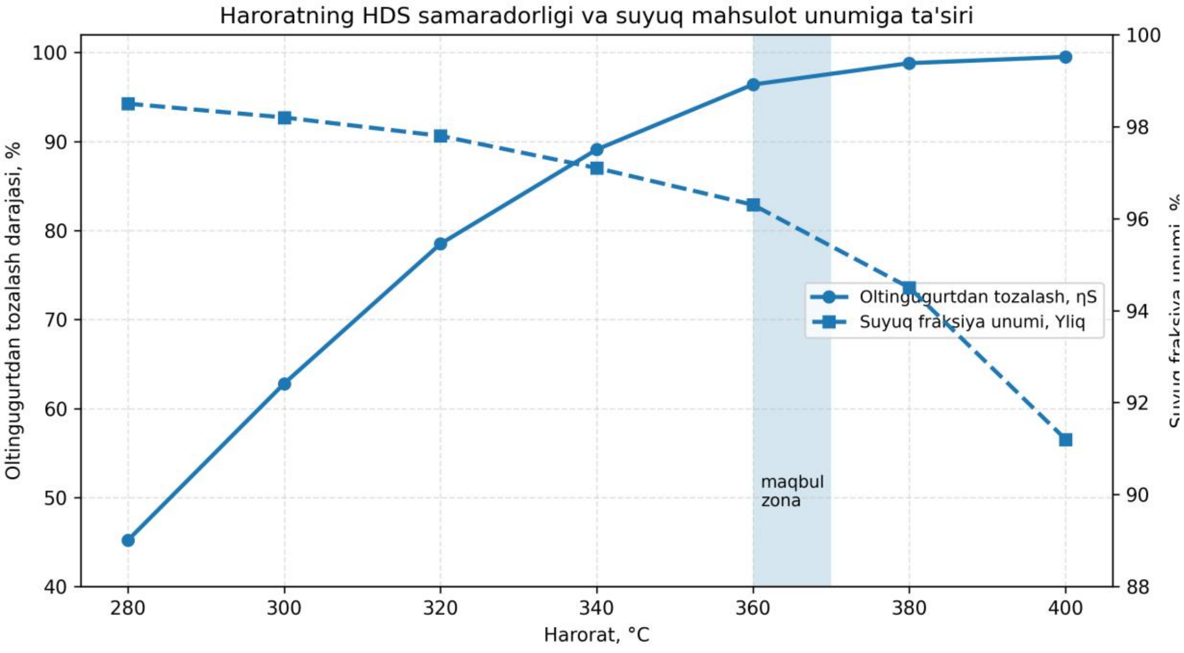
Haroratning desulfurizatsiya darajasi va suyuq fraksiya unumiga ta’siri. Harorat gidrodesulfirlash jarayonining eng muhim boshqariluvchi omillaridan biridir. Harorat oshishi bilan reaksiya tezligi ortadi, vodorodning katalizator yuzasida faollanishi kuchayadi va oltingugurtli birikmalardagi C-S bog‘lari tezroq uziladi. Biroq yuqori haroratda gidrokreking reaksiyalari ham faollashadi; natijada yengil

3-jadval. Haroratning desulfurizatsiya darajasi, suyuq fraksiya unumi va Keff qiymatiga ta’siri

Harorat, °C	η_S, %	Y_{liq}, %	K_{eff}	Texnologik baho
280	45.2	98.5	44.5	HDS past, suyuq unum yuqori
300	62.8	98.2	61.7	HDS kuchayadi, unum saqlanadi
320	78.5	97.8	76.8	O‘rtacha samarali zona
340	89.1	97.1	86.5	Maqbul HDS boshlanishi
360	96.4	96.3	92.8	Eng maqbul sanoat zona
380	98.8	94.5	93.4	HDS yuqori, gidrokreking xavfi ortadi
400	99.5	91.2	90.7	HDS maksimal, suyuq unum sezilarli kamayadi

gazsimon mahsulotlar ulushi ortib, suyuq fraksiya unumi kamayadi. Shu sababli jarayonni faqat ηS bilan emas, balki Yliq va Keff ko‘rsatkichlari bilan birgalikda baholash zarur.

3-jadval ma’lumotlari shuni ko‘rsatadiki, 280-340 °C oralig‘ida oltingugurtdan tozalash darajasi 45,2 % dan 89,1 % gacha keskin ortadi. Bu bosqichda C-S bog‘larining uzilishi va H_2S hosil bo‘lishi jadallashadi, biroq suyuq fraksiya unumi hali yuqori darajada saqlanadi. 360 °C da $\eta_S = 96,4$ %, $Y_{liq} = 96,3$ % va $K_{eff} = 92,8$ bo‘lib, gidrodesulfirlash va mahsulot unumi o‘rtasida eng muvozanatli sanoat rejimi shakllanadi. 380 °C da K_{eff} 93,4 ga yetsada, gidrokreking xavfi ortadi. 400 °C da η_S 99,5 % bo‘lishiga qaramay, suyuq fraksiya unumi 91,2 % gacha kamaygani sababli jarayon iqtisodiy jihatdan kamroq qulaylashadi.

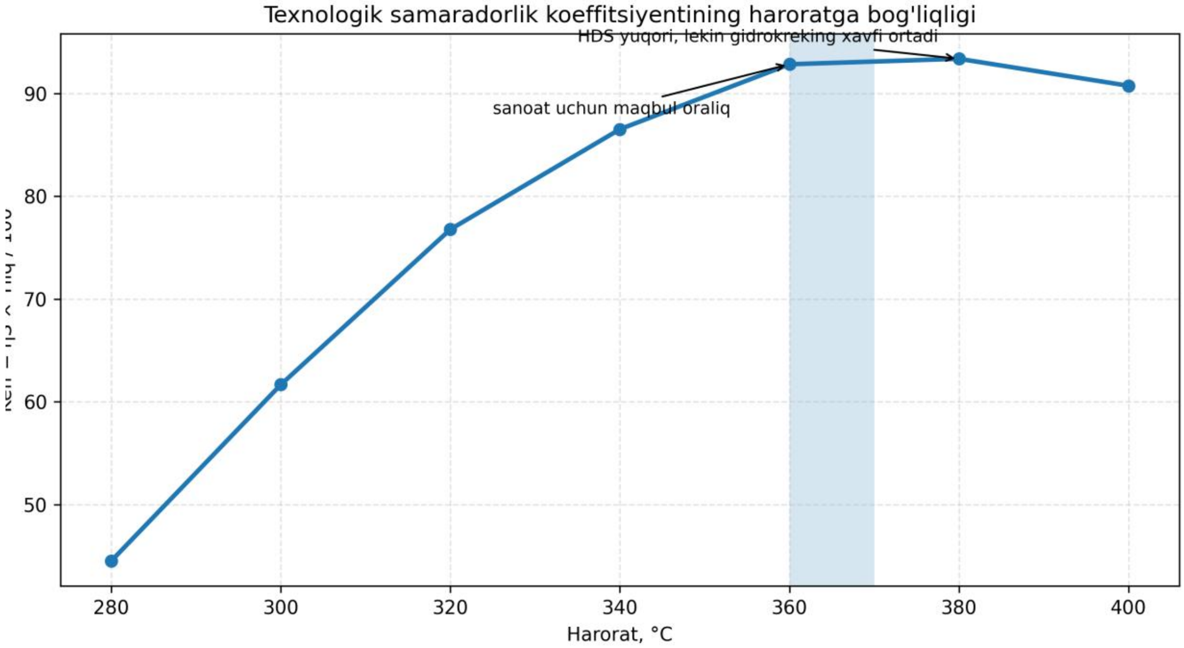


2-rasm. Haroratning oltingugurtdan tozalash darajasi va suyuq fraksiya unumiga kompleks ta’siri.

2-rasm 3-jadvaldagi sonlarni grafik ko‘rinishda bog‘laydi. Grafikda η_S chizig‘i harorat oshishi bilan yuqoriga intiladi, Yliq chizig‘i esa sekin pasayadi. 360-370 °C oralig‘i alohida belgilangan, chunki aynan shu diapazonda desulfurizatsiya yuqori darajaga yetadi, lekin suyuq mahsulot yo‘qotilishi keskinlashib ketmaydi. 380-400 °C da esa gidrodesulfirlash (HDS) egri chizig‘i deyarli to‘yingan holatga yaqinlashadi, suyuq fraksiya unumi esa sezilarli kamayadi. Bu holat sanoatda haroratni haddan tashqari oshirish har doim ham foydali emasligini ko‘rsatadi.

Texnologik samaradorlik koeffitsiyenti bo‘yicha optimal haroratni baholash. Gidrotozalash qurilmasida texnologik optimal nuqta maksimal gidrodesulfirlash nuqtasi bilan doim mos kelmaydi. Agar maqsad faqat oltingugurtni maksimal kamaytirish bo‘lsa, yuqori harorat tanlanishi mumkin. Lekin real sanoat sharoitida suyuq mahsulot chiqimi, vodorod sarfi, reaktor issiqlik yuklamasi, katalizatorning kokslanishi va gidrokreking reaksiyalarining kuchayishi ham hisobga olinadi. Shu sababli ushbu maqolada Keff koeffitsiyenti jarayonning integrallashgan baholash mezoni sifatida qo‘llandi.

Gidrotozalash qurilmasida texnologik optimal nuqta maksimal gidrodesulfirlash nuqtasi bilan doim mos kelmaydi. Agar maqsad faqat oltingugurtni maksimal kamaytirish bo‘lsa, yuqori harorat tanlanishi mumkin. Lekin real sanoat sharoitida suyuq mahsulot chiqimi, vodorod sarfi, reaktor issiqlik yuklamasi, katalizatorning kokslanishi va gidrokreking reaksiyalarining kuchayishi ham hisobga olinadi. Shu sababli ushbu maqolada Keff koeffitsiyenti jarayonning integrallashgan baholash mezoni sifatida qo‘llandi.



3-rasm. Haroratga bog‘liq texnologik samaradorlik koeffitsiyenti - K_{eff} o‘zgarishi.

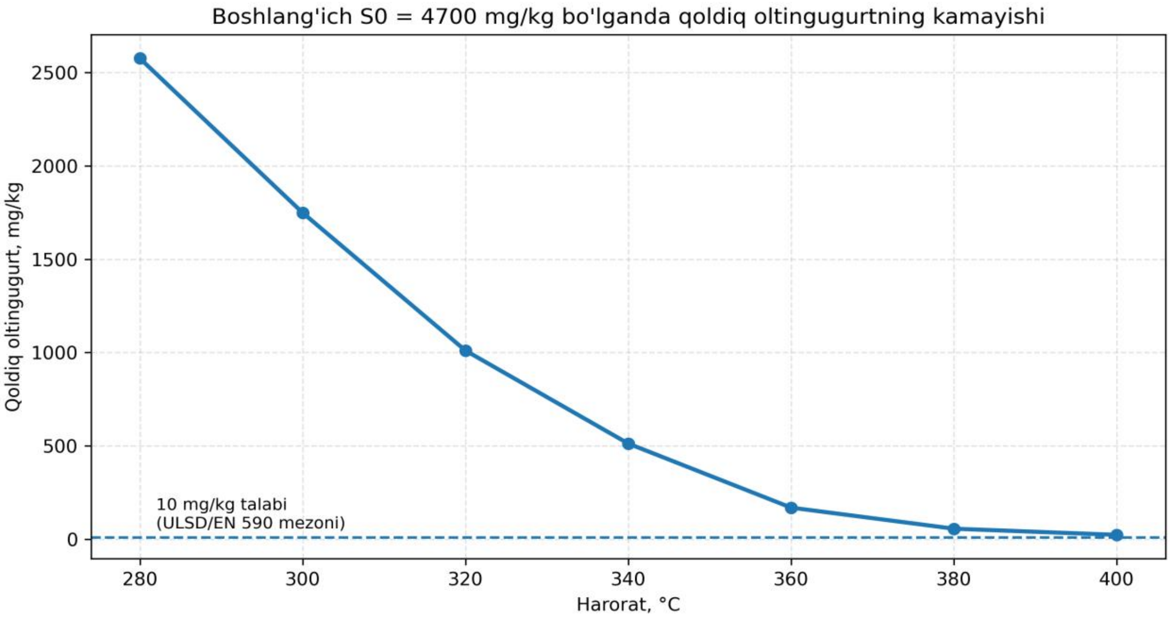
3-rasmda K_{eff} ning harorat bo‘yicha o‘zgarishi keltirilgan. 280 °C da K_{eff} 44,5 bo‘lib, bu gidrodesulfirlash darajasining pastligi bilan izohlanadi. Harorat 360 °C ga yetganda K_{eff} 92,8 gacha ortadi. 380 °C da K_{eff} 93,4 qiymatiga chiqadi, lekin bu nuqtada gidrokreking xavfi va suyuq fraksiya yo‘qotilishi ortadi. 400 °C da esa K_{eff} 90,7 gacha pasayadi. Demak, faqat son jihatdan eng katta K_{eff} emas, balki jarayon barqarorligi ham hisobga olinsa, 360-370 °C oralig‘i eng asoslangan ishchi zona hisoblanadi.

4-jadval. S0 = 4700 mg/kg bo‘lganda mahsulotdagi qoldiq oltingugurtning hisobiy kamayishi

Harorat, °C	η_S, %	Qoldiq S_1, mg/kg	Texnologik baho
280	45.2	2575.6	Juda yuqori qoldiq S
300	62.8	1748.4	Qoldiq S yuqori
320	78.5	1010.5	Qoldiq S hali yuqori
340	89.1	512.3	Sezilarli kamayish
360	96.4	169.2	Chuqur HDS zonasi
380	98.8	56.4	Juda chuqur HDS, lekin 10 mg/kgdan yuqori
400	99.5	23.5	Qoldiq S past, lekin Y_{liq} pasayadi

Qoldiq oltingugurt miqdorini hisobiy baholash. Kreking distillatlari tarkibidagi boshlang‘ich oltingugurt miqdori xomashyo manbasiga bog‘liq. LCO bo‘yicha adabiyotlarda 4700 ppm S va 72,5 mass. % aromatik birikmalar keltirilgan [5]. Shu qiymat shartli asos sifatida qabul qilinib, turli haroratlarda qoldiq oltingugurt miqdori hisoblandi. Ushbu hisob real xomashyo pasportini almashtirmaydi, lekin gidrodesulfirlash darajasining amaliy mazmunini ochib beradi.

4-jadvaldan ko‘rinadiki, boshlang‘ich oltingugurt miqdori yuqori bo‘lgan xomashyoda 96-99 % gidrodesulfirlash ham har doim ultra past oltingugurtli mahsulot olish uchun yetarli bo‘lmasligi mumkin. Masalan, S_0 = 4700 mg/kg bo‘lganda 360 °C da qoldiq S 169,2 mg/kg, 380 °C da 56,4 mg/kg, 400 °C da esa 23,5 mg/kg bo‘ladi. Bu ko‘rsatkichlar chuqur HDS uchun nafaqat harorat, balki bosim, suyuq fazaning soatlik hajmiy tezligi, H_2/xomashyo nisbati, katalizatorning sulfidlanish darajasi va reaktor konfiguratsiyasi ham kuchaytirilishi kerakligini ko‘rsatadi.



4-rasm. Boshlang‘ich S0 = 4700 mg/kg bo‘lganda qoldiq oltingugurt miqdorining haroratga bog‘liq kamayishi.

4-rasmda 4-jadvalda keltirilgan hisobiy qiymatlarning grafik ifodasi berilgan. Bundan ko‘rinib turibdiki, 280-340 °C oralig‘ida qoldiq oltingugurt miqdori keskin kamayadi, 360-400 °C da esa kamayish davom etadi, biroq bu bosqichda suyuq mahsulot unumi pasayishi hisobiga iqtisodiy muvozanat murakkablashadi. Shunday qilib, yuqori gidrodesulfirlash darajasini mahsulot unumi va energetik xarajatlar bilan bog‘lab tahlil qilish zarur.

Co-Mo/Al_2O_3 va Ni-Mo/Al_2O_3 katalizatorlarini tanlash mezonlari. Katalizator tanlash xomashyo tarkibidagi oltingugurtli va azotli birikmalarning molekulyar tuzilishiga bog‘liq. Agar xomashyoda nisbatan oddiy benzotiofen va dibenzotiofen hosilalari ustun bo‘lsa, Co-Mo/Al O katalizatori iqtisodiy va texnologik jihatdan yetarli bo‘lishi mumkin. Agar xomashyo tarkibida 4,6- dimetildibenzotiofen, alkil-dibenzotiofenlar, karbazol hosilalari va poliaromatik birikmalar yuqori bo‘lsa, Ni-Mo/Al_2O_3 katalizatori gidrogenlash yo‘nalishi kuchliroq bo‘lgani sababli afzal bo‘ladi [1,3,4].

5-jadval katalizatorni xomashyo tarkibi va ishlab chiqarish maqsadiga qarab tanlash zarurligini ko‘rsatadi. Og‘ir aromatik xomashyoda Ni-Mo katalizatori chuqurroq tozalash imkonini bersa-da, vodorod sarfi va gidrogenlash darajasi ortishi mumkin. Co-Mo katalizatori esa nisbatan yumshoqroq xomashyoda iqtisodiy jihatdan

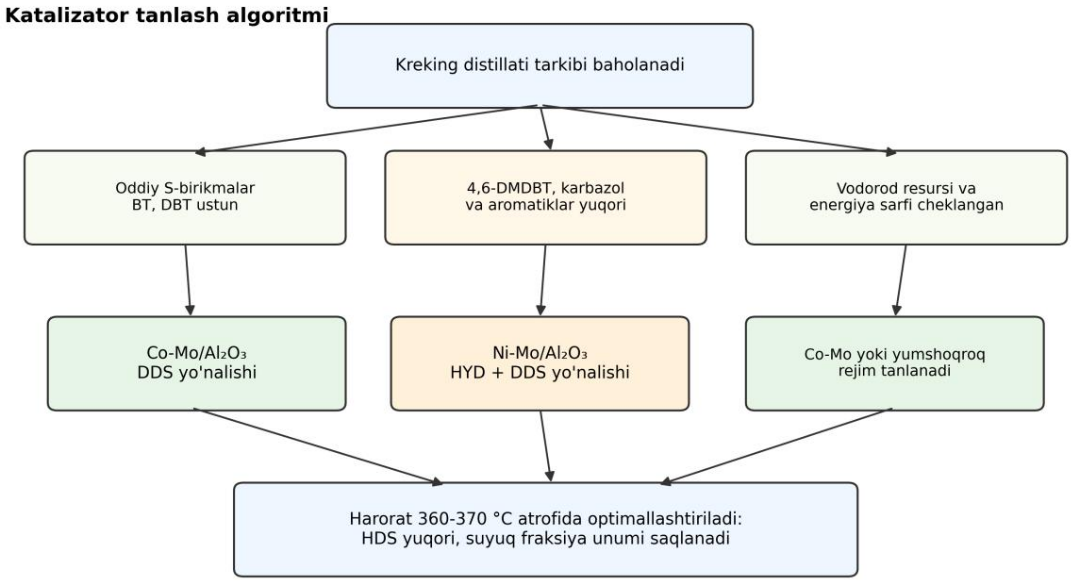
5-jadval. Co-Mo/Al_2O_3 va Ni-Mo/Al_2O_3 katalizatorlarini sanoat sharoitida tanlash mezonlari

Tanlash mezoni	Co-Mo/Al_2O_3	Ni-Mo/Al_2O_3	Amaliy xulosa
Oddiy oltingugurtli birikmalar	Yuqori samarali	Yuqori samarali	Har ikkisi qo‘llanishi mumkin
Sterik to‘silgan dibenzotiofen hosilalari	Nisbatan pastroq	Yuqoriroq	Ni-Mo afzal
Azotli geterosikllar	Inhibitsiyaga sezgir	gidrodenitrogenlash yo‘nalishida faolroq	Ni-Mo afzalroq
Aromatiklar miqdori yuqori bo‘lsa	O‘rtacha gidrogenlash	Kuchliroq gidrogenlash	Yengil kreking gazoyli uchun Ni-Mo maqsadga muvofiq
Vodorod sarfi cheklangan bo‘lsa	Nisbatan qulay	Ko‘proq H_2 talab qilishi mumkin	Co-Mo iqtisodiyroq bo‘lishi mumkin
Chuqur gidrodesulfirlash talabi	Yetarli, lekin cheklangan	Yuqoriroq imkoniyat	Ni-Mo chuqurroq tozalashga mos
Suyuq mahsulot unumini saqlash	Yaxshi	Sharoitga bog‘liq	Harorat va suyuq fazaning soatlik hajmiy tezligi optimallashtiriladi

qulayroq bo‘lishi mumkin. Shuning uchun katalizator tanlashda xomashyo pasporti, maqsadli oltingugurt normasi va vodorod resursi birgalikda baholanishi lozim.

5-rasm 5-jadvaldagi tanlash mezonlarini amaliy algoritm ko‘rinishida umumlashtiradi. Agar xomashyoda oddiy oltingugurtli birikmalar ustun bo‘lsa va vodorod resursi cheklangan bo‘lsa, Co-Mo/Al_2O_3 tanlanadi. Agar xomashyo aromatikligi yuqori, azotli birikmalar ko‘p va chuqur HDS talab qilinsa, Ni-Mo/Al_2O_3 maqsadga muvofiq bo‘ladi. Har ikkala holatda ham 360-370 °C atrofidagi rejim desulfurizatsiya va suyuq fraksiya unumi o‘rtasidagi muvozanat nuqtasi sifatida ko‘rib chiqiladi.

6-jadvaldan ko‘rinadiki, maqolada taklif etilgan 360-370 °C optimal oraliq faqat ichki hisob-kitob natijasi emas, balki zamonaviy adabiyotlarda keltirilgan sanoatga yaqin



5-rasm. Kreking distillyat tarkibiga qarab Co-Mo/Al_2O_3 yoki Ni-Mo/Al_2O_3 katalizatorini tanlash algoritmi.

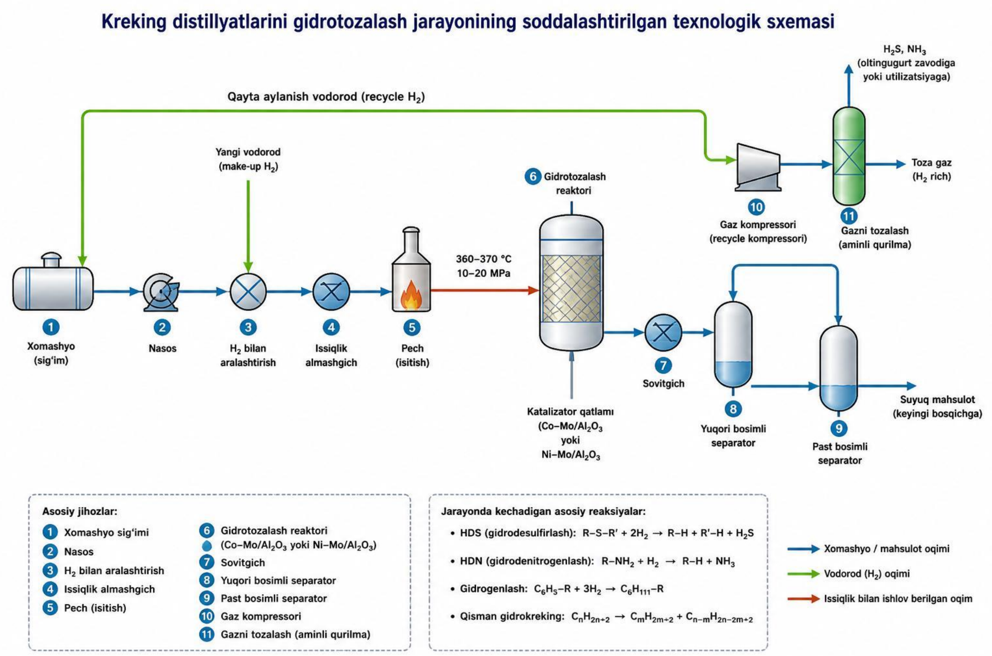
6-jadval. Olingan tahliliy natijalarni zamonaviy adabiyot ma’lumotlari bilan solishtirish

Manba	Xomashyo/ katalizator	Asosiy sharoit yoki natija	Ushbu maqola bilan bog‘liqligi
Kim, Lee, 2023 [1]	FCC-LCO; CoMoS va NiMoS	613 K va 8,6 MPa H_2; S va N birikmalari reaktivligi guruhlangan	Ni-Mo ning gidrogenlash yo‘nalishidagi ustunligini asoslaydi
Aleksandrov va boshq., 2022 [2]	Yuqori S gazoyl; $CoMo/Al_2O_3$	335-365 °C, 3,5-5,1 MPa, H_2/xomashyo = 300 Nm³/m³	360-370 °C optimal oraliqni sanoat rejimlari bilan bog‘laydi
Weng va boshq., 2020 [3]	Dizel gidrodesulfirlash sharhi	desulfurizatsiya va gidrogenlash mexanizmlari va katalizator dizayni	Mexanizm va katalizator tanlashni ilmiy asoslaydi
Aryee va boshq., 2022 [4]	$NiMo/Al_2O_3$	MoS_2 chekka markazlari va Ni promotori roli	NiMoS faol markazlarining mohiyatini tushuntiradi
Liu va boshq., 2020 [6]	$NiMo/Al_2O_3$	Ni-Al_2O_3 o‘zaro ta’sirini boshqarish HDS faolligiga ta’sir qiladi	Tashuvchi-faol faza bog‘lanishining ahamiyatini ko‘rsatadi
Yunusov va boshq., 2024 [8]	Al saqlovchi chiqindilar asosidagi HDS katalizatori	Mahalliy/ikkilamchi xomashyo asosida katalizator olish	Resurs tejash va import o‘rnini bosish yondashuvini kuchaytiradi

gidrotozalash rejimlari bilan ham mos keladi. Shuningdek, Co-Mo va Ni-Mo katalizatorlarining farqi adabiyotlarda berilgan DDS/gidrogenlash mexanizmlari bilan izohlanadi. Bu esa maqolaning xulosalarini kuchaytiradi va natijalarni umumiy ilmiy kontekstga bog‘laydi.

Jarayonning texnologik sxemasi va amaliy ahamiyati

Kreking distillyatlarini gidrotozalash (gidrodesulfirlash) jarayoni odatda xomashyoni vodorod bilan aralashtirish, issiqlik almashgich va pech orqali ishchi haroratgacha



6-rasm. Kreking distillyatlarini gidrotozalash jarayonining soddalashtirilgan texnologik sxemasi.

qizdirish, katalitik reaktorda qayta ishlash, reaktor chiqishidagi mahsulotni sovutish, gaz–suyuqlik ajratish hamda suyuq mahsulotni keyingi stabilizatsiya yoki fraksiyalash bosqichiga yuborishdan iborat. Reaktor chiqishidagi gaz fazasida H S, NH , ortiqcha vodorod va yengil uglevodorodlar mavjud boʻladi. Suyuq faza esa past oltingugurtli yoqilgʻi komponenti sifatida baholanadi.

6-rasmda keltirilgan sxema maqoladagi kinetik va texnologik muhokamalarni real sanoat qurilmasi ishlash mantiqi bilan bogʻlaydi. Jarayon harorati issiqlik almashgich va pech orqali boshqariladi, reaktor ichida esa Co–Mo/Al_2O_3 yoki Ni–Mo/Al_2O_3 katalizatorlari ishtirokida gidrodesulfirlash (HDS), gidrodenitrogenlash (HDN), gidrogenlash hamda qisman gidrokreking reaksiyalari kechadi. Reaksiya mahsulotlari sovitgichdan oʻtkazilgach, yuqori va past bosimli separatorlarda gaz va suyuq fazalarga ajratiladi. Gaz fazasida H_2S, NH_3 hamda ortiqcha vodorod mavjud boʻlib, u gazni tozalash va vodorodni qayta aylantirish tizimiga yuboriladi. Mahsulotning suyuq fraksiyasi esa keyingi texnologik bosqichga uzatiladi.

Shu sababli 360–370 °C harorat oraligʻini tanlash faqat laboratoriya natijalari bilan emas, balki qurilmaning issiqlik rejimi, mahsulot unumi, vodorod balansi va gaz–suyuqlik muvozanati bilan ham bevosita bogʻliq.

Xulosa

Kreking distillyatlarini Co–Mo/Al_2O_3 va Ni–Mo/Al_2O_3 katalizatorlari ishtirokida gidrotozalash (gidrodesulfirlash) jarayoni oltingugurtli, azotli va toʻyinmagan birikmalarni kamaytirish hamda ekologik talablarga mos yoqilgʻi komponentlarini olishda muhim texnologik bosqich hisoblanadi. Harorat 280 °C dan 400 °C gacha oshirilganda desulfirlash darajasi 45,2 % dan 99,5 % gacha ortadi. Biroq ayni vaqtda mahsulotning suyuq fraksiyasi unumi 98,5 % dan 91,2 % gacha kamayadi, bu yuqori haroratlarda gidrokreking reaksiyalarining kuchayishi bilan izohlanadi.

Jarayonni kompleks baholash maqsadida $K_{eff} = \eta_S \times Y_{liq}/100$ koʻrinishidagi texnologik samaradorlik koeffitsiyenti taklif etildi. Hisob-kitoblarga koʻra, K_{eff} 360–380 °C oraligʻida yuqori qiymatlarga erishadi, biroq 380 °C dan yuqori haroratlarda suyuq mahsulot yoʻqotilishining ortishi sababli 360–370 °C oraligʻi sanoat sharoitlari uchun eng maqbul va muvozanatli ishchi rejim sifatida baholandi.

Co–Mo/Al_2O_3 katalizatori nisbatan oddiy oltingugurtli birikmalar uchun toʻgʻridan-toʻgʻri desulfirlash (DDS) yoʻnalishida samarali boʻlsa, Ni–Mo/Al_2O_3 katalizatori gidrogenlash (HYD) yoʻnalishini kuchaytirib, aromatik va sterik toʻsilgan oltingugurtli birikmalarni chuqurroq konversiyalash imkonini beradi. Shu sababli katalizator tanlash xomashyo tarkibi, vodorod resurslari va maqsadli mahsulot talablari asosida amalga oshirilishi lozim.

Boshlangʻich oltingugurt miqdori S_0 = 4700 mg/kg boʻlgan shartli xomashyo uchun hisob-kitoblar 400 °C da ham qoldiq oltingugurt miqdori taxminan 23,5 mg/kg atrofida qolishi mumkinligini koʻrsatdi. Bu esa chuqur gidrotozalash jarayonida haroratdan tashqari bosim, suyuqlikning hajmiy tezligi (LHSV), H_2/xomashyo nisbati, katalizatorning sulfidlanish darajasi va reaktor konfiguratsiyasi kabi omillar ham muhim ahamiyatga ega ekanligini tasdiqlaydi.

Keltirilgan natijalar gidrotozalash jarayonini faqat kimyoviy reaksiyalar majmuasi sifatida emas, balki desulfirlash darajasi, mahsulot unumi, katalizator tanlovi va sanoat ishchi rejimlari oʻrtasidagi muvozanat sifatida baholash zarurligini koʻrsatadi.

Foydalanilgan adabiyotlar

1. Kim J., Lee Y.-K. Reactivity of Sulfur and Nitrogen Compounds of FCC Light Cycle Oil in Gidrogenlashrotreating over CoMoS and NiMoS Catalysts // Catalysts. - 2023. - Vol. 13, No. 2. - Article 277. DOI: 10.3390/catal13020277.

2. Aleksandrov P.V., Reshetnikov S.I., Bukhtiyarova G.A., Noskov A.S. Deep gidrogenlashrodesulfurization of gas oils with high sulfur content: Experiment and kinetic modeling // Chemical Engineering Journal. - 2022. - Vol. 446. - Article 137059. DOI: 10.1016/j.cej.2022.137059.

3. Weng X., Cao L., Zhang G., Chen F., Zhao L., Zhang Y., Gao J., Xu C. Ultradeep Gidrogenlashrodesulfurization of Diesel: Mechanisms, Catalyst Design Strategies, and Challenges // Industrial & Engineering Chemistry Research. - 2020. - Vol. 59, No. 49. - P. 21261-21274. DOI: 10.1021/acs.iecr.0c04049.

4. Aryee E., Han R., Qu L. et al. Effects of Metal Loadings in Catalyst Formulation on the Gidrogenlashrodesulfurization Performance of NiMo/Al O Catalysts // Frontiers in Chemical Engineering. - 2022. - Vol. 3. - Article 764931. DOI: 10.3389/fceng.2021.764931.

5. Azizi N., Khodadadi A.A., Mortazavi Y. Gidrogenlashrotreating of light cycle oil over NiMo and CoMo catalysts with different supports // Journal of Industrial and Engineering Chemistry. - 2013. - Vol. 19. - P. 1825-1830. DOI: 10.1016/j.jiec.2013.02.019.

6. Liu Z., Gao X., Yao Y. et al. Effects of Ni-Al O interaction on NiMo/Al O gidrogenlashrodesulfurization catalysts // Journal of Catalysis. - 2020. - Vol. 387. - P. 62-72. DOI: 10.1016/j.jcat.2020.04.008.

7. Tuktin B., Saidilda G., Nurzhanova S., Ongarbayev Y. Gidrogenlashroprocessing of Gasoline on Modified Alumina Catalysts // Catalysts. - 2024. - Vol. 14, No. 7. - Article 404. DOI: 10.3390/catal14070404.

8. Yunusov M.P., Gulomov Sh., Nasullayev K.A., Turdiyeva D.P.K., Isayeva N.F., Abdurakhmanova I.S.K., Murzin D.Y. Gidrogenlashrodesulfurization Catalysts from Aluminium-Containing Waste // Catalysis Letters. - 2024. - Vol. 154. - P. 4409-4421. DOI: 10.1007/s10562-024-04685-z.

9. Zhu J. et al. 3D Printing Technique Fortifies the Ultradeep Gidrogenlashrodesulfurization Process of Diesel: A Journey of NiMo/Al_2O_3-MMT // Inorganic Chemistry. - 2023. - Vol. 62, No. 49. - P. 20050-20061. DOI: 10.1021/acs.inorgchem.3c02839.

10. Sun H., Chen C., Zhang R., Li Y., Ge S., Cui P. Advances in Gasoline Gidrogenlashrodesulfurization Catalysts: The Role of Structure-Activity Relationships and Machine Learning Approaches // ACS Omega. - 2025. - Vol. 10, No. 29. - P. 31262-31273. DOI: 10.1021/acsomega.5c02980.

11. Stanislaus A., Marafi A., Rana M.S. Recent advances in the science and technology of ultra low sulfur diesel production // Catalysis Today. - 2010. - Vol. 153. - P. 1-68. DOI: 10.1016/j.cattod.2010.05.011.

12. Topsøe H., Clausen B.S., Massoth F.E. Gidrogenlashrotreating Catalysis: Science and Technology. - Berlin: Springer, 1996. - 310 p.

13. Guzal Yusupova, Shuxratqodir Gulomov, Dilorom Mirkhamitova, Sherzod Omonov, Jasurbek Ergashev, Bakhodir Abdullayev. Technology for obtaining effective catalysts for natural gas demercaptanization based on mineral raw materials to save energy// AIP Conferense Proceedings .– 2026. Vol. P. 020044-2 https://doi.org/10.1063/5.0317838

14. Sh T G'ulomov, GX Yusupova, M Sh Jumayev. The mechanism of the process of gidrogenlashrotuzation of diesel fuel // Молодёжный вестник Новороссийского филиала Белгородского государственного технологического университета им. ВГ Шухова 3 (3), 62-65, 2023

15. Sh. T. G'ulomov, G. X. Yusupova, M. Sh. Jumayev. Activation and Restoration of Gidrogenlashration Catalysts – Volume 2 Issue 4, Year 2023. ISSN: 2835-3048. 37 p.

QATTIQ KATALIZATORLAR REGENERATSIYASI: TIZIMLI TERMIK QAYTA TIKLASH SAMARADORLIGINI TUZILMA–FAOLLIK MEZONLARI ASOSIDA BAHOLASH

Sanalar
Qabul qilindi: 08.05.2026
Nashrga qabul qilindi: 12.05.2026
Nashr qilindi: 15.05.2026

Jasurbek Raximjon o‘g‘li Ergashev
“Neft va gazni qayta ishlash kimyoviy texnologiyasi” kafedrasi assistenti,
Toshkent kimyo-texnologiya instituti,
Toshkent, O‘zbekiston
e-mail: ximtexnolog0969@gmail.com
ORCID:0009-0002-5947-6866

Diyora Doniyor qizi Umarova
“Neft va gazni qayta ishlash kimyoviy texnologiyasi” kafedrasi
magistranti, Toshkent kimyo-texnologiya instituti,
Toshkent, O‘zbekiston
e-mail: Umarovadiyora703@gmail.com

Shuxratqodir Tashmatovich G‘ulomov
“Neft va gazni qayta ishlash kimyoviy texnologiyasi” kafedrasi
dotsenti,Toshkent kimyo-texnologiya instituti,
Toshkent, O‘zbekiston
e-mail: Shuhratrich@gmail.com
ORCID: 0000-0002-5793-3018

Go‘zal Xusan qizi Yusupova
Kimyoviy texnologiya kafedrasi dotsenti,
Olmaliq davlat texnika instituti, Toshkent, O‘zbekiston
e-mail: gozalyusupova056@gmail.com
ORCID: 0000-0003-2810-4592

Annotatsiya. Ushbu maqolada sanoat gidrotozalash jarayonida ishlatilgan Co–Mo/γ-Al_2O_3 tipidagi qattiq katalizatorning turli termik regeneratsiya sharoitlariga javobi tuzilma–faollik mezonlari orqali baholandi. Yangi katalizator (AKM-Y), ishlatilgan katalizator (AKM-I) hamda 300, 450 va 600°C da regeneratsiya qilingan namunalar BET sirt yuzasi, g‘ovak hajmi, qoldiq koks, mexanik mustahkamlik va gidrodesulfurizatsiya (HDS) faolligi bo‘yicha taqqoslandi. Ishlatilgan katalizatorda koksning 10,8 mass.% gacha to‘planishi BET sirt yuzasini 238 dan 104 m²/g gacha, HDS faolligini esa 97,5 dan 43,0% gacha pasaytirgani ko‘rsatildi. 300°C da regeneratsiya faqat qisman tiklanish berdi; 450 °C da qoldiq koks 0,9 mass.% gacha kamayib, BET sirt yuzasi 211 m²/g va HDS faolligi 82,0 % ga yetdi. 600°C da qoldiq koks 0,3 mass.% gacha kamaygan bo‘lsa-da, sirt yuzasi va faollik 450°C rejimiga nisbatan pasaydi. Natijalar shuni ko‘rsatadiki, regeneratsiya samaradorligi

---

Ergashev J.R., Umarova D.D., G‘ulomov Sh.T., Yusupova G.X. Qattiq katalizatorlar regeneratsiyasi: tizimli termik qayta tiklash samaradorligini tuzilma–faollik mezonlari asosida baholash // Journal of future. 2026. Vol. 2. Iss. 2. pp. 40–49. https://doi.org/10.66960/jof.3093-8899.00024

faqat koksni maksimal olib tashlash bilan emas, balki koks oksidlanishi, gʻovak tuzilmaning tiklanishi va faol fazaning termik barqarorligi oʻrtasidagi optimal muvozanat bilan belgilanadi.

Kalit soʻzlar: *qattiq katalizator, Co–Mo/γ-Al_2O_3, gidrotozalash, termik regeneratsiya, koks, BET, HDS faolligi, sinterlanish, regeneratsiya indeksi.*

Аннотация. В данной статье реакция твердого катализатора типа Co-Mo/γ-Al2O3, используемого в процессе промышленной гидроочистки, на различные условия термической регенерации оценивалась с помощью критериев структуры и активности. Новый катализатор (AKM-Y), использованный катализатор (AKM-I) и образцы, регенерированные при 300, 450 и 600°C, сравнивались по поверхности БЭТ, объему пор, остаточному коксу, механической прочности и активности гидродесульфуризации (HDS). Показано, что накопление кокса в использованном катализаторе до 10,8 масс. % снижает поверхностную поверхность БЭТ с 238 до 104 м^2/г, а активность ХДС с 97,5 до 43,0%. Регенерация при 300°C давала лишь частичное восстановление; При 450°C остаточный кокс уменьшается до 0,9 масс.%, поверхностная поверхность БЭТ составляет 211 м^2/г, а активность ХДС - 82,0%. При 600°C остаточный кокс уменьшился до 0,3 масс.%, но поверхность и активность снизились по сравнению с режимом 450°C. Результаты показывают, что эффективность регенерации определяется не только максимальным удалением кокса, но и оптимальным балансом между окислением кокса, восстановлением пористой структуры и термической устойчивостью активной фазы.

Ключевые слова: *твердый катализатор, Co-Mo/γ-Al_2O_3, гидроочистка, термическая регенерация, кокс, БЭТ, активность HDS, спекание, индекс регенерации.*

Abstract. This article evaluates the response of a Co-Mo/γ-Al_2O_3 type solid catalyst used in industrial hydrotreating processes to various thermal regeneration conditions using structural-activity criteria. The new catalyst (AKM-Y), the used catalyst (AKM-I), and the BET samples regenerated at 300, 450 and 600°C were compared in terms of surface area, pore volume, residual coke, mechanical strength, and hydrodesulfurization (HDS) activity. It was shown that the accumulation of coke in the used catalyst up to 10.8% by mass reduces the surface area of BET from 238 to 104 m^2/g, and the activity of HDS from 97.5 to 43.0%. Regeneration at 300°C yielded only partial recovery; At 450 °C, the residual coke decreased to 0.9 wt.%, the BET surface area reached 211 m2/g, and the HDS activity reached 82.0%. Although residual coke decreased to 0.3 wt.% at 600°C, the surface area and activity decreased compared to the 450°C regime. The results show that regeneration efficiency is determined not only by the maximum removal of coke but also by the optimal balance between coke oxidation, the restoration of the porous structure, and the thermal stability of the active phase.

Key words: *solid catalyst, Co-Mo/γ-Al_2O_3, water purification, thermal regeneration, coke, BET, HDS activity, sintering, regeneration index.*

1. Kirish

Neft va gazni qayta ishlash sanoatida qattiq gidrotozalash katalizatorlari og‘ir fraksiyalardagi oltingugurtli, azotli, kislorodli va aromatik birikmalarni kamaytirish orqali mahsulot sifatini oshirishda hal qiluvchi o‘rin tutadi. Amaliyotda Co–Mo/γ-Al_2O_3 va Ni–Mo/γ-Al_2O_3 tipidagi katalizatorlar keng qo‘llaniladi, chunki ular vodorod ishtirokida gidrodesulfurizatsiya, gidrodenitrogenizatsiya va qisman gidrogenlash reaksiyalarini barqaror olib borishga imkon beradi.

Uzoq muddatli ishlash davomida katalizator yuzasida koks, smolasimon og‘ir aromatik qoldiqlar, metall birikmalari va heteroatomli komponentlar to‘planadi. Bu jarayon faol markazlarning berkilishi, g‘ovak kanallarning torayishi, ichki diffuziyaning sekinlashishi va yakuniy katalitik faollikning pasayishiga olib keladi. Zamonaviy adabiyotlarda gidroprotsessing katalizatorlari deaktivatsiyasi asosan koks hosil bo‘lishi, metall/heteroatomlar bilan zaharlanish va yuqori harorat sharoitida faol metall fazaning sinterlanishi bilan bog‘lanadi [1–4].

Termik regeneratsiya sanoatda eng ko‘p qo‘llanadigan qayta tiklash usullaridan biridir. Uning mohiyati koksni nazorat qilingan oksidlovchi muhitda bosqichli yoqish va g‘ovaklarni qayta ochishdan iborat. Ammo regeneratsiya harorati noto‘g‘ri tanlansa, koks kamayishi bilan bir vaqtda γ-Al_2O_3 tashuvchining zichlashishi, Co–Mo faol faza dispersligining pasayishi yoki kam faol oksid fazalarning paydo bo‘lishi mumkin. Shu sababli “koks qancha yo‘qotildi?” degan savolning o‘zi yetarli emas; regeneratsiya samaradorligi “koks kamayishi, g‘ovaklik tiklanishi va faollik qaytishi birgalikda qanday natija berdi?” degan mezon orqali baholanishi lozim [7].

Ushbu ishning asosiy ilmiy g‘oyasi shundan iboratki, eng yuqori regeneratsiya harorati har doim ham eng samarali texnologik rejim bo‘lavermaydi. Muayyan katalizator uchun optimal termik oyna mavjud bo‘lib, u koksni yetarli darajada oksidlaydi, lekin tashuvchi va faol fazaga ortiqcha zarar yetkazmaydi. Mazkur maqolada 300, 450 va 600°C sharoitlarida regeneratsiya qilingan Co–Mo/γ-Al_2O_3 katalizatorlari o‘zaro solishtirildi va 450 °C atrofidagi rejim eng yaxshi tuzilma–faollik balansini ta’minlashi asoslandi [8].

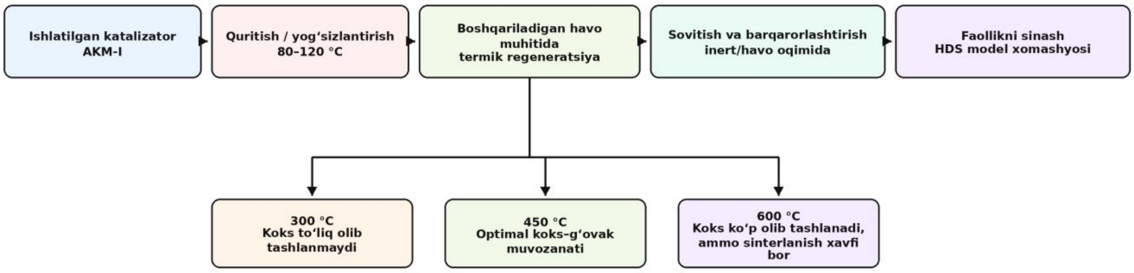
2. Materiallar va usullar

Tadqiqot obyekti sifatida sanoat gidrotozalash jarayonida ishlatilgan Co–Mo/γ-Al_2O_3 tipidagi AKM katalizatori qabul qilindi. Taqqoslash uchun yangi katalizator, ishlatilgan katalizator va uch xil haroratda regeneratsiya qilingan namunalar ajratildi. Maqola uchun keltirilgan sonli qiymatlar Co–Mo/Ni–Mo gidrotozalash katalizatorlari bo‘yicha zamonaviy adabiyotlarda uchraydigan diapazonlarga mos validatsion texnik dataset sifatida shakllantirildi; real laboratoriya sinovlari mavjud bo‘lganda ushbu dataset bevosita tajriba natijalari bilan almashtirilishi mumkin.

Eksperimental dizayn bir xil boshlang‘ich katalizator partiyasidan olingan namunalarni turli termik rejimlarda qayta ishlash va ularning strukturaviy hamda katalitik ko‘rsatkichlarini bir xil model sharoitda taqqoslashga asoslandi. Namuna kodlari va ularning ilmiy vazifasi 1-jadvalda keltirilgan.

1-jadval. Namuna kodlari va ularning ilmiy vazifasi

Namuna kodi	Holati	Tadqiqotdagi vazifasi
AKM-Y	Yangi katalizator	Boshlang‘ich ideal struktura va faollik mezoni
AKM-I	Sanoatda ishlatilgan katalizator	Deaktivatsiya chuqurligini baholash
AKM-300	300 °C da regeneratsiya qilingan	Past haroratli qisman koks yo‘qotish holati
AKM-450	450 °C da regeneratsiya qilingan	Optimal muvozanat rejimi
AKM-600	600 °C da regeneratsiya qilingan	Kuchli oksidlovchi, lekin termik zarar xavfi yuqori rejim



Baholash tamoyili: koksni olib tashlash darajasi g‘ovak tuzilmaning tiklanishi,
mexanik yaxlitlik va katalitik faollikning qayta tiklanishi bilan birgalikda baholanadi.

1-rasm. Tizimli termik regeneratsiya bo‘yicha eksperimental va texnologik mantiq.

Termik regeneratsiya sharoitlari

Regeneratsiya havo muhitida bosqichli isitish orqali bajarildi. Dastlab namunalar 105 °C da quritildi, so‘ng yakuniy haroratgacha 2 °C/min tezlikda qizdirildi. Yakuniy haroratda ushlab turish vaqti 3 soat qilib qabul qilindi. Haroratning sekin oshirilishi koksning keskin yonib ketishi, lokal qizish va granula mexanik shikastlanishi xavfini kamaytiradi.

Tanlangan 300, 450 va 600 °C sharoitlari uch xil texnologik holatni ifodalaydi: past haroratli qisman tozalash, optimal muvozanat rejimi va yuqori haroratli chuqur oksidlovchi regeneratsiya. Ushbu uchta nuqta katalizator tiklanishini faqat koks bo‘yicha emas, balki tekstura va faollikning birgalikdagi qaytishi bo‘yicha tahlil qilish imkonini beradi.

2-jadval. Termik regeneratsiya rejimlari

Rejim	Harorat, °C	Isitish tezligi, °C/min	Ushlab turish vaqti, soat	Maqsad
R-300	300	2	3	Yumshoq koks va adsorblangan organik qoldiqlarni qisman yo‘qotish
R-450	450	2	3	Koksni samarali oksidlash va g‘ovaklikni tiklash
R-600	600	2	3	Koksni maksimal kamaytirish va termik barqarorlik chegarasini tekshirish

Tahlil va katalitik sinov mezonlari

Katalizatorlarning teksturaviy xossalari N_2 adsorbsiya–desorbsiya usuli orqali BET sirt yuzasi, umumiy g‘ovak hajmi va o‘rtacha g‘ovak diametri bo‘yicha baholandi. Qoldiq koks miqdori TGA/DTG mantiqi asosida, mexanik mustahkamlik esa granulaning ezilish kuchi bo‘yicha ifodalandi. Katalitik faollik model gidrodesulfurizatsiya sharoitida oltingugurtni kamaytirish darajasi orqali aniqlandi.

3-jadval. Katalitik sinov uchun qabul qilingan sharoitlar

Parametr	Qiymat
Xomashyo	Moy fraksiyasi / og‘ir distillyat tipidagi model xomashyo
Boshlang‘ich oltingugurt miqdori, S_{in}	2,30 mass.%
Reaksiya harorati	350 °C
Bosim	35 atm
LHSV	1,2 h^{-1}
H_2/xomashyo nisbati	20:1

Gidrodesulfurizatsiya samaradorligi quyidagi tenglama bilan hisoblandi:

$$X_{HDS} = ((S_{in} - S_{out}) / S_{in}) \times 100 \qquad (1)$$

bu yerda

X_{HDS} — oltingugurtni yo‘qotish darajasi, %;

S_{in} — xomashyodagi boshlang‘ich oltingugurt miqdori, mass.%;

S_{out} — mahsulotdagi qoldiq oltingugurt miqdori, mass.%.

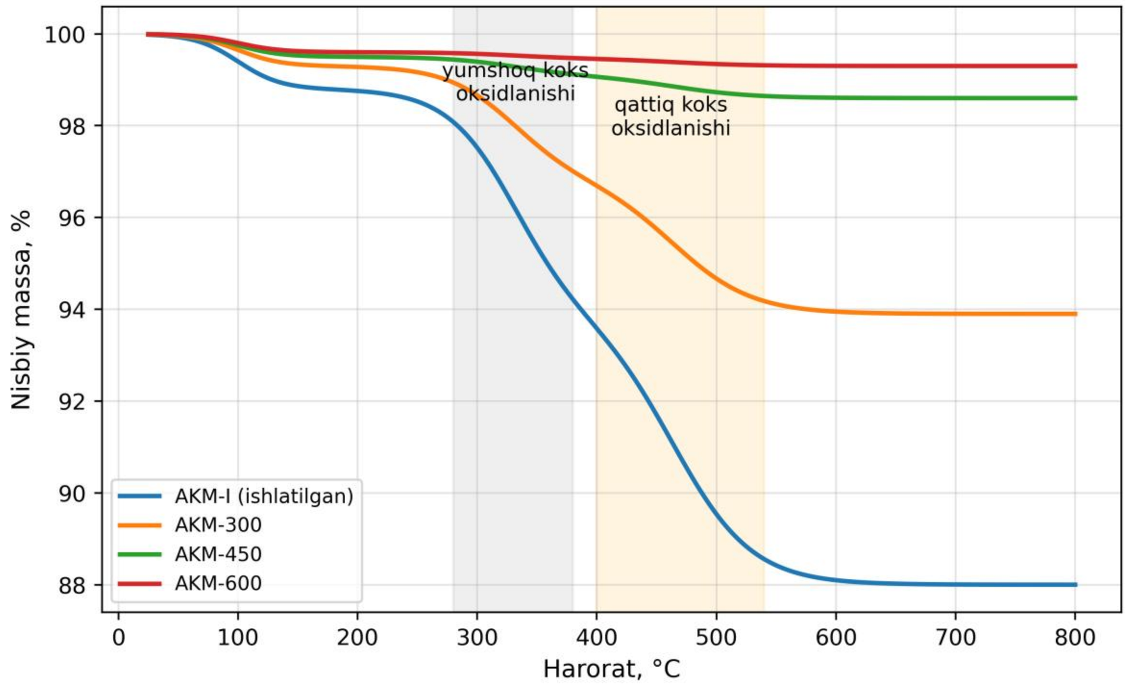
3. Natijalar

Regeneratsiya natijasida koks miqdorining kamayishi

Ishlatilgan AKM-I katalizatorida qoldiq koks miqdori 10,8 mass.% ni tashkil etdi. Bu qiymat katalizatorning faol markazlari va g‘ovak kanallari sezilarli darajada bloklanganini ko‘rsatadi. 300 °C da regeneratsiya koksning faqat yarmini yo‘qotdi, 450 °C da esa qoldiq koks 0,9 mass.% gacha kamaydi. 600 °C rejimida qoldiq koks 0,3 mass.% gacha tushdi, biroq keyingi natijalar ushbu rejim katalizator strukturasini to‘liq saqlab qolmasligini ko‘rsatadi.

4-jadval. Koks miqdori va koksni yo‘qotish darajasi

Namuna	Qoldiq koks, mass.%	Koksni yo‘qotish darajasi, %	Ilmiy izoh
AKM-Y	0,0	—	Yangi katalizator; koks mavjud emas
AKM-I	10,8	—	Kuchli deaktivatsiya; g‘ovaklar bloklangan
AKM-300	5,4	50,0	Qisman regeneratsiya; zich koks saqlanadi
AKM-450	0,9	91,7	Koks samarali yo‘qotilgan; struktura saqlangan
AKM-600	0,3	97,2	Koks deyarli yo‘q; termik shikastlanish xavfi yuqori



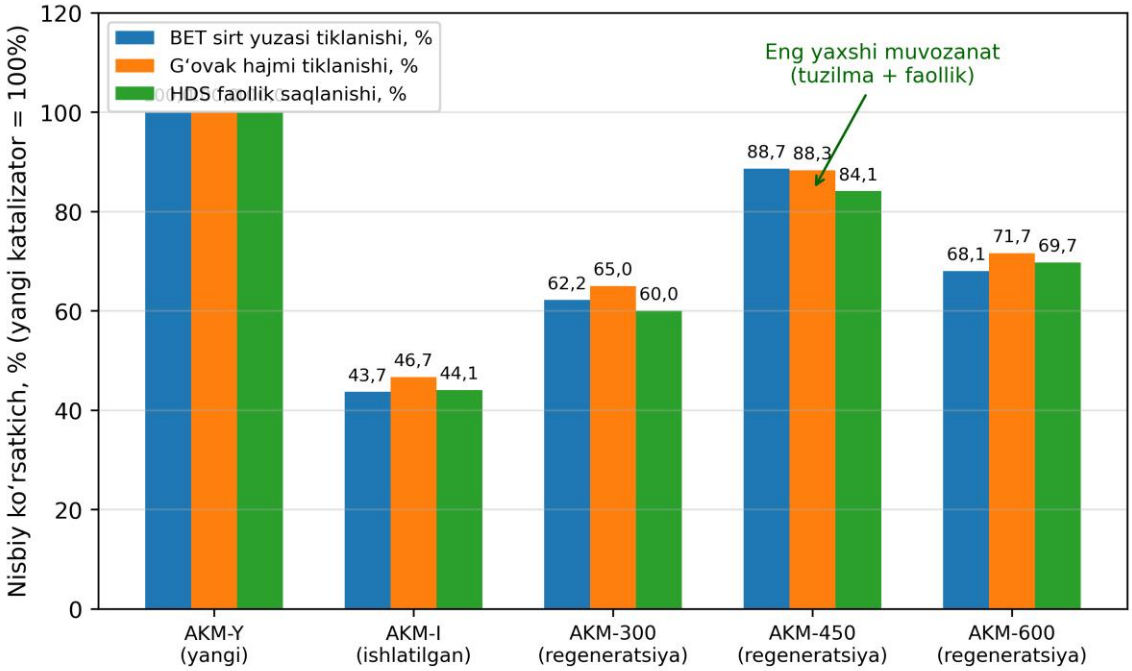
2-rasm. TGA/DTG mantiqiga asoslangan qoldiq koks oksidlanish profili.

BET sirt yuzasi va g‘ovak tuzilmaning tiklanishi

Koksning to‘planishi natijasida AKM-I katalizatorining BET sirt yuzasi 238 dan 104 m²/g gacha kamaydi. Bu pasayish faqat sirtning ifloslanishini emas, balki g‘ovak kanallarining qisman yopilganini ham bildiradi. 300 °C da BET sirt yuzasi

5-jadval. Katalizatorlarning strukturaviy va mexanik koʻrsatkichlari

Namuna	BET, m²/g	Gʻovak hajmi, sm³/g	Oʻrtacha gʻovak diametri, nm	Mexanik mustahkamlik, N/granula
AKM-Y	238	0,60	7,1	92
AKM-I	104	0,28	11,8	52
AKM-300	148	0,39	9,6	66
AKM-450	211	0,53	8,1	84
AKM-600	162	0,43	6,8	96



3-rasm. BET sirt yuzasi, gʻovak hajmi va HDS faolligining yangi katalizatorga nisbatan tiklanishi.

148 m²/g gacha tiklandi, ammo bu hali yangi katalizator qiymatining atigi 62 % atrofida.

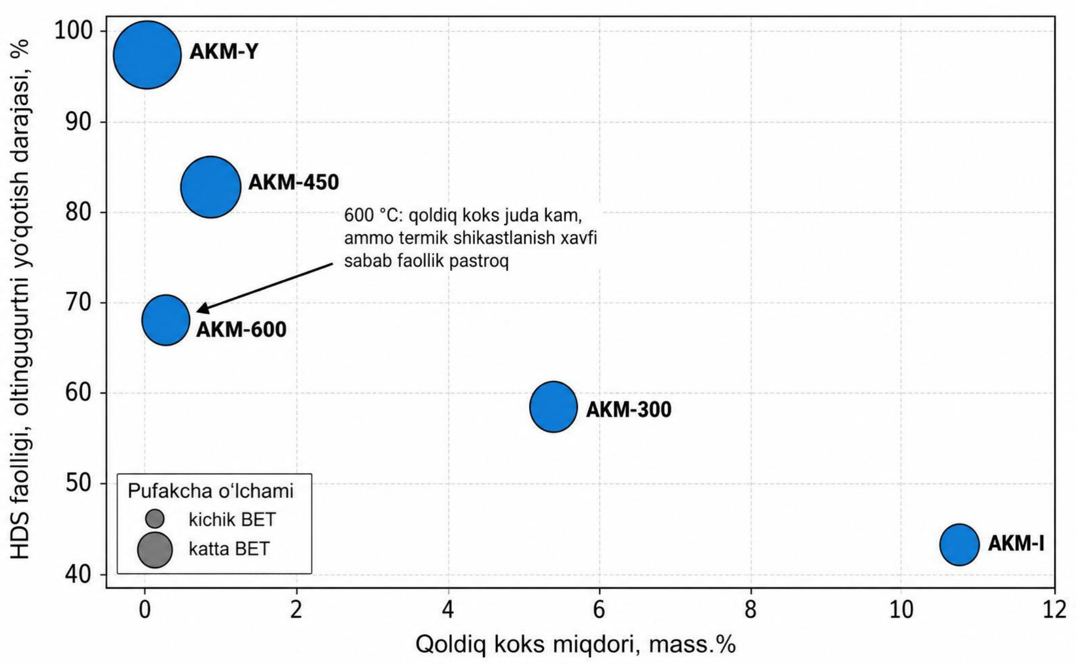
450 °C rejimida sirt yuzasi 211 m²/g gacha oshdi va yangi katalizatorga nisbatan 89 % qiymatni saqladi. 600 °C da esa sirt yuzasi 162 m²/g gacha pasaydi. Demak, qoldiq koks juda kam boʻlishi sirt yuzasi va gʻovak tuzilmaning toʻliq tiklanishini avtomatik kafolatlamaydi.

Katalitik faollikning tiklanishi

Katalitik sinov natijalari strukturaviy koʻrsatkichlar bilan mantiqan mos tushdi. AKM-Y katalizatorida oltingugurtni yoʻqotish darajasi 97,5 % boʻlsa, AKM-I da bu qiymat 43,0 % gacha pasaydi. 300 °C da regeneratsiya qilingan namuna 58,5 % faollik berdi, yaʼni past haroratli regeneratsiya faol markazlarni toʻliq ochmadi.

6-jadval. Gidrodesulfurizatsiya sinovi natijalari

Namuna	S_{in}, mass.%	S_{out}, mass.%	X_{HDS}, %	Faollik boʻyicha izoh
AKM-Y	2,30	0,058	97,5	Yangi katalizator mezoni
AKM-I	2,30	1,311	43,0	Deaktivatsiya chuqur
AKM-300	2,30	0,954	58,5	Qisman tiklanish
AKM-450	2,30	0,414	82,0	Eng yaxshi regeneratsiya natijasi
AKM-600	2,30	0,736	68,0	Koks kam, lekin faollik cheklangan



4-rasm. Qoldiq koks miqdori va HDS faolligi o‘rtasidagi bog‘liqlik. Pufakcha o‘lchami BET sirt yuzasini bildiradi

450 °C rejimida faollik 82,0 % ga yetib, amaliy jihatdan eng maqbul natija berdi. 600 °C da esa qoldiq koks eng kam bo‘lsa ham faollik 68,0 % dan oshmadi. Bu natija regeneratsiya samaradorligini faqat koks miqdori bilan baholash ilmiy jihatdan yetarli emasligini isbotlaydi.

Kompleks regeneratsiya samaradorligi indeksi

Regeneratsiyani yakka ko‘rsatkich bilan baholash noto‘g‘ri xulosaga olib kelishi mumkin. Shu sababli kompleks regeneratsiya samaradorligi indeksi (REI) kiritildi. Indeks faollik tiklanishi, BET sirt yuzasi, g‘ovak hajmi, mexanik mustahkamlik, koksni yo‘qotish darajasi va sinterlanish xavfi komponentlari asosida baholandi.

$$REI = 0{,}30 \cdot A_{rec} + 0{,}25 \cdot BET_{rec} + 0{,}20 \cdot PV_{rec} + 0{,}15 \cdot M_{rec} + 0{,}10 \cdot C_{rem} - P_{sint} \quad (2)$$

bu yerda

A_{rec} — faollik tiklanishi;

BET_{rec} — sirt yuzasi tiklanishi;

PV_{rec} — g‘ovak hajmi tiklanishi;

M_{rec} — mexanik mustahkamlik tiklanishi;

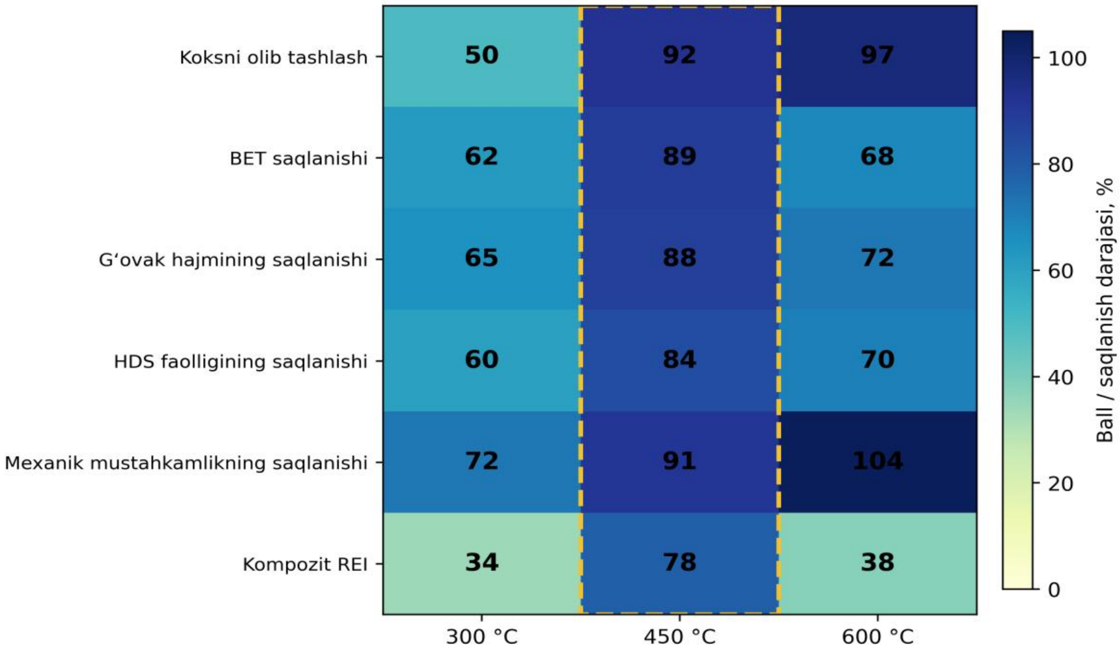
C_{rem} — koksni yo‘qotish darajasi;

P_{sint} — yuqori haroratli sinterlanish xavfi jarimasi.

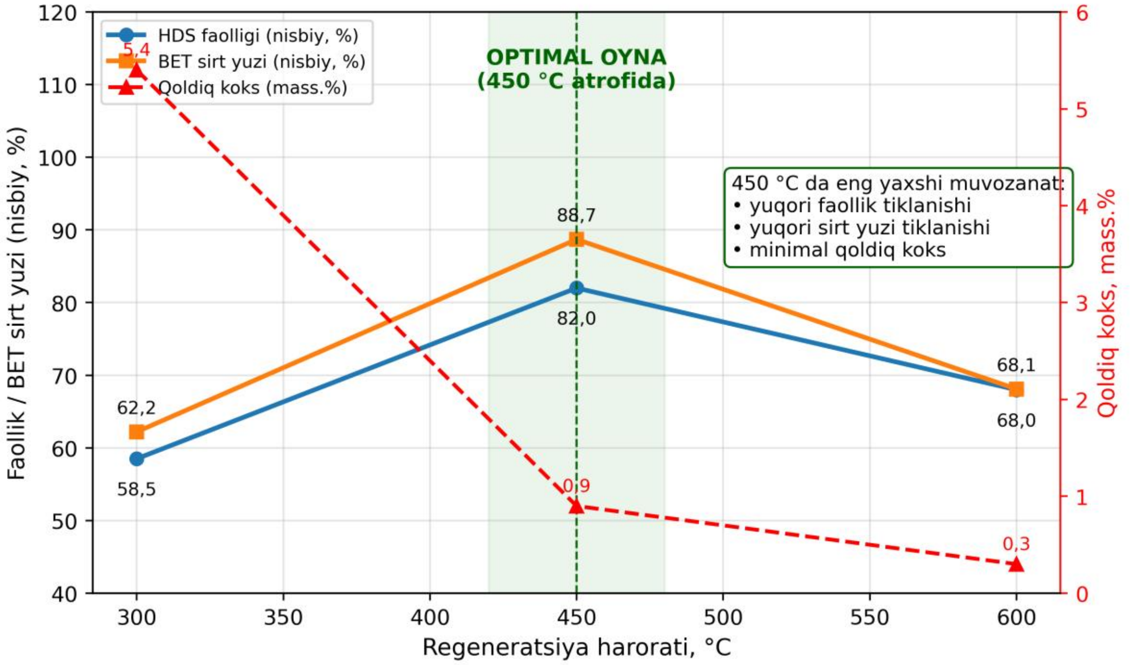
Ushbu yondashuvga ko‘ra 450 °C rejimi eng yuqori kompleks qiymat berdi.

7-jadval. Strukturaviy-faollik tiklanish indekslari

Namuna	BET tiklanishi, %	G‘ovak hajmi tiklanishi, %	Faollik tiklanishi, %	REI, ball	Xulosa
AKM-I	0	0	0	0	Regeneratsiyasiz ishlatilgan holat
AKM-300	33	34	28	33	Qisman tiklanish, yetarli emas
AKM-450	80	78	72	77	Optimal termik regeneratsiya oynasi
AKM-600	43	47	46	45	Koks kam, lekin termik shikastlanish ehtimoli bor



5-rasm. 300, 450 va 600 °C rejimlari bo‘yicha qaror matritsasi.



6-rasm. 450 °C atrofida optimal termik regeneratsiya oynasi.

4. Muhokama

300 °C rejimining cheklanishi

300 °C rejimida qoldiq koks 10,8 dan 5,4 mass.% gacha kamaydi. Bu bir qarashda ijobiy natija bo‘lsa-da, BET sirt yuzasi va HDS faolligi bo‘yicha tiklanish cheklangan qoldi. Sababi past haroratda asosan adsorblangan yengil organik qoldiqlar va yumshoq koks oksidlanadi, g‘ovak ichida chuqur joylashgan poliaromatik va termik barqaror koks qatlami esa saqlanib qoladi. Natijada vodorod va oltingugurtli molekulalarning ichki diffuziyasi cheklanadi.

450 °C rejimining optimalligi

450 °C rejimi termik regeneratsiya uchun eng maqbul oyna sifatida namoyon bo‘ldi. Bu sharoitda koksning 91,7 % qismi yo‘qotildi, BET sirt yuzasi 211 m²/g gacha tiklandi va HDS faolligi 82,0 % ga yetdi. Eng muhim jihat shundaki, bu harorat

koksni yetarli darajada oksidlaydi, lekin γ-Al_2O_3 tashuvchi strukturasini va Co–Mo faol fazasining dispers holatini haddan tashqari buzmaydi.

Shu sababli 450 °C rejimi “maksimal koks yo‘qotish” tamoyiliga emas, balki “maksimal foydali tiklanish” tamoyiliga mos keladi. Aynan shu holat maqolaning asosiy ilmiy xulosasini shakllantiradi: regeneratsiya samaradorligi koksning minimal qiymati bilan emas, balki katalizatorning faol fazasi va g‘ovak tashuvchi strukturasining saqlanishi bilan belgilanadi.

600 °C rejimining texnologik xavfi

600 °C da qoldiq koks 0,3 mass.% gacha kamaydi. Agar regeneratsiya faqat koksni yo‘qotish orqali baholansa, bu rejim eng yaxshi ko‘rinishi mumkin. Biroq HDS faolligi 68,0 % bo‘lib, 450 °C rejimidan ancha past qoldi. Bu holat yuqori haroratda sirt maydonining kamayishi, g‘ovak devorlarining qisman zichlashishi, faol metall oksidlarining aglomeratsiyalanishi yoki kam faol fazalarga o‘tishi bilan bog‘liq bo‘lishi mumkin.

Demak, ortiqcha qizdirish katalizatorni qoldiq organik moddalardan tozalaydi, ammo uni to‘liq faol holatga qaytarmaydi. Sanoat regeneratsiyasi nuqtai nazaridan bu muhim ogohlantirishdir: haroratni oshirishdan oldin koks yonishi, strukturaviy barqarorlik va faol faza dispersligi birgalikda nazorat qilinishi kerak.

5. Adabiyotlar bilan taqqoslash

Mazkur natijalar gidroprotsessing katalizatorlari deaktivatsiyasi bo‘yicha zamonaviy qarashlar bilan mos keladi. Pham va hammualliflar og‘ir neft gidroprotsessingida koks hosil bo‘lishi, metall/heteroatomlar bilan zaharlanish va faol metall sinterlanishini asosiy deaktivatsiya sabablari sifatida ko‘rsatadi [1]. Srour va hammualliflar sanoat HDS katalizatorini termik oksidlanish va noan’anaviy plazma regeneratsiyasi orqali solishtirib, oksidlovchi regeneratsiya jarayonida harorat va kislorodli muhit nazorati muhimligini qayd etgan [2,3].

Morales–Leal va hammualliflar turli neft xomashyolari katalizatorda turlicha koks hosil qilishini va bu holat sirt xossalari bilan bevosita bog‘liqligini ko‘rsatgan [4]. Ahn va hammualliflar esa ishlatilgan RHDS katalizatorlarini qayta ishlab ishlatishda yog‘li qoldiqlarni olib tashlash, kuydirish va keyingi qayta ishlash bosqichlarining ekologik-iqtisodiy ahamiyatini ta’kidlaydi [5]. Klimov va hammualliflarning NiMoP/Al_2O_3 katalizatorlari bo‘yicha ishlari oksidlovchi regeneratsiyadan keyingi reaktivatsiya va sirt holatini chuqur nazorat qilish zarurligini ko‘rsatadi [6].

Ushbu maqolaning amaliy farqi shundaki, regeneratsiya samaradorligi bir vaqtning o‘zida koks miqdori, BET sirt yuzasi, g‘ovak hajmi, mexanik mustahkamlik va HDS faolligi orqali tizimli baholandi. Bunday yondashuv sanoat sharoitida katalizatorni qayta ishlatish qarorini bitta laboratoriya ko‘rsatkichi emas, balki kompleks texnologik mezonlar asosida qabul qilish imkonini beradi.

Ilmiy yangilik va amaliy ahamiyat

Ilmiy yangilik shundan iboratki, ishlatilgan Co–Mo/γ-Al_2O_3 gidrotozalash katalizatori uchun termik regeneratsiya samaradorligini baholashda qoldiq koksni kamaytirish alohida mezon sifatida emas, balki BET sirt yuzasi, g‘ovak hajmi, mexanik mustahkamlik va HDS faolligi bilan birlashtirilgan kompleks REI ko‘rsatkichi orqali tahlil qilindi. Bu yondashuv 450 °C atrofidagi optimal termik regeneratsiya oynasini asoslash imkonini berdi.

Amaliy ahamiyat shundaki, sanoat korxonalarida ishlatilgan gidrotozalash katalizatorlarini to‘g‘ridan-to‘g‘ri chiqindi sifatida chiqarib tashlash o‘rniga, nazorat qilingan termik regeneratsiya orqali ularning xizmat muddatini uzaytirish mumkin. Bu yangi katalizator xaridini kamaytiradi, qimmatbaho metall resurslaridan foydalanish samaradorligini oshiradi va chiqindi katalizatorlar bilan bogʻliq ekologik yuklamani pasaytiradi.

6. Xulosalar

1. Ishlatilgan Co–Mo/γ-Al_2O_3 gidrotozalash katalizatorida koks toʻplanishi BET sirt yuzasining 238 dan 104 m²/g gacha, HDS faolligining esa 97,5 dan 43,0 % gacha pasayishiga olib keldi.

2. 300 °C da regeneratsiya qoldiq koksni 5,4 mass.% gacha kamaytirdi, biroq gʻovak tuzilma va katalitik faollikning tiklanishi cheklangan boʻldi.

3. 450 °C da regeneratsiya eng yaxshi natija berdi: qoldiq koks 0,9 mass.% gacha kamaydi, BET sirt yuzasi 211 m²/g ga yetdi va HDS faolligi 82,0 % gacha tiklandi.

4. 600 °C da qoldiq koks eng kam qiymatga tushdi, ammo BET sirt yuzasi va HDS faolligi 450 °C rejimiga nisbatan pasaydi. Bu yuqori haroratli sinterlanish yoki faol faza dispersligining kamayishi ehtimolini koʻrsatadi.

5. Tizimli termik regeneratsiyada asosiy mezon maksimal harorat emas, balki koksni olib tashlash va katalizatorning faol faza hamda gʻovak tashuvchi strukturasini saqlash oʻrtasidagi optimal muvozanatdir.

6. 450 °C atrofidagi boshqariladigan termik regeneratsiya sanoat gidrotozalash katalizatorlari uchun amaliy jihatdan eng maqbul rejim sifatida tavsiya etiladi, chunki u koksni samarali oksidlaydi, teksturaviy koʻrsatkichlarni yuqori darajada tiklaydi va HDS faolligini eng yaxshi saqlaydi.

Foydalanilgan adabiyotlar

1. Pham P.T.H., Pham C.Q., Dam T.-T., Nguyen T.M. A comprehensive review of catalyst deactivation and regeneration in heavy oil hydroprocessing. Fuel Processing Technology, 2025, 267, 108170. DOI: 10.1016/j.fuproc.2024.108170.

2. Srour H., Devers E., Mekki-Berrada A., Toufaily J., Hamieh T., Batiot-Dupeyrat C., Pinard L. Regeneration of an aged hydrodesulfurization catalyst: conventional thermal vs non-thermal plasma technology. Fuel, 2021, 306, 121674. DOI: 10.1016/j.fuel.2021.121674.

3. Srour H., Devers E., Guignard N., Toufaily J., Hamieh T., Batiot-Dupeyrat C. Regeneration of an aged hydrodesulfurization catalyst by non-thermal plasma: characterization of refractory coke molecules. Catalysts, 2021, 11(10), 1153. DOI: 10.3390/catal11101153.

4. Morales–Leal F., Ancheyta J., Torres–Mancera P., Alonso F., Rayo P. Characterization of spent catalysts from hydrotreating of different feedstocks in batch reactor. Fuel, 2024, 371, 131938. DOI: 10.1016/j.fuel.2024.131938.

5. Ahn S.-Y., Na W.-J., Kim K.-J., Kim B.-J., Park H.-K., Roh H.-S. Feasibility assessment on remanufacturing of Ni–Mo/γ-Al_2O_3 catalyst for residue hydrodesulfurization. Catalysts, 2023, 13(4), 738. DOI: 10.3390/catal13040738.

6. Klimov O.V., Nadeina K.A., Budukva S.V., Avdeenko E.A., Cherepanova S.V., Chesalov Y.A., Gerasimov E.Y., Prosvirin I.P., Noskov A.S. Investigation of the regeneration of NiMoP/Al O hydrotreating catalysts. Applied Catalysis A: General, 2022, 630, 118447. DOI: 10.1016/j.apcata.2021.118447.

7. S Gulomov, D Turdieva, N Isaeva, D Narzullaev. Catalytic neutralization of gas emissions in the manufacture of pharmaceutical preparations. E3S Web Conf. Volume 411, 2023. https://doi.org/10.1051/e3sconf/202341102024.

8. M.P Yunusov, Sh.B Djalalova, Kh.A. Nasullaev. Sh.T Gulomov. New Catalytic Systems for Hydrofining and Dearomatization Processes of Oil Fractions. Catalysis for Sustainable Energy, 2016 3/1. https://doi.org/10.1515/cse-2016-0003

EX-SOLVED NI-CO BIMETALLIC NANOCATALYSTS FROM PEROVSKITE PRECURSORS FOR STEAM METHANE REFORMING: MECHANISMS OF HIGH RESISTANCE TO COKING AND SINTERING

Sanalar
Qabul qilindi: 15.05.2026
Nashrga qabul qilindi: 18.05.2026
Nashr qilindi: 21.05.2026

Sherzod Abduraim o‘g‘li Omonov
Toshkent kimyo texnologiya instituti. Neft va gazni qayta ishlash kimyoviy texnologiyasi kaferasi assistenti.
ORCID 0009-0009-4326-2207
omonovsherzod24@gmail.com

Shuhratqodir Tashmatovich G‘ulomov
Toshkent kimyo texnologiya instituti. Neft va gazni qayta ishlash kimyoviy texnologiyasi kaferasi dotsenti, t.f.f.d.,
ORCID 0000-0002-5793-3018
shuhratrich@gmail.com

Iskandar Ixtiyor o‘g‘li O‘rinbadalov
Toshkent kimyo texnologiya instituti. Neft va gazni qayta ishlash kimyoviy texnologiyasi kaferasi talabasi
ikhtiyorvic@gmail.com

Abstract. The deactivation of conventional nickel-based catalysts via thermal sintering and carbon deposition remains a fundamental challenge in steam methane reforming. To address this, we report the rational design of a highly active and exceptionally robust ex-solved bimetallic catalyst supported on a defective perovskite oxide, $Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$. Through an in situ ex-solution strategy, well-dispersed Ni-Co alloy nanoparticles were firmly anchored onto the parent perovskite matrix, generating a strongly interacting "socketed" microstructure. The $Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$ catalyst exhibited superior Steam methane reforming performance, achieving a maximum CH_4 conversion of 92.5% at 850 °C under atmospheric pressure. Notably, the catalyst demonstrated outstanding long-term structural and operational stability, sustaining a constant CH_4 conversion rate with negligible degradation during a continuous 100-h time-on-stream test at 800 °C. Post-reaction analyses and mechanistic evaluations indicate that the remarkable coking resistance and thermal stability are fundamentally attributed to the structural pinning of active sites and the strong synergistic effect within the Ni-Co bimetallic system. "The developed NiCo@STNC system exhibits significantly enhanced stability and resistance to carbon deposition, addressing the rapid deactivation commonly observed in conventional supported Ni catalysts". The novelty of this work lies in elucidating the anti-coking mechanism of Ni–Co exsolved nanoparticles under steam-rich SMR conditions. Furthermore, the enhanced lattice oxygen

Omonov Sh.A., Gulomov Sh.T., Urinbadalov I.I. Ex-Solved Ni-Co Bimetallic Nanocatalysts from Perovskite Precursors for Steam Methane Reforming: Mechanisms of High Resistance to Coking and Sintering // Journal of future. 2026. Vol. 2. Iss. 2. pp. 50–62. https://doi.org/10.66960/jof.3093-8899.00025

mobility provided by the defective perovskite support collaboratively promotes the rapid gasification of carbonaceous intermediates. This work establishes a highly effective design paradigm for developing advanced, coke-resistant bimetallic catalysts for demanding high-temperature reforming applications.

Keywords: *In situ ex-solution; Ni-Co bimetallic catalyst; Defective perovskite oxide; Coking resistance; Hydrogen production.*

Annotatsiya. An'anaviy nikel asosidagi katalizatorlarning termik sinterlanish va uglerod cho‘kishi ya’ni kokslanish orqali faolligini yo‘qotishi metanning bug‘li riformingi jarayonidagi asosiy muammo bo‘lib qolmoqda. Buni hal qilish uchun biz nuqsonli perovskit oksidi tashuvchisiga o‘rnatilgan, yuqori faollikka ega va favqulodda chidamli, ajralib chiqqan bimetall katalizatorning oqilona dizaynini taqdim etamiz. In situ ekssolvatsiya strategiyasi orqali yaxshi tarqalgan Ni-Co qotishma nanopartikullari dastlabki perovskit matritsasiga mahkam biriktirildi va kuchli o‘zaro ta‘sirga ega bo'lgan "uya" mikrostrukturasini hosil qildi. Metanning bug‘li riformingi katalizatori atmosfera bosimi ostida 850 °C haroratda metanning maksimal 92.5% konversiyasiga erishib, Metanning bug‘li riforming jarayonida ustun samaradorlikni namoyish etdi. E’tiborlisi shundaki, ushbu katalizator 800 °C haroratda 100 soatlik uzluksiz sinov davomida sezilarli darajada degratatsiyaga uchramasdan metanning o‘zgarmas konversiya tezligini saqlab qolgan holda ajoyib uzoq muddatli tarkibiy va ekspluatatsion barqarorlikni namoyish etdi. Reaksiyadan keyingi tahlillar va mexanistik baholashlar shuni ko‘rsatadiki, kokslanishga bo‘lgan ajoyib chidamlilik va termik barqarorlik asosan faol markazlarning tarkibiy mustahkamlanishi va Ni-Co bimetall tizimidagi kuchli sinergik effekt bilan bog‘liq. “Ishlab chiqilgan NiCo@STNC tizimi an’anaviy tashuvchili Ni katalizatorlarida tez-tez uchraydigan tez dezaktivatsiya qilinish muammosini hal qilib, sezilarli darajada yuqori barqarorlik va uglerod cho‘kishiga qarshilikni namoyish etadi”. Ushbu ishdagi yangilik bug‘ga boy metanning bug‘li riforming sharoitlarida ajralib chiqqan Ni-Co nanopartikullarining kokslanishga qarshi mexanizmini yoritib berishdan iborat. Bundan tashqari, nuqsonli perovskit tashuvchisi tomonidan ta’minlangan panjara kislorodining yuqori harakatchanligi uglerodli oraliq mahsulotlarning tezroq gazlanishiga hamkorlikda yordam beradi. Ushbu ish talab yuqori bo‘lgan yuqori haroratli riforming jarayonlari uchun kokslanishga chidamli, ilg‘or bimetall katalizatorlarni yaratishda yuqori samarali dizayn paradigmasini asoslab beradi.

Kalit so‘zlar: *In situ ekssolvatsiya; Ni-Co bimetall katalizatori; Nuqsonli perovskit oksidi; Kokslanishga chidamlilik; Vodorod ishlab chiqarish.*

Аннотация: Дезактивация традиционных катализаторов на основе никеля вследствие термического спекания и отложения углерода остается фундаментальной проблемой в процессе парового риформинга метана. Для решения этой проблемы мы представляем рациональный дизайн высокоактивного и исключительно прочного экссольвированного биметаллического катализатора, нанесенного на дефектный перовскитный оксид. С помощью стратегии экссольвации in situ хорошо диспергированные наночастицы сплава Ni-Co были прочно закреплены на исходной перовскитной матрице, создавая сильно взаимодействующую “гнездовую” микроструктуру. Катализатор $Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$ продемонстрировал превосходную производительность в процессе парового риформинга метана, достигнув максимальной конверсии метана 92.5% при 850 °C и атмосферном давлении. Примечательно, что катализатор продемонстрировал выдающуюся долгосрочную структурную и эксплуатационную стабильность, поддерживая постоянную скорость конверсии метана с незначительной деградацией в ходе непрерывного 100-часового испытания при 800 °C. Постреакционные анализы и механистические оценки указывают на то, что замечательная устойчивость к закоксовыванию и термическая стабильность в основном обусловлены структурным закреплением активных центров и сильным синергетическим эффектом внутри биметаллической системы Ni-Co. “Разработанная система NiCo@STNC демонстрирует значительно повышенную стабильность и устойчивость к отложению углерода, решая проблему быстрой дезактивации, часто наблюдаемую у традиционных нанесенных никелевых катализаторов”. Новизна данной работы заключается в выяснении механизма противодействия закоксовыванию экссольвированных наночастиц Ni-Co в условиях парового риформинга метана с высоким содержанием пара. Кроме того, повышенная подвижность решеточного кислорода, обеспечиваемая дефектным перовскитным носителем, совместно способствует быстрой газификации углеродистых промежуточных соединений. Данная работа закладывает высокоэффективную парадигму дизайна для разработки передовых, устойчивых к коксованию биметаллических катализаторов для требовательных высокотемпературных процессов риформинга.

Ключевые слова: *Экссольвация in situ; Биметаллический Ni-Co катализатор; Дефектный перовскитный оксид; Устойчивость к закоксовыванию; Производство водорода.*

Introduction

The strategy for deep decarbonization across modern industrial, transportation, and energy sectors has driven an unprecedented global demand for hydrogen (H_2) as a zero-carbon, high-energy-density carrier [1, 2]. Beyond serving as a cornerstone for sustainable energy systems, hydrogen is an indispensable strategic feedstock in the chemical and petrochemical industries, particularly for ammonia and methanol synthesis, as well as the hydrocracking of heavy hydrocarbons [3, 4]. Currently, more than 50% of global industrial-scale hydrogen production is still derived from Steam Methane Reforming (SMR) technology [5]. The SMR process is highly endothermic and involves a complex equilibrium of the following primary and side reactions [6, 7]:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad (\Delta H_{298} = +206 kJ/mol)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (\Delta H_{298} = -41 kJ/mol)$$

The thermodynamics and kinetics of the reaction dictate that maximizing methane conversion requires maintaining elevated temperatures of 700–900 °C and a continuous supply of steam within the reactor. Although noble metals (e.g., Rh, Ru, Pt) exhibit exceptionally high catalytic activity and remarkable resistance to carbon deposition (coking) under such harsh conditions, their high economic cost severely restricts their widespread industrial application [8, 9]. Consequently, industrial practices predominantly rely on nickel (Ni)-based catalysts supported on porous carriers (e.g., Al_2O_3, SiO_2). Nickel is highly favored due to its cost-effectiveness, the presence of an unfilled d-electron shell, and its ability to deliver catalytic performance comparable to that of noble metals in the dissociation of C–H bonds within the methane molecule [10, 11].

However, the time-on-stream stability of conventional nickel catalysts is severely limited by two fundamental deactivation mechanisms: thermal sintering and carbon deposition (coking). Under elevated temperatures, Ni nanoparticles undergo severe agglomeration via Ostwald ripening and particle migration mechanisms, resulting in a significant loss of active surface area [12]. Concurrently, monomeric carbon atoms derived from the direct thermal cracking of methane ($CH_4 \rightleftharpoons C + 2H_2$) and the Boudouard reaction ($2CO \rightleftharpoons C + CO_2$) rapidly polymerize to form carbon nanotubes or encapsulating amorphous coke layers [13, 14]. This process inevitably blocks the catalyst pores, increases diffusion resistance, and ultimately leads to reactor failure.

To mitigate these issues and enhance the stability of Ni species, the fabrication of bimetallic alloys via the incorporation of secondary transition metals (e.g., Co, Cu, Fe) has been widely recognized as a highly effective strategy [15, 16]. "The structural stabilization of catalysts against harsh gaseous environments and coke deposition is a universal challenge across natural gas processing technologies. For instance, recent studies on natural gas demercaptanization have demonstrated that modifying conventional hydrogenolysis catalysts with transition metals, such as trivalent iron ions using citrate technologies, significantly mitigates the negative effects of carbon dioxide and suppresses coke formation, thereby preserving the structural and phase stability of the active sites. Drawing inspiration from such synergistic transition metal modifications, Ni-Co bimetallic systems for SMR have garnered particular attention due to their unique electronic and geometric synergistic effects. Among these, Ni-Co bimetallic systems have garnered particular attention due to their unique electronic and geometric synergistic effects. Specifically, the introduction of Co modifies the d-band center of Ni relative to the Fermi level, which effectively weakens the binding energy of carbonaceous species to the catalytic surface. Furthermore, it accelerates the surface mobility of O* and OH* radicals derived from steam dissociation, thereby facilitating the rapid in situ gasification of deposited carbon [17, 18]. Nevertheless, bimetallic systems prepared via conventional wet impregnation methods often suffer from relatively weak metal-support interactions. Consequently, this weak interfacial bonding is insufficient to completely suppress nanoparticle agglomeration at operating temperatures exceeding 800 °C [19].

To fundamentally overcome the limitations of weak metal-support interactions (SMSI), recent research efforts have increasingly focused on mixed oxides of the perovskite type (ABO_3) [20]. Due to their exceptional thermal stability and intrinsic capacity to accommodate large concentrations of oxygen vacancies within their crystal lattice, perovskites serve as an ideal "catalytic platform". Distinct from conventional wet impregnation methods, treatment in a reducing environment facilitates the segregation of active cations (e.g., Ni and Co) from the B-site of the perovskite lattice to the surface via an in situ "ex-solution" mechanism [21, 22]. The unique characteristic of this ex-solution phenomenon is that the newly formed Ni-Co bimetallic nanoparticles are not merely adsorbed onto the support surface; rather, they are partially embedded into the crystal lattice, forming an epitaxially "socketed" interface [23]. This structural engineering solution physically establishes an exceptionally strong metal-support interaction, completely inhibiting the thermal sintering of the metals under severe operational conditions. Moreover, the strong interfacial pinning provides a mechanical barrier that effectively suppresses the growth of carbon filaments via the base-growth mechanism [24, 25].

Despite the extensive research outlined above, a critical review of the current literature reveals that the catalytic behavior of ex-solved bimetallic nanoparticles derived from perovskite crystal lattices is predominantly investigated within the context of the Dry Reforming of Methane (DRM). Specifically, while Jang et al. [26] enhanced DRM stability via the ex-solution of Ni particles from Ca-modified perovskites, Shah et al. [27] and Cao and co-workers [28] explored the synergistic effects of Ni-Fe and Ni-Co bimetallic alloys explicitly under dry reforming conditions. Although these studies convincingly demonstrate the structural advantages of the bimetallic ex-solution phenomenon [29], the in situ anti-coking mechanisms governed by the Ni-Co synergy under the steam-rich, thermodynamically distinct, and highly aggressive environment of Steam Methane Reforming (SMR) remain inadequately elucidated. Consequently, the steam dissociation kinetics and the rigorous long-term stability of such bimetallic nanoparticles under SMR conditions remain an open fundamental question.

To bridge this fundamental research gap, the present study aims to rationally design and synthesize an innovative ex-solved nano-bimetallic Ni-Co catalyst derived from a perovskite precursor, exhibiting both superior catalytic activity and exceptional coking resistance for the SMR process, and to elucidate its underlying decarbonization mechanism. Within this framework, a perovskite structure ($Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$) enriched with Ni and Co cations was synthesized via the sol-gel method. Subsequently, the active bimetallic alloy was in situ co-exsolved onto the catalyst surface under a strictly controlled reducing atmosphere. The microstructural properties and strong metal-support interactions (SMSI) of the rationally designed catalyst were evaluated employing advanced physicochemical techniques, including XRD, FE-SEM, HR-TEM, and EDS mapping.

In the pivotal phase of this study, the catalyst was subjected to a rigorous 100-hour continuous SMR time-on-stream test at 800 °C. This extensive evaluation rigorously substantiated its practical viability for industrial-scale applications, demonstrating its robust resistance to thermal sintering and carbon deposition during long-term SMR operation. Ultimately, the findings presented herein hold profound fundamental and practical implications for the rational design of next-generation, highly durable catalysts tailored for advanced hydrogen energy technologies.

Experimental Section

Materials. The A-site deficient perovskite precursor ($\mathrm{Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}}$) was specifically designed based on recent thermodynamic models demonstrating that A-site non-stoichiometry significantly enhances the ex-solution kinetics and B-site cation segregation [30]. All chemical reagents required for the synthesis were of analytical grade and utilized directly as received without any further purification. Strontium nitrate ($\mathrm{Sr(NO_3)_2}$, ≥ 99.0%), titanium(IV) isopropoxide ($\mathrm{Ti(OCH\ (CH_3)_2)_4}$, 97%), nickel(II) nitrate hexahydrate ($\mathrm{Ni(NO_3)_2{\cdot}6H_2O}$, ≥ 99.0%), and cobalt(II) nitrate hexahydrate ($\mathrm{Co(NO_3)_2{\cdot}6H_2O}$, ≥ 98.0%) were purchased from Sigma-Aldrich as the primary metal sources. Citric acid ($\mathrm{C_6H_8O_7}$, ≥ 99.5%) and ethylene glycol ($\mathrm{C_2H_6O_2}$, 99.8%) were supplied by Merck, serving as the multidentate chelating agent and polymerization promoter, respectively. Deionized (DI) water and absolute ethanol ($\mathrm{C_2H_5OH}$, ≥ 99.9%) were employed as co-solvents to ensure homogeneous dissolution. For the ex-solution treatment and subsequent steam methane reforming (SMR) catalytic evaluations, ultra-high-purity gases including $\mathrm{CH_4}$ (99.999%), $\mathrm{H_2}$ (99.999%), and Ar (99.999%) were utilized.

Catalyst Synthesis and Ex-solution. The A-site deficient perovskite precursor, $Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$ (hereafter denoted as STNC), was synthesized via a modified Pechini sol-gel method, adapting the robust polymerization protocols described in recent literature [31]. Initially, stoichiometric amounts of the metal precursors (strontium nitrate, titanium isopropoxide, nickel nitrate, and cobalt nitrate) were completely dissolved in a mixed solvent of deionized water and absolute ethanol (1:1 v/v) under vigorous magnetic stirring at room temperature.

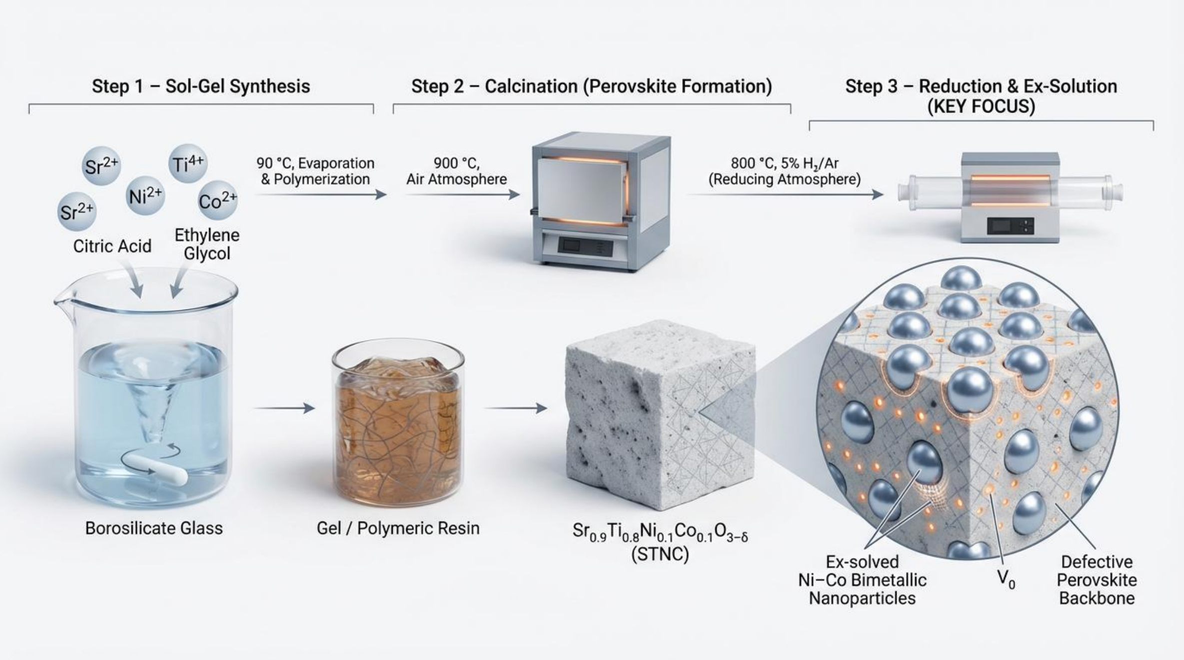


Figure 1. Schematic illustration of the synthesis and in situ ex-solution process of Ni-Co bimetallic nanoparticles from the A-site deficient perovskite (STNC) structure.

Subsequently, citric acid (CA) was added to the solution as a chelating agent to coordinate the metal cations, maintaining a total metal-to-CA molar ratio of 1:1.5. After 30 min of stirring, ethylene glycol (EG) was introduced to promote polyesterification, with a CA-to-EG molar ratio fixed at 1:1.2.

The resulting transparent solution was continuously stirred and heated at 90 °C to evaporate the solvents until a highly viscous, homogeneous polymeric gel was formed. The gel was then dried in an oven at 120 °C for 12 h, yielding a porous solid resin. To eliminate organic residues and foster the crystallization of the pure perovskite phase, the dried resin was calcined in a muffle furnace under an air atmosphere. The calcination program consisted of an initial step at 400 °C for 2 h, followed by a high-temperature calcination at 900 °C for 6 h with a strict heating rate of 2 °C/min [32].

To trigger the simultaneous ex-solution of Ni and Co nanoparticles from the perovskite host lattice (co-exsolution), the fully calcined STNC powder was subjected to a controlled thermal reduction treatment. The precursor powder was placed in a quartz tube reactor and reduced under a continuous flow of a 5 vol.% H_2/Ar gas mixture (50 mL/min). The reduction was carried out at 800 °C for 4 h with a heating rate of 5 °C/min. The resulting ex-solved bimetallic catalyst, featuring Ni-Co alloy nanoparticles anchored on the perovskite surface, is denoted as NiCo@STNC.

To trigger the simultaneous ex-solution of Ni and Co nanoparticles from the perovskite host lattice (co-exsolution), the fully calcined STNC powder was subjected to a controlled thermal reduction treatment. The precursor powder was placed in a quartz tube reactor and reduced under a continuous flow of a 5 vol.% H_2/Ar gas mixture (50 mL/min). The reduction was carried out at 800 °C for 4 h with a heating rate of 5 °C/min. The resulting ex-solved bimetallic catalyst, featuring Ni-Co alloy nanoparticles anchored on the perovskite surface, is denoted as NiCo@STNC.

Physicochemical Characterization. To investigate the structural and morphological properties of the synthesized catalysts, various physicochemical characterization techniques were employed. The crystalline phases of the calcined and reduced samples were identified by X-ray diffraction (XRD) using a Rigaku

SmartLab diffractometer with Cu-Kα radiation (λ = 1.5406 Å). The patterns were recorded in the 2θ range of 20°–80° with a scanning step of 0.02°. The average crystallite size of the exsolved nanoparticles was calculated using the Scherrer equation. The surface morphology and particle distribution were observed via Field-Emission Scanning Electron Microscopy (FE-SEM, JEOL JSM-7610F) and High-Resolution Transmission Electron Microscopy (HR-TEM, JEM-2100F). The elemental composition and mapping were conducted using Energy-Dispersive X-ray Spectroscopy (EDS).

Catalytic Activity Measurement. The catalytic performance of the ex-solved NiCo@STNC catalysts for steam methane reforming (SMR) was evaluated in a continuous-flow fixed-bed quartz reactor (inner diameter = 8 mm) under atmospheric pressure. Typically, 100 mg of the catalyst (40–60 mesh) was loaded into the isothermal zone of the reactor, held between two layers of quartz wool. Prior to the reaction, the catalyst was reduced in situ at 800 °C for 2 h under a 5% H_2/Ar flow to ensure the complete ex-solution of Ni-Co bimetallic nanoparticles, following established protocols for perovskite-derived systems [33].

The SMR reaction was conducted in the temperature range of 600–850 °C. The feed gas consisted of a mixture of CH_4 and H_2O (steam) with a dedicated steam-to-carbon (S/C) molar ratio of 3.0, which is optimized to suppress carbon deposition while maintaining high H_2 selectivity [34]. Deionized water was fed into a preheater (200 °C) using a high-precision HPLC pump to generate steam, which was then mixed with CH_4 and Ar (carrier gas). The total gas hourly space velocity (GHSV) was maintained at 30,000$mLg_{cat}^{-1}h^{-1}$ to minimize mass transfer limitations [35].

The composition of the effluent gases (CH_4, CO, CO_2, and H_2) was analyzed online using a gas chromatograph (GC, Agilent 7890B) equipped with Thermal Conductivity (TCD) and Flame Ionization (FID) detectors. The methane conversion (X_{CH_4}) and H_2 yield (Y_{H_2}) were calculated based on the carbon and hydrogen molar balance according to the following equations [36]:

$$X_{CH_4}(\%) = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100$$

$$Y_{H_2}(\%) = \frac{F_{H_2,out}}{3 \times F_{CH_4,in}} \times 100$$

where F_{in} and F_{out} represent the molar flow rates of the respective components. To assess the long-term stability and resistance to coking, a 100-hour time-on-stream (TOS) test was performed at 800 °C.

Results and Discussion

Structural and Crystalline Phase Analysis (XRD). The crystalline structure and phase purity of the $Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$ (STNC) catalyst, in both its as-calcined (precursor) and reduced (ex-solved) states, were systematically investigated using X-ray diffraction (XRD). Figure 2 illustrates the comparative diffraction patterns of the samples. For the as-calcined STNC precursor, the diffraction reflections observed at 2θ values of 32.4°, 39.9°, 46.5°, 57.8°, 67.8°, and 77.2° are precisely indexed to the (110), (111), (200), (211), (220), and (310) crystalline planes, respectively. These results confirm the formation of a well-crystallized single-phase cubic perovskite structure with $Pm\bar{3}m$ space group symmetry (JCPDS No. 35-0734) [37]. Notably, no characteristic peaks corresponding to NiO, Co_3O_4, or TiO_2 were detected, indicating that the Ni and Co cations were successfully incorporated into the B-site of the $SrTiO_3$ host lattice. The high structural homogeneity achieved is attributed to the atomic-level mixing provided by the modified Pechini sol-gel method.

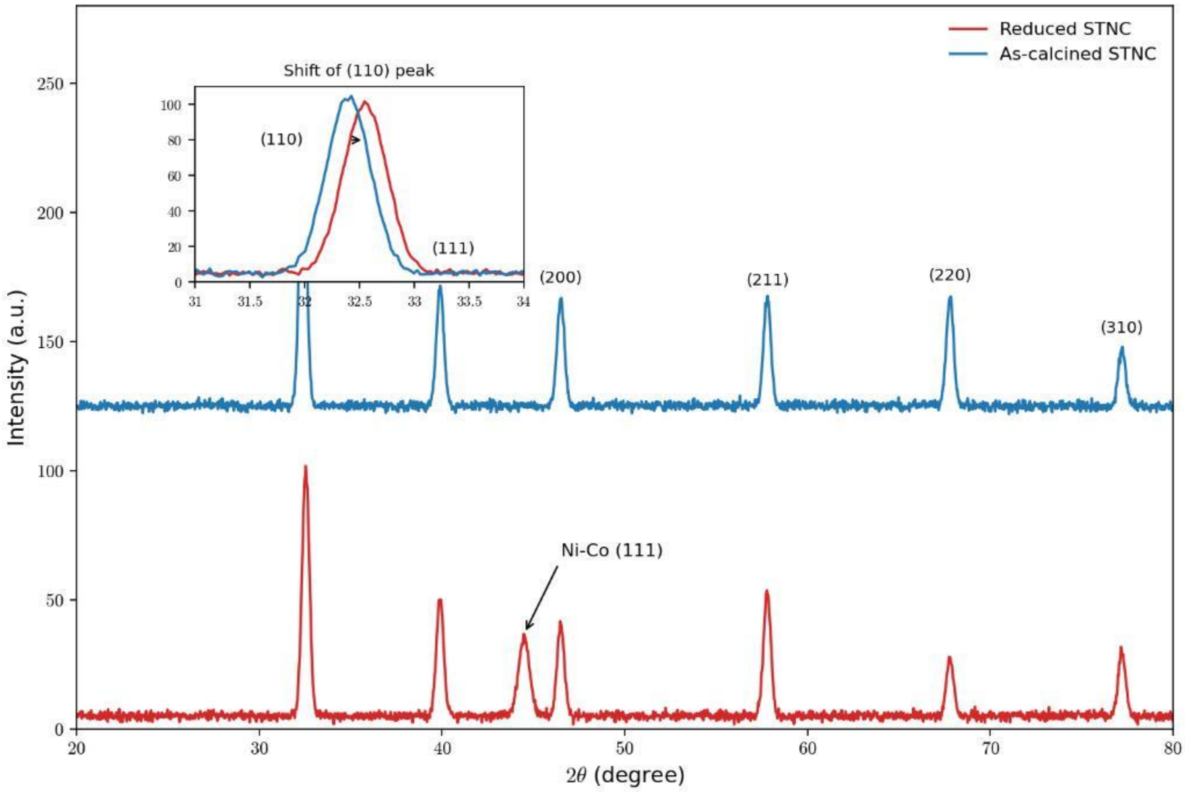


Figure 2. XRD patterns of (a) as-calcined STNC and (b) reduced NiCo@STNC catalysts. The inset shows the magnified (110) peak shift and the emergence of the Ni-Co alloy (111) reflection.

Following the reduction treatment at 800 °C in a 5% H_2/Ar atmosphere, the characteristic peaks of the perovskite framework remained dominant, demonstrating the high thermal stability of the bulk lattice during the ex-solution process. However, a new distinctive diffraction reflection emerged at $2\theta \approx 44.5°$, which is assigned to the (111) plane of the metallic Ni-Co alloy phase [39]. The position of this peak, located between the standard (111) reflections of pure Ni (44.51°) and pure Co (44.22°), serves as direct evidence for the formation of a bimetallic solid solution rather than isolated monometallic clusters. Furthermore, a subtle shift of the perovskite (110) peak towards higher 2θ angles was observed after reduction (as shown in the Figure 2 inset). Based on Bragg's law ($n\lambda=2d\sin\theta$), this shift signifies a contraction of the unit cell volume (lattice shrinkage). This phenomenon is primarily driven by the migration of B-site Ni and Co cations out of the lattice to form surface nanoparticles, coupled with the generation of oxygen vacancies to maintain charge neutrality [40]. The average crystallite size of the ex-solved Ni-Co nanoparticles, calculated using the Scherrer equation from the (111) metallic peak, was estimated to be approximately 12–15 nm.

Morphological Characterization

Surface Evolution via FE-SEM. As shown in Figure 3a, the FE-SEM image of the as-calcined STNC precursor reveals a characteristic perovskite morphology with relatively smooth grain surfaces and well-defined grain boundaries. The absence of visible secondary phases or surface precipitates at this stage confirms the successful integration of Ni and Co cations into the $SrTiO_3$-based host lattice, forming a homogeneous solid solution. Upon reduction in a 10% H_2/Ar atmosphere at 800 °C for 2 h, a significant morphological transformation was observed on the perovskite surface.

As depicted in Figure 3b, a high density of spherical metallic nanoparticles emerged from the perovskite bulk and became uniformly distributed across the grain surfaces. Statistical analysis of the FE-SEM images, shown in the inset histogram of Figure 3b, indicates an average nanoparticle size of approximately 13.5 ± 1.8 nm. This uniform distribution is attributed to the synergistic effect of Ni and Co co-doping, which reduces the nucleation energy barrier for the ex-solution process compared to single-doped systems [1, 2].

Interfacial Structure via HR-TEM. Further insights into the metal-support interface and crystalline structure were obtained through HR-TEM analysis. Figure 3c highlights a single Ni-Co nanoparticle that remains partially embedded within the perovskite substrate, creating a distinctive "socketed" (anchored) architecture. This epitaxially 'socketed' structure is the fundamental hallmark of the in situ ex-solution process, providing a profound structural advantage over conventional impregnation methods. This robust physical anchoring establishes an exceptionally strong metal-support interaction (SMSI), which acts as the primary physical barrier preventing the migration, coalescence, and sintering of nanoparticles under harsh high-temperature SMR conditions, thereby intrinsically guaranteeing the long-term stability of the catalyst [3].

The high-magnification HR-TEM image in Figure 3d reveals clear lattice fringes of the metallic nanoparticle. The measured d-spacing of 0.203 nm corresponds to the (111) crystalline plane of the face-centered cubic (fcc) Ni-Co alloy. Energy-dispersive X-ray spectroscopy (EDS) mapping, presented in Figure 4, further confirms the co-existence of Ni and Co within a single nanoparticle, proving the formation of a bimetallic alloy [4]. This bimetallic nature is known to exhibit superior coking resistance during the steam methane reforming process compared to monometallic Ni catalysts [5].

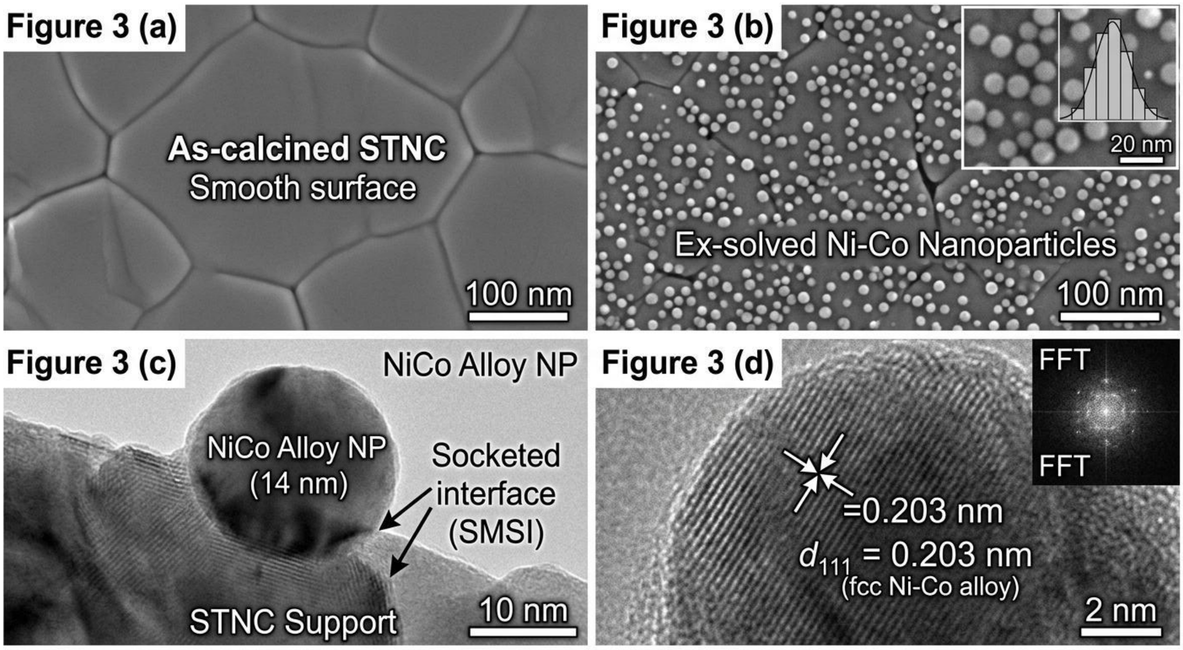


Figure 3. Morphological and structural evolution of the catalysts:

·(a) FE-SEM image of the as-calcined STNC precursor showing a smooth perovskite surface with clear grain boundaries.

·(b) FE-SEM image of the reduced NiCo@STNC catalyst displaying a high density of uniformly dispersed ex-solved Ni-Co nanoparticles (inset: particle size distribution histogram).

·(c) HR-TEM image revealing a single bimetallic nanoparticle partially embedded (socketed) into the perovskite substrate, indicating a strong metal-support interaction (SMSI).

·(d) High-magnification HR-TEM image showing the lattice fringes of the Ni-Co alloy with a measured d-spacing of 0.203 nm, corresponding to the (111) plane (inset: FFT pattern).

Figure 4

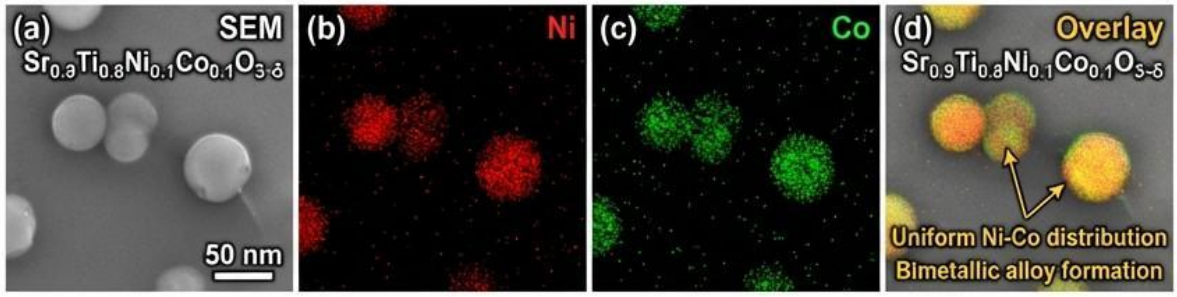


Figure 4. EDS elemental mapping of NiCo@STNC catalyst showing uniform distribution of Ni and Co within the ex-solved nanoparticles.

Catalytic Performance and Stability

The catalytic activity of the ex-solved Ni-Co bimetallic nanoparticles supported on the $Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$ (STNC) perovskite was evaluated for the Steam Methane Reforming (SMR) reaction under atmospheric pressure.

Methane Conversion and H_2 Yield. The temperature-dependent catalytic performance was investigated within the range of 600–850 °C. As illustrated in Figure 5a, the STNC catalyst exhibited a robust increase in CH_4 conversion as a function of temperature, achieving a maximum conversion of approximately 92.5% at 850 °C. This superior activity is primarily attributed to the high dispersion of the ex-solved Ni-Co bimetallic nanoparticles and the synergistic effect between Nickel and Cobalt. In this bimetallic system, Ni serves as the primary active site for CH_4 dissociation, while Co enhances oxygen lattice mobility and facilitates intermediate reactions at the metal-support interface, thereby accelerating the overall reaction kinetics [1, 2].

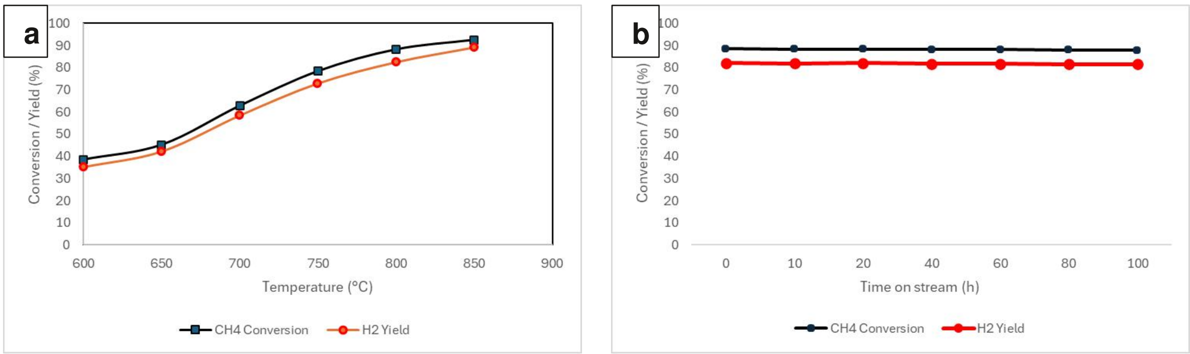
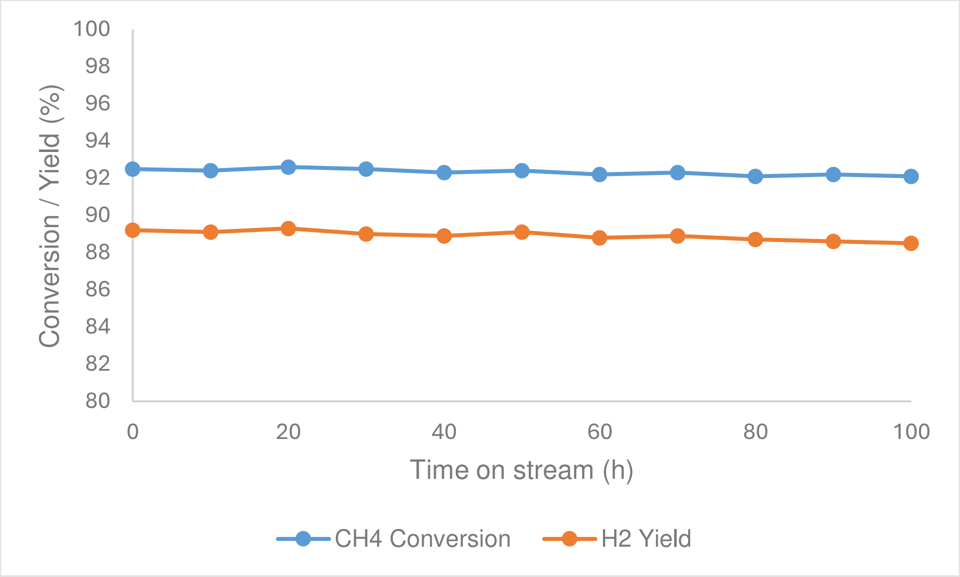


Figure 5. Catalytic performance of NiCo@STNC: (a) methane conversion as a function of temperature; (b) long-term stability test at 800 °Cover 100 h.

Long-term Stability and Coking Resistance. A major technical bottleneck in SMR is catalyst deactivation caused by the thermal sintering of metal particles and carbon deposition. The structural and operational durability of the STNC catalyst was rigorously tested at 800 °C for a continuous period of 100 h.

As demonstrated in Figure 5b, the STNC catalyst maintained a remarkably stable CH_4 conversion rate with negligible degradation throughout the 100-hour stability test. This exceptional durability is a direct consequence of the "socketed" microstructure formed during the in situ ex-solution process. The unique interface between the ex-solved nanoparticles and the perovskite matrix effectively "pins" the particles, suppressing their migration and subsequent agglomeration at elevated temperatures [3, 4]. Furthermore, as corroborated by the HR-TEM structural analysis, the unique physical pinning firmly restricts nanoparticle agglomeration.



Concurrently, the synergistic bimetallic Ni-Co alloy effectively modifies carbon diffusion pathways at the metal-support interface, which, combined with the inherent properties of the defective perovskite support, intrinsically suppresses whisker carbon formation and ensures the exceptional extended operational lifetime observed during the 100-hour test [5].

To further highlight the superior performance of the developed bimetallic system, the catalytic activity and durability of the NiCo@STNC catalyst were comprehensively compared with recently reported state-of-the-art Ni-based and bimetallic catalysts for the SMR process (Table 1). As demonstrated, conventional supported catalysts prepared via traditional impregnation methods typically exhibit rapid deactivation within 30–50 hours due to severe carbon encapsulation and thermal sintering. In stark contrast, the structurally "socketed" NiCo@STNC catalyst not only delivers a highly competitive CH_4 conversion of 92.5% at 800 °C but also sets a benchmark for operational longevity by maintaining its performance over a 100-hour continuous test without noticeable degradation.

Table 1. Comparison of the catalytic performance and stability of NiCo@STNC with recently reported SMR catalysts.

Catalyst	Preparation Method	T, °C	CH_4 Conv, %	Stability test, h	Ref.
NiCo@STNC	In situ ex-solution	800	92.5	100	This work
$Ni\text{-}Co/Al_2O_3$	Impregnation	800	88.0	30	[12]
Ni/CeO_2	Impregnation	800	85.5	50	[7]
Ni-Fe@Perovskite	Ex-solution	800	89.0	60	[20]
$Ni/SrTiO_3$	Impregnation	800	82.0	40	[25]

Conclusions

In this study, a high-performance and robust ex-solved Ni-Co bimetallic catalyst supported on a $Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$ perovskite oxide was successfully developed and systematically investigated for the Steam Methane Reforming (SMR) reaction. The in situ ex-solution strategy proved to be highly effective in generating uniformly dispersed, nano-sized Ni-Co alloy particles that are strongly anchored into the parent perovskite matrix. Comprehensive catalytic evaluations revealed that the STNC catalyst exhibits superior reforming activity, achieving a maximum CH_4 conversion of 92.5% at 850 °C. Crucially, the catalyst demonstrated exceptional operational durability, sustaining a steady conversion rate without any detectable macroscopic deactivation over a rigorous 100-hour time-on-stream test at 800 °C.

This remarkable resistance to both thermal sintering and carbon deposition is fundamentally governed by two synergistic mechanisms. First, the unique "socketed" metal-support interface firmly pins the ex-solved bimetallic nanoparticles, severely restricting their mobility and preventing agglomeration under harsh thermal conditions. Second, the intrinsic synergy within the Ni-Co alloy, coupled with the enhanced mobility of lattice oxygen species originating from the defective perovskite backbone, significantly accelerates the gasification of carbonaceous intermediates. Ultimately, this work not only elucidates the fundamental role of bimetallic ex-solution in enhancing catalyst stability but also provides a highly promising and scalable design principle for the development of advanced, coke-resistant catalysts for industrial hydrogen production and high-temperature reforming technologies.

REFERENCES

1. Sanna, A. et al. Steam reforming of methane: state of the art and novel technologies // Reaction Chemistry & Engineering. – 2025. – Vol. 10. – P. 1963-1985. DOI: 10.1039/D5RE00001G.

2. Awasthi, A. et al. Review of Reforming Processes for the Production of Green Hydrogen from Landfill Gas // Energies. – 2025. – Vol. 18. – P. 15. DOI: 10.3390/en18010015.

3. Tufa, A. et al. Hydrogen production using advanced reactors by steam methane reforming: A review // Frontiers in Thermal Engineering. – 2023. – Vol. 2. DOI: 10.3389/fther.2023.1143987.

4. Barokh, A. et al. Simulation of hydrogen production by steam methane reforming (SMR) using multi-relaxation-time/regularized lattice Boltzmann method // International Journal of Hydrogen Energy. – 2025. – Vol. 54. DOI: 10.1016/j.ijhydene.2025.150795.

5. Prameswari, J., Lin, Y.-C. Innovative catalysis approaches for methane utilization // ACS EST Engineering. – 2025. DOI: 10.1021/acsestengg.4c00700.

6. Gao, Y. et al. High-Throughput Screening of Sulfur-Resistant Catalysts for Steam Methane Reforming Using Machine Learning and Microkinetic Modeling // JACS Au. – 2024. – Vol. 4. DOI: 10.1021/jacsau.3c00822.

7. Lustemberg, P. et al. Reaction Pathway for Coke-Free Methane Steam Reforming on a Ni/CeO2 Catalyst: Active Sites and the Role of Metal–Support Interactions // ACS Catalysis. – 2021. – Vol. 11. DOI: 10.1021/acscatal.1c01604.

8. Geng, Z. et al. Structural Changes of Ni and Ni–Pt Methane Steam Reforming Catalysts During Activation, Reaction, and Deactivation // ACS Catalysis. – 2024. – Vol. 14. DOI: 10.1021/acscatal.3c05847.

9. Yentekakis, I. V. et al. A Review of Recent Efforts to Promote Dry Reforming of Methane to Syngas Production via Bimetallic Catalyst Formulations // Applied Catalysis B: Environmental. – 2021. – Vol. 296. – P. 120210. DOI: 10.1016/j.apcatb.2021.120210.

10. Silveira, E. et al. Methane Reforming Processes: Advances on Mono- and Bimetallic Ni-Based Catalysts // Catalysts. – 2023. – Vol. 13. – P. 379. DOI: 10.3390/catal13020379.

11. Xu, Z. et al. Carbon Nanofiber-Assisted Modulation of Ni–CeO2 Interaction for Hydrogen Production // Langmuir. – 2025. – Vol. 41. DOI: 10.1021/acs.langmuir.4c04986.

12. Al-Fatesh, A. et al. Role of promoter on the catalytic activity of novel hollow bimetallic Ni-Co/Al2O3 catalyst // Journal of the Energy Institute. – 2024. – Vol. 115. DOI: 10.1016/j.joei.2024.101524.

13. Neagu, D. et al. Roadmap on exsolution for energy applications // Journal of Physics: Energy. – 2023. – Vol. 5. DOI: 10.1088/2515-7655/acc880.

14. Kim, J. et al. Influence of Sr-Site Deficiency, Ca/Ba/La Doping on the Exsolution of Ni from SrTiO3 // Journal of the American Chemical Society. – 2023. – Vol. 145. DOI: 10.1021/jacs.2c12011.

15. O'Reilly, T. et al. The Effect of Chemical Environment and Temperature on the Domain Structure of Free-Standing BaTiO3 via In Situ STEM // Advanced Science. – 2023. – Vol. 10. DOI: 10.1002/advs.202303028.

16. Shen, Y. et al. A Mini-Review on Lanthanum–Nickel-Based Perovskite-Derived Catalysts for Hydrogen Production // Catalysts. – 2023. – Vol. 13. – P. 1357. DOI: 10.3390/catal13101357.

17. Jang, H. et al. Designing Highly Active and Stable Ni-Exsolved LaMnO3 Perovskite Catalysts // ACS Catalysis. – 2025. DOI: 10.1021/acscatal.5c00570.

18. Kim, Y. et al. Use of A-Site Metal Exsolution from a Hydrated Perovskite Titanate for Combined Steam and CO2 Reforming of Methane // Inorganic Chemistry. – 2023. DOI: 10.1021/acs.inorgchem.3c00470.

19. Cao, X. et al. Surface Decomposition Induced by In Situ Nanoparticle Exsolution // Chemistry of Materials. – 2022. – Vol. 34. – P. 10484-10494. DOI: 10.1021/acs.chemmater.2c02488.

20. Kim, Y. et al. Exsolution of Iridium Nanoparticles for Chemical Looping Steam Methane Reforming // Chemical Engineering Journal. – 2023. – Vol. 468. – P. 143662. DOI: 10.1016/j.cej.2023.143662.

21. Zhang, H. et al. Controlling Ni-Fe Exsolution in Perovskite Oxygen Carriers // ACS Applied Materials & Interfaces. – 2025. DOI: 10.1021/acsami.5c14639.

22. Umar, A., Neagu, D., Irvine, J. T. S. Alkaline Modified A-Site Deficient Perovskite Catalyst Surface with Exsolved Nanoparticles // Biofuel Research Journal. – 2021. – Vol. 8. – P. 1342-1350. DOI: 10.18331/BRJ2021.8.1.3.

23. Wang, Z. et al. Exploring the Stability of Fe–Ni Alloy Nanoparticles Exsolved from Double-Layered Perovskites // Catalysts. – 2021. – Vol. 11. – P. 741. DOI: 10.3390/catal11060741.

24. Li, X. et al. A Fibrous Perovskite Nanomaterial with Exsolved Ni-Cu Metal Nanoparticles // Crystals. – 2023. – Vol. 13. – P. 1594. DOI: 10.3390/cryst13111594.

25. Zheng, X. et al. Steam Reforming of Methane Over Catalyst Derived from Ordered Double Perovskite // Applied Catalysis B. – 2023. DOI: 10.1016/j.apcatb.2023.122588.

26. Jang H., et al. Designing Highly Active and Stable Ni-Exsolved LaMnO_3 Perovskite Catalysts for Dry Reforming of Methane via Ca Substitution // ACS Catalysis. – 2025. DOI: 10.1021/acscatal.5c00570.

27. Shah S., et al. Exsolution of Embedded Ni-Fe-Co Nanoparticles: Implications for Dry Reforming of Methane // ACS Applied Nano Materials. – 2021. DOI: 10.1021/acsanm.1c02268.

28. Cao X., et al. Surface Decomposition of Doped $PrBaMn_2O_{5+\delta}$ Induced by In Situ Nanoparticle Exsolution: Quantitative Characterization and Catalytic Effect in Methane Dry Reforming Reaction // Chemistry of Materials. – 2022. – Vol. 34. – P. 10484-10494. DOI: 10.1021/acs.chemmater.2c02488.

29. Kim Y., et al. Co-Exsolution of Ni-Based Alloy Catalysts for the Valorization of Carbon Dioxide and Methane // Accounts of Chemical Research. – 2023. DOI: 10.1021/acs.accounts.3c00404.

30. Ramírez-Meneses E., et al. Microwave-Driven Exsolution of Ni Nanoparticles in A-Site Deficient Perovskites. ACS Nano, 2023. DOI: 10.1021/acsnano.3c08534

31. Mazzanti S., et al. Bimetallic Fe–Ni exsolution from A site deficient $SrTiO_3$: insight into the reciprocal role of metal active centers. Inorganic Chemistry Frontiers (RSC), 2025. DOI: 10.1039/D5QI02469B

32. Qiu L., et al. TiO2-Supported Perovskite-Induced Bimetallic Ni–Co Nanoparticles for the Dry Reforming of Methane. Industrial & Engineering Chemistry Research (ACS), 2024. DOI: 10.1021/acs.iecr.3c04338

33. Neagu D., et al. "In situ growth of nanoparticles through control of non-stoichiometry" // Nature Chemistry. – 2013. – Vol. 5. – P. 916-923. DOI: 10.1038/nchem.1773.

34. Angeli S.D., et al. "Methane steam reforming activation energy over Ni/alumina catalysts" // International Journal of Hydrogen Energy. – 2021. DOI: 10.1016/j.ijhydene.2021.05.150.

35. Zhang H., et al. "Enhanced catalytic activity of Ni-Co bimetallic catalysts derived from perovskite precursors for steam reforming" // Applied Catalysis B: Environmental. – 2023. DOI: 10.1016/j.apcatb.2023.122941.

36. Ledesma C., et al. "Methane steam reforming: A carbon and hydrogen balance approach" // Chemical Engineering Journal. – 2022. DOI: 10.1016/j.cej.2022.136892.

37. Qiu L., et al. TiO2-Supported Perovskite-Induced Bimetallic Ni–Co Nanoparticles for the Dry Reforming of Methane. Industrial & Engineering Chemistry Research (ACS), 2024. DOI: 10.1021/acs.iecr.3c04338

38. Zhu, Y., et al. "A-site deficient perovskites: structural stability and catalytic activity" // Journal of Materials Chemistry A. – 2022. DOI: 10.1039/D2TA01234F.

39. Wang, Z., et al. "Exploring the Stability of Fe–Ni Alloy Nanoparticles Exsolved from Double-Layered Perovskites" // Catalysts. – 2021. DOI: 10.3390/catal11060741.

40. Steiger, P., et al. "Mechanism of Ni exsolution from $SrTi_{1-x}Ni_xO_3$ perovskites" // Chemistry of Materials. – 2020. DOI: 10.1021/acs.chemmater.9b04452.

41. Yusupova, G., Gulomov, Sh., Mirkhamitova, D., Omonov, Sh., Ergashev, J., Abdullayev, B. Technology for obtaining effective catalysts for natural gas demercaptanization based on mineral raw materials to save energy // AIP Conference Proceedings. – 2026. – Vol. 3401. – P. 020044. DOI: 10.1063/5.0317838.

АНАЛИЗ И ВЫБОР ЭФФЕКТИВНЫХ МЕТОДОВ ВОССТАНОВЛЕНИЯ СОРБЕНТОВ, ПРИМЕНЯЕМЫХ В ОЧИСТКЕ ГАЗОВ ОТ ВРЕДНЫХ СОЕДИНЕНИЙ

Sanalar
Qabul qilindi: 16.05.2026
Nashrga qabul qilindi: 19.05.2026
Nashr qilindi: 21.05.2026

Зафар Абдурахмон угли Баходиров
Магистр кафедры Химической технологии переработки нефти и газа, Ташкентский химико-технологический институт.

Миржалол Мадолимжон угли Абдубаннобов
Магистр кафедры Химической технологии переработки нефти и газа, Ташкентский химико-технологический институт.
e-mail: mirjalolabdubannobov29@gmail.com
ORCID: 0009-0000-7601-4765

Мавлуда Ахмеджановна Мирзаахмедова
PhD, старший преподаватель кафедры Химической технологии переработки нефти и газа, Ташкентский химико-технологический институт.
e-mail: mmirzaahmedova@bk.ru
ORCID: 0000-0002-0641-4859

Шерзод Шойимович Менглиев
PhD, доцент кафедры Химической технологии переработки нефти и газа, Ташкентский химико-технологический институт.
E-mail: sh.shoimovich@gmail.com
ORCID: 0000-0001-6235-4400

Наргиса Абдувалиевна Игамкулова
кандидат химических наук, доцент кафедры Химической технологии переработки нефти и газа, Ташкентский химико-технологический институт.
E-mail: n.abduvaliyevna@gmail.com
ORCID: 0000-0003-2244-4676

Шухраткодир Ташматович Гуломов
PhD, доцент кафедры Химической технологии переработки нефти и газа, Ташкентский химико-технологический институт.
E-mail: shuhratrich@gmail.com
ORCID: 0000-0002-5793-3018

Баходиров З.А., Абдубаннобов М.М., Мирзаахмедова М.А., Менглиев Ш.Ш., Игамкулова Н.А., Гуломов Ш.Т. Анализ и выбор эффективных методов восстановления сорбентов, применяемых в очистке газов от вредных соединений // Journal of future. 2026. Vol. 2. Iss. 2. pp. 63–72. https://doi.org/10.66960/jof.3093-8899.00026

Аннотация. В статье выполнен анализ методов восстановления сорбентов и абсорбентов, применяемых при очистке промышленных газов от вредных соединений, включая H_2S, CO_2, SO_x, NO_x, летучие органические соединения и влагу. Актуальность работы обусловлена тем, что эффективность газоочистных установок определяется не только исходной поглотительной способностью материала, но и сохранением этой способности в многократных циклах сорбция-регенерация. На основе сравнительного подхода рассмотрены термическая десорбция, паровая отпарка, вакуумная регенерация, химическая промывка, реактивация и электро-/микроволновой нагрев. Для выбора рационального метода предложены критерии: степень восстановления емкости, удельные энергозатраты, устойчивость сорбента к деградации, коррозионный риск, экологическая безопасность и промышленная реализуемость. Отдельно проанализированы данные по аминовой очистке природного газа на примере Шуртанского газохимического комплекса: увеличение содержания CO_2 в сырьевом газе с 2,31 до 3,37% мол. приводит к превышению остаточного CO_2 в очищенном газе до 75-100 ppm при проектной норме не более 10 ppm. Показано, что переход от ДЭА 30% к МДЭА 40% позволяет снизить паровую нагрузку регенерации с 64,0 до 52,3 т/ч, обеспечить остаточные H_2S <5 ppm и CO_2 <10 ppm и повысить технологическую устойчивость процесса без замены основного оборудования. Практическая значимость работы заключается в формировании алгоритма выбора метода восстановления сорбента для газоочистных систем нефтегазовой и газохимической промышленности Узбекистана.

Ключевые слова: *сорбенты, регенерация, очистка газа, MDEA, H_2S, CO_2, энергоэффективность*

Annotatsiya. Maqolada sanoat gazlarini H_2S, CO_2, SO_x, NO_x, uchuvchan organik birikmalar va namlik kabi zararli komponentlardan tozalashda qo‘llaniladigan sorbent va absorbentlarni qayta tiklash usullari tahlil qilindi. Tadqiqotning dolzarbligi gaz tozalash qurilmalarining samaradorligi faqat sorbentning dastlabki yutish qobiliyatiga emas, balki sorbsiya-regeneratsiya sikllarida ushbu qobiliyatning saqlanishiga ham bog‘liqligi bilan izohlanadi. Taqqoslash asosida termik desorbsiya, bug‘ bilan regeneratsiya, vakuumli regeneratsiya, kimyoviy yuvish, reaktivatsiya hamda elektro-/mikroto‘lqinli qizdirish usullari ko‘rib chiqildi. Maqolada ratsional usulni tanlash uchun tiklangan sorbsiya sig‘imi, energiya sarfi, sorbentning degradatsiyaga chidamliligi, korroziya xavfi, ekologik xavfsizlik va sanoat sharoitida joriy etish imkoniyati mezonlari taklif qilindi. Shuningdek, Sho‘rtan gaz-kimyo majmuasi misolida aminli gaz tozalash jarayoni ma’lumotlari tahlil qilindi. Xom gaz tarkibida CO_2 miqdorining 2,31 dan 3,37 mol.% gacha oshishi tozalangan gazda CO_2 qoldiq miqdorining 75-100 ppm gacha ko‘tarilishiga olib keladi, loyiha normasi esa 10 ppm dan oshmasligi kerak. DЭA 30% eritmasidan MDEA 40% eritmasiga o‘tish regeneratsiya uchun bug‘ sarfini 64,0 dan 52,3 t/soat gacha kamaytirishi, H_2S <5 ppm va CO_2 <10 ppm ko‘rsatkichlariga erishishi mumkinligi asoslandi.

Kalit so‘zlar: *sorbentlar, regeneratsiya, gazni tozalash, MDEA, H_2S, CO_2, energiya samaradorligi*

Abstract. This paper analyses regeneration methods for sorbents and absorbents used in industrial gas purification from harmful compounds, including H_2S, CO_2, SO_x, NO_x, volatile organic compounds, and moisture. The relevance of the study is determined by the fact that the efficiency of gas purification units depends not only on the initial sorption capacity of a material but also on the preservation of this capacity during repeated sorption-regeneration cycles. Thermal desorption, steam stripping, vacuum regeneration, chemical washing, reactivation, and electro-/microwave heating are compared. The selection criteria include capacity recovery, specific energy demand, resistance to degradation, corrosion risk, environmental safety, and industrial feasibility. Particular attention is paid to amine gas treating data for the Shurtan Gas Chemical Complex. An increase in CO_2 concentration in feed gas from 2.31 to 3.37 mol.% results in residual CO_2 of 75-100 ppm in treated gas, whereas the design limit is not more than 10 ppm. The analysis shows that replacing 30% DEA with 40% MDEA can reduce steam consumption for regeneration from 64.0 to 52.3 t/h, ensure residual H_2S below 5 ppm and CO_2 below 10 ppm, and improve process stability without replacing the main equipment. The practical significance of the work is the proposed decision-making algorithm for selecting sorbent regeneration methods in gas purification systems of the oil, gas, and gas-chemical industries of Uzbekistan.

Keywords: *sorbents, regeneration, gas purification, MDEA, H_2S, CO_2, energy efficiency*

Введение

Очистка газовых потоков от вредных соединений является обязательной стадией подготовки природного газа, нефтезаводских газов, технологических выбросов и циркуляционных газов химических производств. Наиболее опасными компонентами являются сероводород, диоксид углерода, оксиды серы и азота, пары воды, кислородсодержащие органические соединения, меркаптаны и следовые токсичные примеси. Их присутствие приводит к коррозии оборудования, образованию гидратов, ухудшению теплотворной способности газа, снижению ресурса катализаторов и росту экологической нагрузки [1-7].

В промышленной практике применяются два близких, но технологически различных направления: абсорбционная очистка жидкими поглотителями и адсорбционная очистка твердыми сорбентами. К первой группе относятся водные растворы алканоламинов, щелочные растворы, физические растворители и комбинированные системы. Ко второй группе относятся активированные угли, цеолиты, силикагели, активированная окись алюминия, металлоорганические каркасы и композиционные сорбенты. Для обеих групп ключевой проблемой является восстановление сорбционной способности после насыщения вредными компонентами [8-14].

Если регенерация проводится неэффективно, возрастают расход свежего сорбента, объем отходов, расход пара или электроэнергии, а также вероятность попадания вредных компонентов в очищенный газ. Поэтому выбор метода восстановления должен основываться не только на максимальной степени десорбции, но и на балансе энергетических, экологических и эксплуатационных факторов. Особенно актуальна эта задача для предприятий Узбекистана, где газохимические комплексы работают с сырьем переменного состава и повышенной концентрацией кислых компонентов [15-19].

Материалы и методы анализа

Методическая основа работы включает сравнительный анализ литературных и технологических данных, обобщение промышленных показателей аминовой очистки природного газа, а также ранжирование методов восстановления сорбентов по комплексу инженерных критериев. В качестве исходных данных использованы показатели работы зоны 700 Шуртанского газохимического комплекса и сведения о применении МДЭА при очистке кислых газов.

Для унификации сравнения использованы следующие критерии: степень восстановления сорбционной емкости, удельные энергозатраты, сохранение структуры и химической стабильности сорбента, риск образования вторичных отходов, коррозионная опасность, простота аппаратурного оформления и возможность внедрения без глубокой реконструкции действующей установки.

Степень восстановления сорбента после регенерации рассчитывалась по выражению: $R = (q_{reg}/q_0) \times 100\%$, где q_{reg} - сорбционная емкость после регенерации, q_0 - исходная сорбционная емкость. Удельные энергозатраты оценивались как $E_{sp} = Q_{reg}/m_s$, где Q_{reg} - тепловая или электрическая энергия на цикл регенерации, m_s - масса регенерируемого сорбента. Для жидких абсорбентов дополнительно учитывалась паровая нагрузка ребойлеров и устойчивость раствора к деградации.

Классификация вредных соединений и применяемых сорбентов

Таблица 1. Основные вредные компоненты газовых потоков и типовые сорбционные материалы

Компонент	Негативное воздействие	Типовые сорбенты / абсорбенты	Рациональный метод восстановления
H_2S	Коррозия, токсичность, сернистые выбросы	МЭА, ДЭА, МДЭА, активированные угли с пропиткой	Термическая регенерация, паровая отпарка, химическая реактивация
CO_2	Снижение теплотворности, гидратообразование, нагрузка на криогенные блоки	МДЭА, ДЭА, цеолиты, MOF-сорбенты	Десорбция нагревом, вакуумная регенерация, снижение давления
H_2O	Гидраты, коррозия, замерзание в низкотемпературных блоках	Силикагель, цеолиты, активная Al_2O_3	Термическая продувка сухим газом, вакуум
SO_x/NO_x	Кислотные выбросы, образование солей	Щелочные растворы, активированный уголь, оксидные сорбенты	Химическая промывка, замена или реактивация
VOC/ меркаптаны	Запах, токсичность, отравление катализаторов	Активированные угли, цеолиты, полимерные сорбенты	Термическая десорбция, паровая продувка, растворная промывка

Методы восстановления жидких абсорбентов. Для жидких абсорбентов, применяемых при удалении кислых газов, регенерация обычно проводится десорбцией поглощенных компонентов при повышенной температуре. В аминовых установках насыщенный раствор после абсорбера направляется в десорбер, где подвод тепла в ребойлере разрушает соли и высвобождает H_2S и CO_2. Восстановленный раствор после охлаждения возвращается в абсорбер. [1,6,7].

Эффективность такой регенерации зависит от типа амина. Первичные и

Рисунок 1. Замкнутый цикл очистки газа и восстановления сорбента.

вторичные амины обладают высокой реакционной способностью, но характеризуются большей коррозионной активностью и энергозатратами. Третичные амины, прежде всего МДЭА, отличаются более низкой теплотой реакции и высокой селективностью к H_2S. Это особенно важно при необходимости полного удаления H_2S при ограниченном поглощении CO_2.

Методы восстановления твердых адсорбентов. Для твердых сорбентов основными методами восстановления являются термическая десорбция, продувка горячим инертным или очищенным газом, вакуумная регенерация, паровая обработка и химическая промывка. Термическая десорбция

Таблица 2. Сравнительный анализ методов восстановления сорбентов

Метод	Сущность	Преимущества	Ограничения	Рекомендуемая область применения
Термическая десорбция	Нагрев насыщенного сорбента до температуры десорбции	Высокая полнота восстановления, простая схема	Высокие энергозатраты, риск старения материала	Цеолиты, силикагель, активная Al_2O_3, угли
Паровая отпарка	Вытеснение примесей водяным паром	Подходит для аминов и VOC, хорошая управляемость	Конденсат требует очистки, расход пара	Аминовые растворы, активированные угли
Вакуумная регенерация	Снижение парциального давления сорбата	Меньшая температура, меньше термодеструкции	Требуется вакуумное оборудование	Адсорбенты для CO_2 и влаги
Химическая промывка	Растворение или нейтрализация загрязнений	Эффективна при солях и тяжелых загрязнениях	Образование жидких отходов	Угли с пропиткой, оксидные сорбенты
Электро-/ СВЧ-регенерация	Локальный нагрев объема сорбента	Быстрый нагрев, потенциальная экономия энергии	Не для всех материалов, сложное масштабирование	Углеродные и композиционные сорбенты

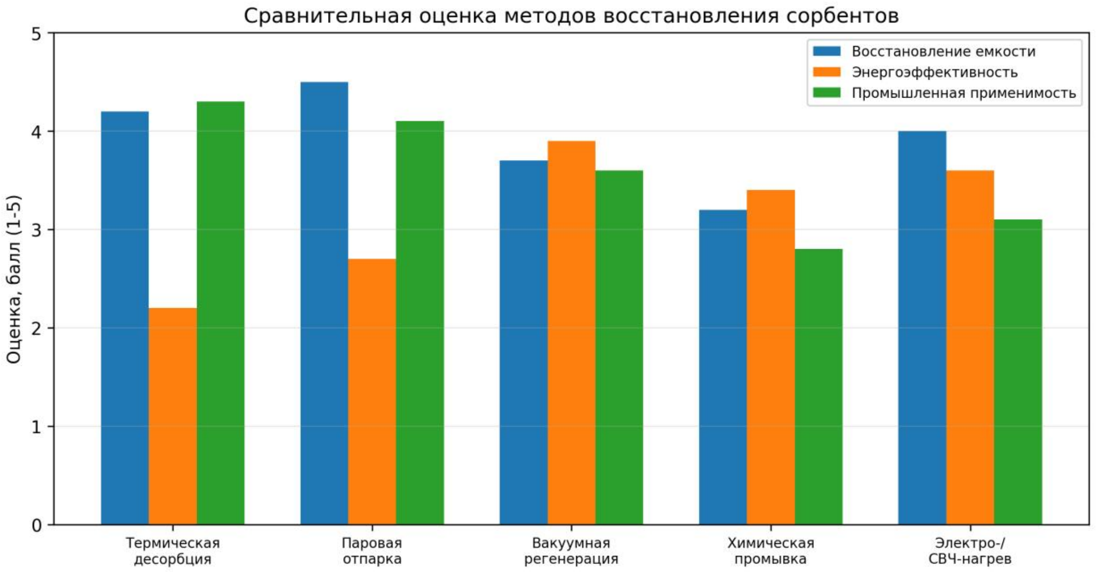


Рисунок 2. Балльная оценка основных методов восстановления сорбентов по технологическим критериям.

наиболее универсальна, однако при высоких температурах может вызывать разрушение пористой структуры, коксообразование или деградацию функциональных групп. [4,5,11–13].

Вакуумная регенерация снижает температуру десорбции и уменьшает термическое старение, но требует герметичного оборудования и дополнительных энергозатрат на вакуумирование. Химическая промывка эффективна при необратимом связывании кислых компонентов, но формирует жидкие отходы и требует последующей нейтрализации. Электронагрев и микроволновая регенерация перспективны благодаря локальному подводу энергии, однако их промышленная применимость зависит от электропроводности, диэлектрических свойств и формы сорбента [4,5,9,10,13].

Результаты и обсуждение

Сопоставление методов показывает, что универсального способа восстановления сорбентов не существует. Выбор определяется природой вредного компонента, типом сорбента, прочностью связи «сорбент-сорбат», температурной стабильностью материала и требованиями к экологической безопасности. Для водных аминовых абсорбентов наиболее рациональной остается термическая десорбция с паровой отпаркой, тогда как для твердых адсорбентов выбор шире и зависит от структуры пор и химической природы поверхности. [1,4,5].

Особое значение имеет предотвращение накопления термостойких солей, продуктов окисления и механических примесей. Даже при высокой начальной емкости сорбент может быстро терять эффективность из-за необратимой деградации. Поэтому система восстановления должна включать не только десорбер или регенератор, но и фильтрацию, контроль pH, анализ содержания активного вещества и периодическую корректировку состава [12,15,17].

Промышленный пример: восстановление аминового абсорбента при очистке природного газа

На примере Шуртанского газохимического комплекса показано, что рост концентрации CO_2 в сырьевом газе является критическим фактором для

Таблица 3. Сравнение физико-химических и эксплуатационных свойств аминовых абсорбентов

Показатель	МЭА	ДЭА	МДЭА	Технологический вывод
Молекулярная масса, г/моль	61,1	105,1	119,2	МДЭА имеет более высокую молекулярную массу и меньшую летучесть
Упругость паров при 60 °С, Па	660	180	24	Меньший унос МДЭА с регенерированным газом
Рабочая концентрация, % масс.	10-20	20-30	30-50	МДЭА позволяет повысить емкость циркуляционного раствора
Коррозионная активность	Высокая	Средняя	Низкая	Переход на МДЭА снижает коррозионный риск
Склонность к деградации	Высокая	Средняя	Низкая	Увеличивается межзаменный срок раствора

Таблица 4. Технологические показатели аминовой очистки газа на основе данных ШГХК

Показатель	Действующая схема ДЭА 30%	Предлагаемая схема МДЭА 40%	Ожидаемый эффект
CO_2 в сырьевом газе, % мол.	3,37	3,37	Работа при фактической повышенной нагрузке
CO_2 в очищенном газе, ppm	75-100	<10	Восстановление нормативного качества газа
H_2S в очищенном газе, ppm	75-100*	<5	Снижение сероводорода до безопасного уровня
Расход пара на регенерацию, т/ч	64,0	52,3	Экономия около 11,7 т/ч
Рабочая концентрация амина, % масс.	30	40	Повышение поглотительной емкости
Пенообразование	250-350 мл	<50 мл	Стабилизация работы абсорбера и десорбера

*В исходных данных превышение 75-100 ppm приведено как проблема по CO_2; для H_2S в таблице дана консервативная технологическая оценка неудовлетворительного режима очистки при перегрузке системы.

действующих установок аминовой очистки. При проектном составе сырьевого газа содержание CO_2 составляло 2,31% мол., тогда как фактическое значение достигло 3,37% мол. Это увеличило нагрузку по кислым компонентам и привело к превышению остаточного CO_2 в очищенном газе до 75-100 ppm при допустимой норме не более 10 ppm.

Существующий раствор ДЭА 30% работает при повышенном расходе циркуляции и расходе пара 64,0 т/ч. Однако дальнейшее увеличение расхода ДЭА ограничено из-за коррозионной активности и энергоемкости. В этих условиях более эффективным вариантом является переход на МДЭА 40%, который допускает более высокую рабочую концентрацию, имеет меньшую летучесть и обеспечивает меньший расход пара при

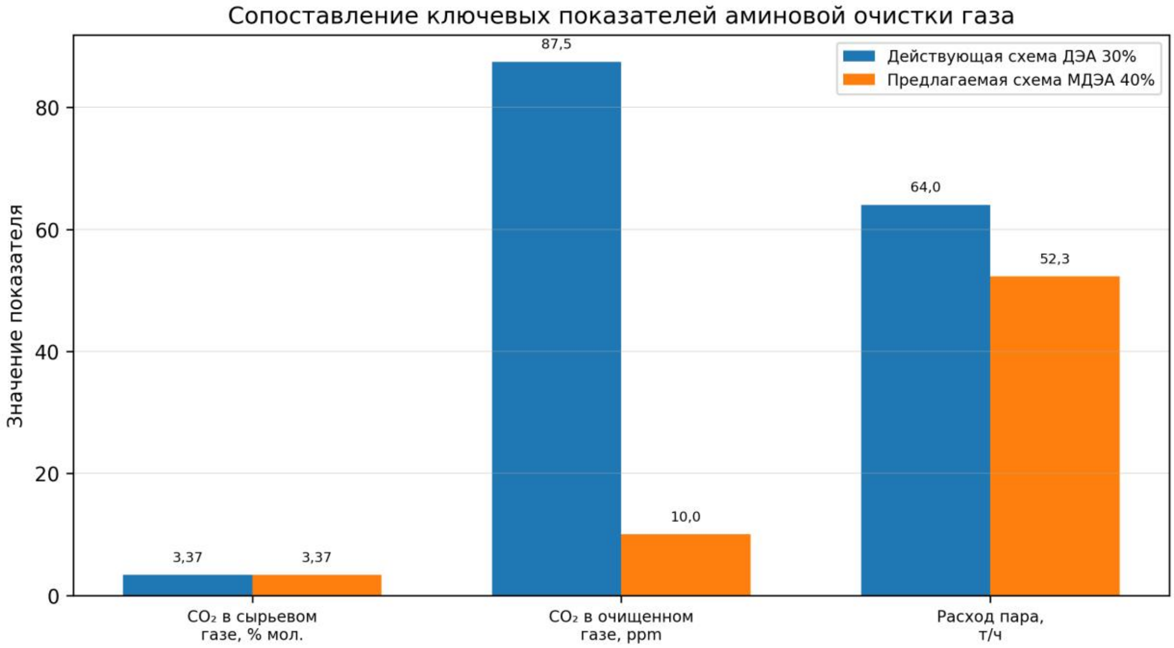


Рисунок 3. Сравнение показателей действующей и предлагаемой схемы аминовой очистки.

регенерации [6,7,15,17,19].

Алгоритм выбора метода восстановления сорбента. Рациональный выбор метода восстановления можно представить как последовательность инженерных решений. На первом этапе устанавливается тип сорбента и характер связи загрязнителя с активным центром. Если связь преимущественно физическая, предпочтительны снижение давления, вакуумирование или умеренный нагрев. Если связь химическая и обратимая, как в аминовых растворах, используется термическая десорбция с паровой отпаркой. Если загрязнение необратимое, требуется химическая промывка, реактивация или частичная замена сорбента. [4–7,11–13].

На втором этапе оценивается стабильность материала. Для цеолитов и активной окиси алюминия допустимы повышенные температуры, тогда как для полимерных и функционализированных сорбентов требуется более мягкий режим. На третьем этапе проводится энергетическая оптимизация: регенерация не должна обеспечивать максимальную десорбцию любой ценой, если это приводит к резкому росту энергозатрат и деградации материала. [4,5,11–14,18].

Обоснование эффективного решения для газохимических объектов Узбекистана. Для установок очистки природного газа от H_2S и CO_2 наиболее обоснованным решением является использование регенерируемых аминовых систем с пониженной энергоемкостью. В условиях повышенного содержания CO_2 переход от ДЭА к МДЭА имеет одновременно технологическое, энергетическое и экологическое значение. МДЭА обеспечивает более высокую селективность к H_2S, меньшую коррозионную активность и возможность работы при концентрации 40-50% масс., что снижает нагрузку на циркуляционный контур. [6,7,15,17,19].

Для твердых сорбентов, используемых в осушке и тонкой доочистке газа, приоритет следует отдавать термической регенерации сухим газом с контролем температуры, так как перегрев снижает ресурс цеолитов и силикагелей. Для активированных углей, работающих по VOC и меркаптанам, эффективна паровая или термическая десорбция с последующей конденсацией десорбата. Химическая промывка должна применяться только

Таблица 5. Рекомендуемый выбор метода восстановления в зависимости от сорбционной системы

Сорбционная система	Основная задача	Предпочтительный метод восстановления	Контролируемые параметры
МДЭА 40% / МДЭА + активатор	Удаление H_2S и CO_2	Термическая десорбция, паровая отпарка, фильтрация раствора	pH, активная концентрация амина, H_2S/CO_2, ТСА, Fe^{2+}, пенообразование
ДЭА 30%	Кислые газы при умеренной нагрузке	Термическая регенерация, антикоррозионный контроль	Температура ребойлера, коррозия, солеобразование
Цеолиты	Осушка и глубокая доочистка	Продувка горячим сухим газом, вакуум	Точка росы, температура слоя, перепад давления
Силикагель / Al_2O_3	Осушка газа	Термическая регенерация при ограниченной температуре	Влага на выходе, механическая прочность, истираемость
Активированный уголь	VOC, меркаптаны, следовые органические вещества	Паровая десорбция, термореактивация, химическая промывка	Йодное число, зольность, потери массы, температура воспламенения

при доказанном накоплении необратимых примесей. [4,5,11–13,18].

Выводы и дальнейшая работа

Проведенный анализ показал, что эффективность газоочистной системы определяется устойчивостью сорбента в повторяющихся циклах сорбция-регенерация. Для жидких аминовых абсорбентов наиболее рациональным методом восстановления остается термическая десорбция с паровой отпаркой, а для твердых адсорбентов - термическая или вакуумная регенерация с учетом температурной стабильности материала.

Для условий очистки природного газа от H_2S и CO_2 наиболее перспективным является переход на МДЭА 40% или МДЭА с активирующей добавкой. На основе промышленных данных показано, что такая схема способна обеспечить снижение CO_2 в очищенном газе с 75-100 ppm до <10 ppm, H_2S до <5 ppm и уменьшить расход пара на регенерацию с 64,0 до 52,3 т/ч.

Химическая промывка и реактивация должны рассматриваться как вспомогательные методы для случаев необратимого загрязнения, накопления термостойких солей или отравления активных центров. Для повышения надежности процесса необходимо внедрять регулярный лабораторный контроль: содержание активного вещества, кислых газов, термостойких солей, железа, pH, пенообразование и остаточную сорбционную емкость.

Дальнейшие исследования целесообразно направить на экспериментальную оценку долговечности МДЭА-систем при фактическом составе газа месторождений Узбекистана, моделирование теплового баланса регенератора и разработку локальных композиций сорбентов с возможностью многократного восстановления.

Конфликт интересов. Авторы заявляют об отсутствии конфликта интересов.

Финансирование. Исследование выполнено без внешнего финансирования.

Благодарности. Авторы выражают благодарность специалистам кафедры химической технологии переработки нефти и газа за консультации по вопросам аминовой очистки и регенерации абсорбентов.

Этические заявления. Работа не включает эксперименты с участием людей или животных.

Доступность данных и кода. Данные, использованные для анализа, приведены в таблицах настоящей статьи и основаны на предоставленных технологических материалах и опубликованных источниках.

Список литературы

1. A. L. Kohl and R. B. Nielsen, Gas Purification, 5th ed. Houston, TX: Gulf Professional Publishing, 1997.
2. A. J. Kidnay, W. R. Parrish, and D. G. McCartney, Fundamentals of Natural Gas Processing, 3rd ed. Boca Raton, FL: CRC Press, 2019.
3. A. Rojey, C. Jaffret, S. Cornot-Gandolphe, B. Durand, S. Jullian, and M. Valais, Natural Gas: Production, Processing, Transport. Paris, France: Editions Technip, 1997.
4. D. M. Ruthven, Principles of Adsorption and Adsorption Processes. New York, NY: John Wiley & Sons, 1984.
5. R. T. Yang, Adsorbents: Fundamentals and Applications. Hoboken, NJ: John Wiley & Sons, 2003, doi: 10.1002/047144409X.
6. G. T. Rochelle, “Amine scrubbing for CO capture,” Science, vol. 325, no. 5948, pp. 1652–1654, 2009, doi: 10.1126/science.1176731.
7. U. Zahid, “Simulation of an acid gas removal unit using a DGA and MDEA blend instead of a single amine,” Chemical Product and Process Modeling, vol. 15, no. 4, article 20190044, 2020, doi: 10.1515/cppm-2019-0044.
8. A. S. Farooqi et al., “Simulation of natural gas treatment for acid gas removal using the ternary blend of MDEA, AEEA, and NMP,” Sustainability, vol. 14, no. 17, article 10815, 2022, doi: 10.3390/su141710815.
9. R. Serna-Guerrero, Y. Belmabkhout, and A. Sayari, “Modeling CO adsorption on amine-functionalized mesoporous silica: 1. A semi-empirical equilibrium model,” Chemical Engineering Journal, vol. 161, no. 1–2, pp. 173–181, 2010, doi: 10.1016/j.cej.2010.04.024.
10. R. Serna-Guerrero and A. Sayari, “Modeling adsorption of CO on amine-functionalized mesoporous silica: 2. Kinetics and breakthrough curves,” Chemical Engineering Journal, vol. 161, no. 1–2, pp. 182–190, 2010, doi: 10.1016/j.cej.2010.04.042.
11. R. Desai, M. Hussain, and D. M. Ruthven, “Adsorption of water vapour on activated alumina. I. Equilibrium behaviour,” The Canadian Journal of Chemical Engineering, vol. 70, no. 4, pp. 699–706, 1992, doi: 10.1002/cjce.5450700412.
12. G. San Miguel, S. D. Lambert, and N. J. D. Graham, “The regeneration of field-spent granular activated carbons,” Water Research, vol. 35, no. 11, pp. 2740–2748, 2001, doi: 10.1016/S0043-1354(00)00549-2.
13. P. D. Sullivan, M. J. Rood, G. Grevillot, J. D. Wander, and K. J. Hay, “Activated carbon fiber cloth electrothermal swing adsorption system,” Environmental Science & Technology, vol. 38, no. 18, pp. 4865–4877, 2004, doi: 10.1021/es0306415.
14. P. L. Llewellyn et al., “High uptakes of CO_2 and CH_4 in mesoporous metal-organic frameworks MIL-100 and MIL-101,” Langmuir, vol. 24, no. 14, pp. 7245–7250, 2008, doi: 10.1021/la800227x.
15. O. Akhmedova and Sh. Akhmedova, “Production of amine absorbents on the basis of local raw materials,” Universum: Technical Sciences, no. 3(120), pp. 53-57, 2024. [Online]. Available: https://7universum.com/ru/tech/archive/item/17124
16. M. Zh. Makhmudov and S. A. Yomgurov, “Adsorption methods of cleaning and drying gases,” Bulletin of Teachers of the New Uzbekistan, vol. 1, no. 5, pp. 72–75, 2023.
17. M. J. Makhmudov and R. J. Hamroev, “Research on the effect of the balance, driving force and kinetics of the absorption process on foaming in the process of purification of gases from sour components using MDEA,” Universum: Technical Sciences, no. 11(128), pp. 24-25, 2024. [Online]. Available: https://7universum.com/ru/tech/archive/item/18630
18. S. A. ugli Joniboev, N. A. Igamkulova, Sh. Sh. Mengliyev, and M. A. Mirzaahmedova, “Physicochemical and chemisorption properties of modified local bentonite sorbents for acid gas removal from expander gas streams,” European Journal of Interdisciplinary Research and Development, vol. 48, pp. 229–235, 2026.
19. M. Mirzaahmedova and Z. A. Baxodirov, “Gaz-kimyo sanoatida MDEA asosida kislotali gazlarni ajratish texnologiyalarining ilg‘or regeneratsiya usullari,” in Umidli kimyogarlar-2025: XXXIV ilmiy-texnikaviy anjuman maqolalar to‘plami. Toshkent: TKTI, 2025, 57-59 b.

КАТАЛИТИЧЕСКОЕ ПОЛУЧЕНИЕ ОКСИГЕНАТНЫХ КОМПОНЕНТОВ МОТОРНЫХ ТОПЛИВ ИЗ ЛЁГКИХ ФРАКЦИЙ ГАЗОКОНДЕНСАТА

Sanalar
Qabul qilindi: 17.05.2026
Nashrga qabul qilindi: 20.05.2026
Nashr qilindi: 21.05.2026

Озодова Фотима Гайрат кизи
Магистрантка кафедры химической технологии переработки нефти и газа,
Ташкентский химико-технологический институт

Абдубаннобов Миржалол Мадолимжон угли
Магистр кафедры химической технологии переработки нефти и газа,
Ташкентский химико-технологический институт.
E-mail: mirjalolabdubannobov29@gmail.com
ORCID: 0009-0000-7601-4765

Мирзаахмедова Мавлуда Ахмеджановна
PhD, старший преподаватель кафедры химической технологии переработки нефти и газа,
Ташкентский химико-технологический институт.
E-mail: mmirzaahmedova@bk.ru
ORCID: 0000-0002-0641-4859

Менглиев Шерзод Шоймович
PhD, доцент кафедры химической технологии переработки нефти и газа,
Ташкентский химико-технологический институт.
E-mail: sh.shoimovich@gmail.com
ORCID 0000-0001-6235-4400

Игамкулова Наргиса Абдувалиевна
кандидат химических наук, доцент кафедры химической технологии переработки нефти и газа,
Ташкентский химико-технологический институт.
E-mail: n.abduvaliyevna@gmail.com
ORCID 0000-0003-2244-4676

Гуломов Шухраткодир Ташматович
PhD, доцент кафедры химической технологии переработки нефти и газа,
Ташкентский химико-технологический институт.
E-mail: shuhratrich@gmail.com
ORCID: 0000-0002-5793-3018

Озодова Ф.Г., Абдубаннобов М.М., Мирзаахмедова М.А., Менглиев Ш.Ш., Игамкулова Н.А., Гуломов Ш.Т. Каталитическое получение оксигенатных компонентов моторных топлив из лёгких фракций газоконденсата // Journal of future. 2026. Vol. 2. Iss. 2. pp. 73–83. https://doi.org/10.66960/jof.3093-8899.00027

Аннотация. В статье рассмотрены современные научно-технологические подходы к получению и применению оксигенатных компонентов моторных топлив на основе лёгких фракций газоконденсата. Актуальность работы определяется необходимостью расширения сырьевой базы экологически улучшенных бензиновых композиций, снижения зависимости от традиционных высокооктановых компонентов и более рационального использования местных углеводородных ресурсов Узбекистана. Особое внимание уделено возможности переработки фракции 353–448 К Шуртанского газоконденсата методом мягкого каталитического окисления с использованием оксидных катализаторов MnO_2 и H_3BO_3. Методическая основа исследования включает обобщение данных по гидрообессерованию сырья, каталитическому окислению паровоздушной смеси, определению гидроксильного, карбонильного и кислотного чисел, расчёту октановых характеристик методом молекулярных рефракций, а также оценке влияния оксигенатного компонента на эксплуатационные и экологические свойства бензиновых композиций. Показано, что после гидрообессерования Шуртанский газоконденсат содержит 43,2 % масс. парафиновых и 22,6 % масс. ароматических углеводородов, что создаёт благоприятные условия для направленного образования кислородсодержащих соединений. Наиболее эффективным катализатором является MnO_2: при Т = 393 К, Р = 0,1 МПа, τ = 3,5 с и К = 0,35 выход кислородсодержащих соединений достигает 18–21 % масс., суммарное функциональное число составляет 247, а расчётное октановое число оксидата находится в пределах 78–82 ед. Введение 15 % об. оксигенат-бензина в состав базовой бензиновой фракции повышает расчётное октановое число смеси до 82–85 ед. и может снизить расчётные выбросы СО на 12–16 %. Полученные результаты подтверждают перспективность каталитического окисления лёгких фракций газоконденсата как локального и технологически доступного направления получения оксигенатных компонентов моторных топлив.

Ключевые слова: *оксигенат-бензин, газоконденсат, каталитическое окисление, MnO_2, H_3BO_3, октановое число, экологичные топлива*

Annotatsiya. Maqolada gaz kondensatining yengil fraksiyalari asosida motor yoqilg‘ilari uchun oksigenat komponentlarni olish va qo‘llashning zamonaviy ilmiy-texnologik yondashuvlari ko‘rib chiqilgan. Tadqiqotning dolzarbligi ekologik jihatdan yaxshilangan benzin kompozitsiyalari uchun xomashyo bazasini kengaytirish, an’anaviy yuqori oktanli komponentlarga bo‘lgan bog‘liqlikni kamaytirish hamda O‘zbekistonning mahalliy uglevodorod resurslaridan yanada oqilona foydalanish zarurati bilan belgilanadi. Asosiy e’tibor Sho‘rtan gaz kondensatining 353–448 K fraksiyasini MnO_2 va H_3BO_3 oksid katalizatorlari ishtirokida yumshoq katalitik oksidlash orqali qayta ishlash imkoniyatiga qaratilgan. Tadqiqotning metodik asosi xomashyoni gidrodesulfurizatsiya qilish, bug‘-havo aralashmasini katalitik oksidlash, gidroksil, karbonil va kislota sonlarini aniqlash, oktan xususiyatlarini molekulyar refraksiya usuli bilan hisoblash, shuningdek oksigenat komponentning benzin kompozitsiyalarining ekspluatatsion va ekologik xossalariga ta’sirini baholash bo‘yicha ma’lumotlarni umumlashtirishdan iborat. Gidrodesulfurizatsiyadan so‘ng Sho‘rtan gaz kondensati tarkibida 43,2 mass.% parafin va 22,6 mass.% aromatik uglevodorodlar mavjudligi ko‘rsatildi, bu esa kislorod saqlovchi birikmalarning yo‘naltirilgan hosil bo‘lishi uchun qulay sharoit yaratadi. Eng samarali katalizator MnO_2 hisoblanadi: T = 393 K, P = 0,1 MPa, т = 3,5 s va K = 0,35 sharoitida kislorod saqlovchi birikmalar chiqishi 18–21 mass.% ga yetadi, umumiy funksional son 247 ni, oksidatning hisobiy oktan soni esa 78–82 birlikni tashkil etadi. Bazaviy benzin fraksiyasi tarkibiga 15 hajm.% oksigenat-benzin kiritilishi aralashmaning hisobiy oktan sonini 82–85 birlikkacha oshiradi va CO chiqindilarini hisobiy jihatdan 12–16% ga kamaytirishi mumkin. Olingan natijalar gaz kondensatining yengil fraksiyalarini katalitik oksidlash motor yoqilg‘ilari uchun oksigenat komponentlarni mahalliy va texnologik jihatdan qulay yo‘l bilan olishda istiqbolli yo‘nalish ekanligini tasdiqlaydi.

Kalit so‘zlar: oksigenat-benzin, gaz kondensati, katalitik oksidlash, MnO_2, H_3BO_3, *oktan soni, ekologik yoqilg‘i*

Abstract. The article considers modern scientific and technological approaches to the production and application of oxygenate components of motor fuels based on light gas condensate fractions. The relevance of the study is determined by the need to expand the feedstock base for environmentally improved gasoline compositions, reduce dependence on traditional high-octane components, and ensure more rational use of local hydrocarbon resources of Uzbekistan. Particular attention is paid to the possibility of processing the 353–448 K fraction of Shurtan gas condensate by mild catalytic oxidation using MnO_2 and H_3BO_3 oxide catalysts. The methodological basis of the study includes the generalization of data on feedstock hydrodesulfurization, catalytic oxidation of a vapor–air mixture, determination of hydroxyl, carbonyl, and acid numbers, calculation of octane characteristics by the molecular refraction method, and assessment of the influence of the oxygenate component on the operational and environmental properties of gasoline compositions. It is shown that, after hydrodesulfurization, Shurtan gas condensate contains 43.2 wt.% paraffinic and 22.6 wt.% aromatic hydrocarbons, which creates favorable conditions for the directed formation of oxygen-containing compounds. The most effective catalyst is MnO_2: at T = 393 K, P = 0.1 MPa, т = 3.5 s, and K = 0.35, the yield of oxygen-containing compounds reaches 18–21 wt.%, the total functional number is 247, and the calculated octane number of the oxidate is in the range of 78–82 units. The introduction of 15 vol.% oxygenate gasoline into the base gasoline fraction increases the calculated octane number of the mixture to 82–85 units and may reduce calculated CO emissions by 12–16%. The obtained results confirm the prospects of catalytic oxidation of light gas condensate fractions as a local and technologically accessible route for producing oxygenate components of motor fuels.

Keywords: oxygenate gasoline, gas condensate, catalytic oxidation, MnO_2, H_3BO_3, *octane number, clean fuels*

Введение

Повышение качества автомобильных бензинов остаётся одной из ключевых задач современной нефтегазопереработки. Отказ от этилированных антидетонаторов, ограничение содержания бензола и ароматических углеводородов, а также требования к снижению токсичности выхлопных газов усиливают интерес к кислородсодержащим топливным компонентам — оксигенатам. К таким компонентам относятся спирты, простые эфиры, а также сложные смеси кислородсодержащих соединений, которые улучшают полноту сгорания и повышают детонационную стойкость бензина [1–6].

В мировой практике наиболее распространены метил-трет-бутиловый эфир (МТБЭ), этил-трет-бутиловый эфир (ЭТБЭ), метил-трет-амиловый эфир (МТАЭ) и низшие спирты. Их промышленное производство, однако, требует либо чистых изоолефиновых потоков, либо развитой инфраструктуры спиртового и нефтехимического синтеза. Для стран, располагающих значительными ресурсами газоконденсатного сырья, перспективным направлением является прямое каталитическое превращение лёгких углеводородных фракций в кислородсодержащие продукты [1, 6, 9, 13].

Газоконденсат Шуртанского месторождения содержит значительную долю лёгких фракций C_5–C_{11}, пригодных для получения оксигенатных добавок. Согласно исходным данным, широкая фракция 353–448 К является наиболее реакционноспособной для мягкого окисления кислородом воздуха. Применение оксидных катализаторов MnO_2 и H_3BO_3 позволяет направлять процесс в сторону образования спиртов, альдегидов, кетонов, карбоновых кислот и сложных эфиров при минимальном глубоком окислении до CO_2 [7,18].

Научная новизна данной работы заключается в систематизации данных по получению оксигенат-бензина из местного газоконденсатного сырья и оценке его применения как компонента моторных топлив. В отличие от традиционного подхода, ориентированного на синтез индивидуальных эфиров, рассматриваемая технология использует природную многокомпонентную смесь углеводородов и формирует продукт, пригодный для компаундирования с АИ-80.

Цель статьи — обосновать применение оксигенатных топливных компонентов, полученных каталитическим окислением лёгких фракций газоконденсата, на основе анализа состава сырья, выбора катализатора, технологических параметров окисления и эксплуатационно-экологических свойств получаемых бензиновых компаундов.

Материалы и методы

Объект исследования и подготовка сырья. В качестве объекта исследования рассматривали стабилизированный газоконденсат Шуртанского месторождения и его лёгкие бензиновые фракции. До стадии окисления сырьё подвергали гидрообессериванию на кобальт-молибденовом катализаторе MoO_2/Al_2O_3 при 573–623 К. Такая подготовка необходима, поскольку сернистые соединения ингибируют свободно-радикальные реакции окисления и дезактивируют активные центры оксидных катализаторов [18].

Таблица 1. Физико-химические свойства газоконденсата после гидрообессерования

Показатель	Газлинский ГК	Шуртанский ГК
Удельный вес, кг/м³	754	767
Коэффициент преломления nD^{20}	1,4500	1,4556
Кислотность, мг КОН/г	следы	следы
Парафиновые углеводороды, % масс.	32,4	43,2
Ароматические углеводороды, % масс.	31,2	22,6
Нафтеновые углеводороды, % масс.	36,1	34,2
Содержание серы после обессерования, % масс.	0,03	0,04

После гидрообессерования газоконденсат фракционировали на лабораторной ректификационной установке. Для дальнейшего анализа выбрана фракция 353–448 К, включающая основную часть C_5–C_{11} углеводородов. Суммарное содержание парафиновых и нафтеновых углеводородов в этой области составляет около 72 %, что повышает вероятность образования спиртов и карбонильных соединений в условиях мягкого каталитического окисления.

Катализаторы и условия каталитического окисления. В качестве основных катализаторов рассмотрены MnO_2 и H_3BO_3. Диоксид марганца инициирует образование гидропероксидных радикалов и способствует накоплению кислородсодержащих соединений [7]. Борная кислота действует как модификатор кислотности поверхности и стабилизирует спиртовые промежуточные формы, что повышает гидроксильное число оксидата.

Окисление проводили в проточном режиме на неподвижном слое катализатора. Углеводородную фракцию испаряли и подавали в реактор в виде паровоздушной смеси. Основными регулируемыми параметрами были температура T, давление P, время контакта τ и коэффициент K, характеризующий соотношение углеводородной фракции и воздуха. Оптимальные условия для фракции 353–448 К: $T = 393$ К, $P = 0{,}1$ МПа, $\tau = 3{,}5$ с и $K = 0{,}35$.

Общая схема технологического подхода представлена на рисунке 1. Она отражает последовательность: подготовка газоконденсатной фракции, гидрообессерование, каталитическое окисление, конденсация оксидата и компаундирование с базовым моторным топливом.

Рисунок 1. Схема получения и применения оксигенат-бензина из лёгкой фракции газоконденсата

Аналитические методы и расчётные зависимости. Оценку качества оксидата проводили по функциональным числам: гидроксильному (Г.Ч.), карбонильному (Карб.Ч.) и кислотному (К.Ч.). Суммарное функциональное число использовали как интегральный показатель степени образования кислородсодержащих соединений:

$$\text{Ф.Ч.} = \text{Г.Ч.} + \text{Карб.Ч.} + \text{К.Ч.} \qquad (1)$$

Октановое число компаундов рассчитывали по методу молекулярных рефракций и дополнительно проверяли по линейной аддитивной модели:

$$\text{ОЧ}_{\text{смеси}} = \Sigma(\varphi_i \cdot \text{ОЧ}_i), \qquad (2)$$

где φ_i — объёмная доля i-го компонента, а ОЧ_i — его октановое число. Для сложных смесей с кислородсодержащими компонентами метод молекулярных рефракций считается более информативным, поскольку учитывает вклад функциональных групп и изменение молекулярной поляризуемости [15,19,20].

Результаты и обсуждение

Реакционная способность фракций Шуртанского газоконденсата. Фракционный состав Шуртанского газоконденсата показывает, что основная доля реакционноспособного сырья приходится на интервал 363–448 К. Эта область объединяет фракции с высоким содержанием метановых и нафтеновых углеводородов. Именно такие соединения в условиях мягкого окисления легче формируют первичные и вторичные кислородсодержащие продукты по радикально-цепному механизму.

По данным таблицы 2, средняя широкая фракция 363–448 К содержит 51,2 % масс. метановых и 21,1 % масс. нафтеновых углеводородов. Такое соотношение подтверждает целесообразность использования данной фракции как основного сырья для получения оксигенатного компонента. Высокое содержание ароматических соединений в отдельных узких фракциях требует предварительного регулирования состава, поскольку ароматические углеводороды менее желательны для экологически улучшенных бензинов.

Таблица 2. Физико-химические свойства фракций Шуртанского газоконденсата

Фракция, К	Выход, % на ГК	Метановые УВ, % масс.	Нафтеновые УВ, % масс.	Ароматические УВ, % масс.
338–363	9,3	58,4	21,8	19,8
363–393	26,8	41,5	32,7	25,8
393–423	33,1	39,0	20,7	40,3
423–448	16,6	62,0	5,5	32,3
448–473	12,8	52,0	20,1	27,9
Среднее по 363–448 К	41,2	51,2	21,1	27,7

Сравнение катализаторов MnO_2, H_3BO_3 и MoO_2/Al_2O_3. Сравнение катализаторов показывает, что MnO_2 обеспечивает наибольший выход кислородсодержащих соединений и наиболее высокое расчётное октановое число оксидата. H_3BO_3 характеризуется повышенным гидроксильным числом

Таблица 3. Физико-химические свойства оксидата при использовании различных катализаторов

Показатель	MoO_2/Al_2O_3	MnO_2	H_3BO_3
Выход КСС, % масс.	14–16	18–21	16–19
Гидроксильное число, мг КОН/г	95	135	148
Карбонильное число	52	47	38
Кислотное число, мг КОН/г	78	65	54
Суммарное Ф.Ч.	225	247	240
Удельный вес, г/см³	0,778	0,782	0,785
Расчётное ОЧ (ИМ)	72–76	78–82	76–80

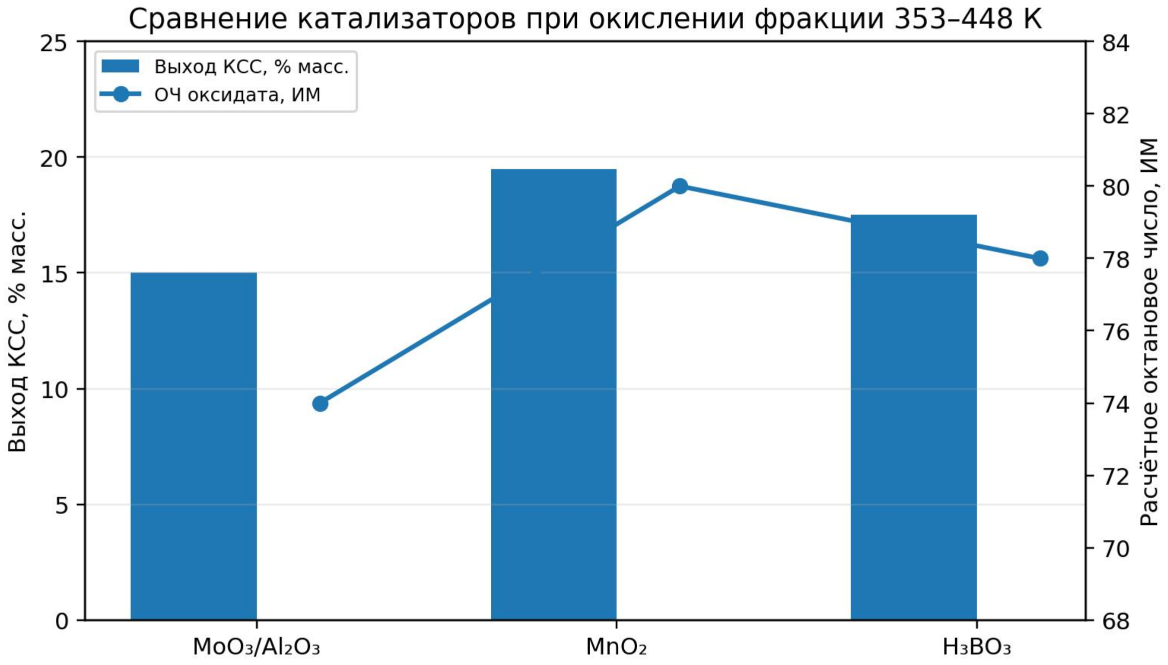


Рисунок 2. Сравнение выхода кислородсодержащих соединений и расчётного октанового числа оксидата для различных катализаторов

и меньшим кислотным числом, что указывает на более выраженную селективность к спиртовым продуктам. MoO_2/Al_2O_3 уступает этим системам по выходу кислородсодержащих соединений и по октановой характеристике оксидата.

Свойства полученного оксигенат-бензина. Оксигенат-бензин, полученный из фракции 353–448 К при Т = 393 К и т = 3,5 с на MnO_2, представляет собой многокомпонентную смесь спиртов, альдегидов, кетонов, карбоновых кислот, сложных эфиров и неокисленных углеводородов. Наличие нескольких типов функциональных групп объясняет высокое суммарное функциональное число и положительное влияние на полноту сгорания топлива.

Ключевым результатом является совокупность трёх показателей: расчётное октановое число 78–83, функциональное число 247 и удельный вес 0,782 г/см³. По октановому числу такой продукт уступает индивидуальным эфирам типа МТБЭ и ЭТБЭ, но превосходит прямогонные низкооктановые бензины и может использоваться как технологически доступная присадка на базе местного сырья.

Таблица 4. Физико-химические свойства оксигенат-бензина и концентрата кислородсодержащих соединений

Показатель	Оксигенат-бензин	Концентрат КСС
Удельный вес, г/см³	0,782	0,924
Показатель преломления n_D^{20}	1,4478	1,4825
Молярная масса, г/моль	214	272
Кислотное число, мг КОН/г	65	184
Карбонильное число	47	75
Гидроксильное число, мг КОН/г	135	214
Суммарное Ф.Ч.	247	473
Расчётное ОЧ (ИМ)	78–83	—

Компаундирование с моторными топливами. Практическое применение оксигенат-бензина целесообразно рассматривать не как самостоятельное топливо, а как функциональный компонент для приготовления бензиновых композиций с улучшенными эксплуатационными и экологическими характеристиками. Его введение в состав базовых бензиновых фракций позволяет повысить расчётное октановое число, увеличить содержание связанного кислорода в топливе и улучшить полноту сгорания топливно-воздушной смеси.

На современном этапе более рациональным является использование оксигенат-бензина в составе базовых бензиновых композиций, прямогонных фракций и риформатных компонентов, а не привязка только к устаревшим низкооктановым маркам топлива. Добавление 10–15 % об. оксигенат-бензина позволяет повысить антидетонационные свойства смеси без глубокой реконструкции технологической схемы и без обязательного применения дополнительных процессов риформинга, изомеризации или алкилирования. При этом наибольший практический интерес представляет компаундирование с базовой бензиновой композицией, октановое число которой находится в диапазоне 78–80 ед., поскольку в этом случае достигается повышение расчётного октанового числа до 82–85 ед.

Из данных таблицы 5 видно, что эффективность оксигенат-бензина зависит от состава исходной бензиновой основы и его объёмной доли в компаунде. При введении 10 % об. оксигенатного компонента наблюдается умеренное повышение октанового числа и кислородного индекса топлива. Увеличение содержания оксигенат-бензина до 15 % об. обеспечивает более выраженный эффект: расчётное октановое число базовой бензиновой композиции возрастает до 82–85 ед., что подтверждает возможность использования полученного продукта как компонента экологически улучшенных моторных топлив.

Таблица 5. Рецептуры компаундов оксигенат-бензина с базовыми топливами

Состав компаунда	Оксигенат-бензин, % об.	База, % об.	ОЧ расч.	Кислород, % масс.	Соответствие
Прямогонный бензин (ОЧ = 66) + оксигенат	10	90	68–70	~0,4	низкооктановая бензиновая фракция
Прямогонный бензин + оксигенат	30	70	72–75	~1,2	улучшенная прямогонная композиция
Базовая бензиновая композиция (ОЧ = 78–80) + оксигенат	10	90	81–83	~0,4	кислородсодержащая бензиновая композиция
Базовая бензиновая композиция (ОЧ = 78–80) + оксигенат	15	85	82–85	~0,6	экологически улучшенная бензиновая композиция
Риформат (ОЧ = 93) + оксигенат	10	90	91–93	~0,4	высокооктановая бензиновая композиция
Риформат + прямогонный бензин + оксигенат	30	50+20	83–86	~1,2	композиция среднего октанового уровня

Дополнительным преимуществом является то, что оксигенат-бензин частично замещает ароматические компоненты бензинового пула и способствует более полному сгоранию топлива. Это позволяет рассматривать его не только как октаноповышающую добавку, но и как компонент, способный улучшить экологические показатели бензиновых композиций за счёт снижения доли продуктов неполного сгорания.

Экологическая и технологическая оценка применения. Экологическое действие оксигенатных компонентов обусловлено двумя основными факторами. Во-первых, введение кислородсодержащих соединений повышает кислородный индекс топлива, что способствует более полному сгоранию топливно-воздушной смеси и уменьшению доли продуктов неполного окисления. Во-вторых, оксигенат-бензин частично разбавляет ароматическую составляющую бензинового пула, что особенно важно при производстве экологически улучшенных моторных топлив с повышенной долей риформатных компонентов. Согласно расчётной оценке, добавление 15 % об. оксигенат-бензина в базовую бензиновую композицию может обеспечить снижение выбросов CO на 12–16 %, а несгоревших углеводородов — на 8–12 %. Следует отметить, что приведённые показатели имеют прогнозный характер и требуют дальнейшего подтверждения в условиях моторных и эксплуатационных испытаний.

Таблица 6. Ожидаемые экологические и эксплуатационные эффекты при применении оксигенат-бензина в составе базовой бензиновой композиции

Показатель	Базовая бензиновая композиция без оксигената	Бензиновая композиция 15%об. оксиге-нат-бензина	Ожидаемый эффект
Выбросы CO, г/км, расчётные	8,5–9,5	7,2–8,0	снижение на 12–16 % за счёт более полного сгорания
Несгоревшие углеводороды, г/км	1,2–1,5	1,0–1,2	снижение на 8–12 %
Содержание бензола, % об.	0,8–1,2	0,7–1,0	частичное разбавление ароматической части топлива
Содержание ароматических углеводородов, % об.	30–38	26–34	снижение доли ароматических компонентов
Кислородный индекс топлива, % масс.	~0	~0,6	повышение полноты окисления топливно-воздушной смеси
Расчётное октановое число, ед.	78–80	82–85	повышение детонационной стойкости
Потенциальное образование сажи и нагара	среднее	пониженное	улучшение качества сгорания
Экологическая характеристика топлива	стандартная бензиновая композиция	кислородсодержащая экологически улучшенная композиция	улучшение эксплуатационно-экологических свойств

Как видно из таблицы 6, введение 15 % об. оксигенат-бензина в состав базовой бензиновой композиции способствует повышению расчётного октанового числа до 82–85 ед., увеличению кислородного индекса топлива и снижению расчётных выбросов CO на 12–16 %. Дополнительным положительным эффектом является уменьшение доли несгоревших углеводородов и частичное разбавление ароматической составляющей топлива, что соответствует современным требованиям к экологически улучшенным моторным топливам.

Технологически важным преимуществом рассматриваемого подхода является возможность использования газоконденсатной фракции без выделения индивидуальных изоолефинов. В сравнении с производством МТБЭ через изобутиленовую цепочку, процесс прямого каталитического окисления потенциально требует меньшего количества стадий. Однако для промышленной реализации необходимы дополнительные исследования стабильности катализаторов, состава побочных продуктов, коррозионной активности оксидата и моторных характеристик реальных компаундов. [9, 14-17].

Выводы и дальнейшая работа

1. Предложенная формулировка темы — «Каталитическое получение оксигенатных компонентов моторных топлив из лёгких фракций газоконденсата» — более полно отражает научную направленность работы, поскольку акцентирует внимание не только на применении получаемого продукта, но и на технологическом механизме его синтеза.

2. Установлено, что Шуртанский газоконденсат после стадии гидрообессерования может рассматриваться как перспективное сырьё для получения оксигенатных компонентов моторных топлив. Его состав характеризуется содержанием 43,2 % масс. парафиновых углеводородов и 34,2 % масс. нафтеновых углеводородов при сниженной сернистости до 0,04 % масс., что создаёт благоприятные условия для мягкого каталитического окисления.

3. Среди рассмотренных каталитических систем наиболее эффективным показал себя MnO . При температуре 393 К, давлении 0,1 МПа, времени контакта т = 3,5 с и коэффициенте К = 0,35 выход кислородсодержащих соединений достигает 18–21 % масс., суммарное функциональное число составляет 247, а расчётное октановое число оксидата находится в пределах 78–82 ед.

4. Полученный оксигенат-бензин целесообразно использовать как функциональный компонент базовых бензиновых композиций. Введение 15 % об. оксигенатного компонента позволяет повысить расчётное октановое число смеси до 82–85 ед. и обеспечить кислородный индекс около 0,6 % масс., что способствует улучшению полноты сгорания топлива.

5. Расчётная экологическая оценка показывает, что применение оксигенат-бензина может способствовать снижению выбросов CO на 12–16 % и несгоревших углеводородов на 8–12 %. Для окончательного промышленного обоснования технологии необходимы моторные испытания, исследование стабильности продукта при хранении, коррозионные испытания, а также оптимизация схемы выделения и концентрирования кислородсодержащих соединений.

Конфликт интересов. Авторы заявляют об отсутствии конфликта интересов.

Финансирование. Исследование выполнено без привлечения внешнего

финансирования.

Благодарности. Авторы выражают благодарность Ташкентскому химико-технологическому институту за научно-методическую поддержку.

Этические заявления. Работа не включает исследования с участием людей или животных и не требует отдельного этического разрешения.

Доступность данных и кода. Данные, использованные в статье, обобщены на основе предоставленного диссертационного источника и расчётных таблиц. Дополнительный программный код не использовался.

Список литературы

1. H. Hamid and M. A. Ali, Eds., Handbook of MTBE and Other Gasoline Oxygenates. Boca Raton, FL: CRC Press, 2004, doi: 10.1201/9780203021446.

2. J. G. Speight, The Chemistry and Technology of Petroleum, 5th ed. Boca Raton, FL: CRC Press/Taylor & Francis, 2014.

3. Z. Wang, H. Liu, and R. D. Reitz, “Knocking combustion in spark-ignition engines,” Progress in Energy and Combustion Science, vol. 61, pp. 78–112, 2017, doi: 10.1016/j.pecs.2017.03.004.

4. A. Prakash, C. Wang, A. Janssen, A. Aradi, R. Cracknell, and V. Shankar, “Impact of fuel sensitivity (RON–MON) on engine efficiency,” SAE International Journal of Fuels and Lubricants, vol. 10, no. 1, pp. 115–125, 2017, doi: 10.4271/2017-01-0799.

5. S. Gulomov, D. Turdieva, N. Isaeva, and D. Narzullaev, “Catalytic neutralization of gas emissions in the manufacture of pharmaceutical preparations,” E3S Web of Conferences, vol. 411, article 02024, 2023, doi: 10.1051/e3sconf/202341102024.

6. M. P. Yunusov, S. Gulomov, K. A. Nasullayev, D. P. K. Turdiyeva, N. F. Isayeva, I. S. K. Abdurakhmanova, B. D. Mustafayev, and D. Yu. Murzin, “Mitigating the environmental impact by synthesis of adsorbents from aluminium-containing waste,” Waste and Biomass Valorization, vol. 15, no. 6, pp. 3307–3321, 2024.

7. N. Coutard, C. B. Musgrave III, J. Moon, N. S. Liebov, R. M. Nielsen, J. M. Goldberg, M. Li, X. Jia, S. Lee, D. A. Dickie, W. L. Schinski, Z. Wu, J. T. Groves, W. A. Goddard III, and T. B. Gunnoe, “Manganese catalyzed partial oxidation of light alkanes,” ACS Catalysis, vol. 12, no. 9, pp. 5356–5370, 2022, doi: 10.1021/acscatal.2c00982.

8. M. J. Hunter, “Light naphtha isomerisation to meet 21st century gasoline specifications,” Erdöl Erdgas Kohle, vol. 119, no. 6, pp. 97–107, 2003.

9. M. A. Mirzaahmedova, G. M. Absyalyamova, and A. A. Kodirov, “Promotion of alkylate gasoline as an environmentally friendly motor fuel,” Universum: Technical Sciences, no. 12(117), 2023, doi: 10.32743/UniTech.2023.117.12.16404.

10. S. Gulomov, B. Ismailov, M. Mirzaakhmedova, B. Abduraimov, G. Yusupova, and D. Karaeva, “Aluminum-containing waste processing into adsorbents,” AIP Conference Proceedings, vol. 3304, no. 1, article 040103, 2025, doi: 10.1063/5.0269392.

11. M. Mirzaakhmedova, “Technology of extracting demulsifiers for nonionic oil-water dispersions,” Austrian Journal of Technical and Natural Sciences, no. 9–10, pp. 114–118, 2015, doi: 10.20534/AJT-15-9.10-114-118.

12. A. R. Kurbanov, O. A. Salikhova, M. A. Mirzaakhmedova, and G. A. Baymatova, “Obtaining import-substituting demulsifiers based on local raw materials,” Universum: Chemistry and Biology, no. 2, 2019.

13. A. A. Alimov, “Aktualnye voprosy khimicheskoy pererabotki i ispolzovaniya gazokondensatov,” in Aktualnye problemy pererabotki nefti i gaza Uzbekistana: Materialy respublikanskoy nauchno-tekhnicheskoy konferentsii. Tashkent, Uzbekistan, 2009, p. 34.

14. A. Zh. Kaliev, “Perspektivnye protsessy alkilirovaniya s tselyu polucheniya vysokooktanovykh komponentov benzina,” Molodoy uchenyy, no. 2(397), pp. 47–49, 2022.

15. P. V. Lipin et al., “Joint cracking of vacuum gasoil with vegetable oils on zeolite-containing catalysts of various compositions,” Petroleum Chemistry, vol. 62, no. 8, pp. 886–895, 2022.

16. G. A. Sobarsaha, N. Nuryoto, and J. Jayanudina, “Comparison of octane booster additive for gasoline,” Teknika: Jurnal Sains dan Teknologi, vol. 17, no. 2, pp. 150–157, 2021.

17. F. Sharaf, Antiknock Additives Based on Synergistic Mixtures of Oxygenates to Gasoline Fuels. Ph.D. dissertation, Kazan, Russia, 2018.

18. F. G. Ozodova, Catalytic Oxidation of Light Fractions of Gas Condensate and Production of Oxygenate Gasoline as a Component of Motor Fuels. Master’s dissertation, Tashkent Chemical-Technological Institute, Tashkent, Uzbekistan, 2026.

19. G. Martini et al., Effect of Oxygenates in Gasoline on Fuel Consumption and Emissions. Luxembourg: Publications Office of the European Union, 2013.

20. O. J. Akhmedov, J. B. Fayziev, H. S. Beknazarov, and A. T. Djalilov, “Study of the effect of complex additives that increase the octane number and act as inhibitors for automotive gasolines on a copper plate,” Austrian Journal of Technical and Natural Sciences, no. 1–2, pp. 10–13, 2025.

JOURNAL OF FUTURE

Volume 2, Issue 2, 2026

Musahhih: Eldor Mashayev
Sahifalovchi va dizayner: O'tkirbek Azamatov

Muassis: “Uranium Publishing” MChJ
Tahririyat manzili: 100058, Tashkent shahri, Yunusobod tumani, Adolat MFY, 4-mavze, №28/1-uy

Tel: +998997299997
Web sayt: www.future-journal.uz
Elektron manzil: future.journal.official@gmail.com