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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

PRODUCTION OF ECOLOGICALLY CLEAN DIESEL FUEL THROUGH MAGNETIC FIELD APPLICATION

Speciality: 2314.01 – Petrochemical

Field of science: Technical sciences

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Baku – 2025

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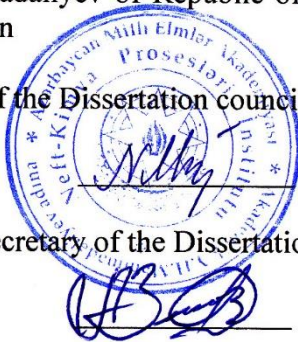
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OVERVIEW OF THE RESEARCH SCOPE

Relevance of the topic and level of advancement

Diesel fuel stands as one of the most sought-after petroleum products globally. It is more cost-effective than gasoline, with diesel engines demonstrating 25-30% lower fuel consumption compared to their gasoline counterparts. The exceptional reliability and efficiency of diesel engines have further contributed to their extensive utilization. Consequently, the demand for diesel fuel in the energy market has escalated to millions of tons annually.

The demand for diesel fuel in the Republic of Azerbaijan is substantial, with the nation's oil refinery producing approximately 2 million tons of diesel fuel annually.¹

Enhancing the quality of diesel fuel remains a critical priority, as the “Euro” standards implemented across numerous countries, particularly within the European Union, impose stringent limitations on the concentration of various emissions released into the atmosphere by internal combustion engines.

The primary driver behind the increasing environmental regulations for diesel fuel is the detrimental impact of sulfur compounds, as well as aromatic and polycyclic hydrocarbons. Given that sulfur is predominantly embedded within the structure of polycyclic aromatic hydrocarbons, their removal has become a pressing concern. Purification of diesel fuels from polycyclic hydrocarbons significantly reduces the presence of carcinogenic and hazardous substances in exhaust emissions, thereby addressing critical environmental and health issues.²

In the modern oil refining industry, the dearomatization and desulfurization of diesel fractions are achieved through various processes, often involving high-pressure systems with intricate technological configurations utilizing hydrogen and catalysts.

¹SOCAR illik hesabat: [Electronic resource] / – Bakı: Socar, – 2023, – 64 s.
<https://socar.az/az/page/illik-hesabatlar>

²Patel, A.B. Polycyclic aromatic hydrocarbons: sources, toxicity, and remediation approaches / A.B. Patel, S. Shaikh, K.R. Jain [et al.] // Front. Microbiol, –2020, Vol.11, 562813.

Furthermore, identifying and implementing a more efficient purification method is of paramount importance, as the potential of the hydrogenation process for removing aromatic hydrocarbons and sulfur compounds from diesel fractions has been extensively utilized.

Minimizing the cost of raw materials and energy resources, as well as introducing innovative purification technologies to address these shortcomings, represents a pressing challenge.

In this regard, the application of a waste-free liquid-phase extraction method for removing aromatic and sulfur compounds from diesel fuel is of particular significance. This method offers the advantages of easy regeneration and enables the separation and reintegration of the extractant into the process, ensuring both efficiency and sustainability.

The advantages of the extraction process are determined by the following factors:

- extraction occurs under moderate conditions, specifically at ambient temperature and pressure, ensuring operational efficiency.
- the process requires no reagents other than the extractant, which simplifies process control and facilitates the easy separation of the raffinate and extract phases.
- the extraction can be performed under both batch and continuous modes, offering flexibility in operation.
- the process does not necessitate additional energy input, contributing to its cost-effectiveness and sustainability.
- it is a waste-free process, promoting environmental responsibility.
- the extracted material can be recycled back into the system, allowing for its reuse and enhancing the overall sustainability of the process.

A critical aspect of extracting both aromatic and sulfur compounds from the diesel fraction is the selection and justification of an appropriate selective solvent.

The requirements for the solvent are as follows:

- a high capacity to dissolve aromatic and sulfur compounds;
- a density that differs from that of the diesel fraction;
- a high dispersion coefficient, which helps reduce solvent

- consumption per unit of raw material;
- feasibility of production;
- cost-effectiveness.

Experiments were conducted to identify solvents that meet the specified requirements, with N-methylpyrrolidone, commonly used in the purification of the diesel fraction, selected as the extractant. While this extractant produced better results than other solvents, the resulting diesel fuel did not meet the EURO-5 standards.

To address these shortcomings, enhance the regulation of technological parameters, improve their efficiency, and reduce the cost of the produced raffinate, the objective was set to perform the extraction process using a magnetic field. For the first time, extraction under the influence of a magnetic field was implemented to purify the diesel fraction from aromatic hydrocarbons and sulfur compounds, with the goal of producing diesel fuel that complies with EURO-5 standards.

In petrochemical production, various catalysts and chemical reagents are employed to prepare raw materials in technological processes. However, traditional chemical methods and standard technologies often fall short in terms of effectiveness. In recent years, researchers have increasingly focused on physical methods for activating hydrocarbon feedstocks, with the magnetic field effect gaining prominence as a highly versatile and influential tool.

Research object and subject.

The research involves the development of a process for purifying the diesel fraction derived from the primary oil processing at the Oil Refinery named after H.Aliyev, specifically targeting the removal of aromatic hydrocarbons and sulfur compounds through extraction under the influence of a magnetic field. The selection and rationale behind the choice of solvent and extractant for this process constitute the focus of the study.

The goals and objectives of the research.

The objective of this research is to produce diesel fuel that meets EURO-5 standards regarding the content of aromatic hydrocarbons in the diesel fraction derived from the primary oil processing at the Oil Refinery named after H.Aliyev.

This dissertation investigates the dearomatization process of the diesel fraction under the influence of a magnetic field, utilizing N-methylpyrrolidone as an extractant, along with its mixtures with acetic, phosphoric, and sulfuric acids.

Research methodology.

In the course of the experiments, advanced analytical techniques such as liquid chromatography, infrared (IR) spectroscopy, and nuclear magnetic resonance (NMR) were employed. Quality parameters were assessed in accordance with GOST and ASTM standards, and a mathematical model was developed.

Fundamental assertions for the defense.

To obtain environmentally friendly diesel fuel through the dearomatization and desulfurization of the diesel fraction derived from the primary oil processing at the Oil Refinery named after H.Aliyev, the following key issues were identified and addressed:

- selection and justification of the process;
- identification of an efficient extractor to facilitate the extraction process;
- choice of an extractant that ensures optimal process performance;
- incorporation of various solvents into the extractant to enhance the economic efficiency of the process;
- investigation of the influence of a magnetic field on the process;
- determination of the optimal process parameters;
- development of a mathematical model for the process;
- calculation of the technical and economic indicators for extraction;
- formulation of regulations considering their practical application to the industry.

The scientific novelty of the research is outlined as follows:

- For the first time, a liquid-phase extraction process was implemented using N-methylpyrrolidone as the solvent, combined with the application of a magnetic field, to treat the diesel fraction obtained from the primary petroleum refining process.
- As a result of the research, diesel fuel was obtained that complies with EURO-5 standards in terms of the amount of aromatic hydrocarbons and has a sulfur content of 0.026% (mass).

- A mathematical model was developed to accurately describe the mechanism of the magnetic field's influence, thus enabling the potential industrialization of the process.
- Utilizing the developed mathematical model, the research provides a detailed description of the mass transfer in both integral and dispersed phases, identifies the driving force behind the process, and examines the characteristics of the boundary layer of the intermediate phases.
- The investigation revealed that the application of a magnetic field induces the formation of a new homogeneous, ordered, and low-viscosity structure in the diesel fuel, thereby facilitating the transition of aromatic hydrocarbons and sulfur compounds into the solvent via both molecular and convective diffusion mechanisms.

The theoretical and practical significance of the study.

For the first time, the extraction of a diesel fraction derived from the primary petroleum refining process was conducted under the influence of a magnetic field. This resulted in the production of diesel fuel that meets the EURO-5 standards in terms of aromatic hydrocarbon content.

The mechanism of the magnetic field's impact on the process was elucidated.

The technical and economic indicators of the process were calculated. Based on laboratory studies, the cost of the product was determined to be 292 AZN/ton. In comparison, the price of unpurified diesel fuel produced through hydrogenation is 583 AZN/ton, indicating an economic benefit of 291 AZN/ton for each ton of product.

A mathematical model of the process was developed

A regulation was established to facilitate its implementation in industrial applications.

The validation and application of the research. A total of 23 scientific publications related to the dissertation topic have been produced, including 10 articles (one published internationally) and 12 theses (two presented abroad). Additionally, one patent has been granted. The findings of the dissertation were presented at numerous

national and international conferences, including:

Euro-eco Hannover 2014 (Environmental and Engineering Aspects for Sustainable Living), Hannover, Germany, November 27-28, 2014; IXth Conference “Current Problems of Chemistry,” dedicated to the 92nd anniversary of the founding of chemistry, attended by PhD students, graduate students, and young researchers. Republican Scientific Conference on the Birth of National Leader Heydar Aliyev, Baku, Azerbaijan, May 7, 2015; IV International Scientific Conference of Young Researchers, Baku, Azerbaijan, April 29-30, 2016; 72nd International Youth Scientific Conference “Oil and Gas - 2018,” Moscow, Russia, April 23-26, 2018; Current Problems of Contemporary Natural and Economic Sciences, Ganja, Azerbaijan, May 4-8, 2018; Current Problems of Contemporary Natural and Economic Sciences, Ganja, Azerbaijan, May 3, 2019; GTDOEK 2020, 100th Anniversary of Azerbaijan State Oil and Industry University, Online Scientific Conference of Young Researchers and Doctoral Students, Baku, Azerbaijan, May 7-8, 2020; Republican Scientific Conference on “New Directions of Agricultural Development and Environmental Protection,” Baku, Azerbaijan, January 30, 2021; RRPCS-2021 International Scientific Conference “Reconstruction and Recovery in Post-Conflict Situations,” Baku, Azerbaijan, February 25-26, 2021; ISCRPCS-2022 II International Scientific Conference “Reconstruction and Recovery in Post-Conflict Situations,” Baku, Azerbaijan, February 24-25, 2022; National Republican Scientific Conference of Young Researchers and Doctoral Students Dedicated to the 100th Anniversary of the Birth of National Leader Heydar Aliyev, GTDREK 2023, Baku, Azerbaijan, May 4-5, 2023; Conference “Modern,” National Republican Scientific Conference of Young Researchers and Doctoral Students Dedicated to the 100th Anniversary of the Birth of National Leader Heydar Aliyev, GTDREK 2023, Baku, Azerbaijan, May 4-5, 2023; Nature and International Scientific Conference on “Current Problems of Economic Sciences,” Ganja, Azerbaijan, May 5-6, 2023.

The institution where the research for this dissertation work was carried out. This dissertation work was completed at the Department of Petrochemical Technology and Industrial Ecology at

Azerbaijan State Oil and Industry University.

Author's personal contribution. The author actively participated in formulating the research questions, conducting the experiments, analyzing and interpreting the obtained results, and preparing the articles.

The total length of the dissertation work, including the individual word count for each structural section of the dissertation:

The dissertation work comprises 180 pages, including an introduction and four chapters, featuring 89 figures, 4 diagrams, 31 tables, and a reference list containing 180 sources. Excluding the tables, figures, diagrams, and reference list, the dissertation contains a total of 177,405 characters (introduction - 11,680, Chapter I - 51,590, Chapter II - 41,945, Chapter III - 65,930, Chapter IV - 4,040, conclusion - 2,220).

The introduction outlines the key concepts of the dissertation work, emphasizing the significance of the research, the study's objectives, and the issues it addresses. It also highlights the scientific novelty, practical implications, and potential applications of the findings.

Chapter one provides a comprehensive review of the literature concerning the demand for diesel fuels, their production processes, and the methods used for removing aromatic hydrocarbons and sulfur compounds. Liquid phase extraction is selected and justified as the method of choice for purification.

The second chapter focuses on the selection and justification of the solvent and extractor used in the extraction purification of the diesel fraction, as well as the research methods employed (IR, NMR, and Liquid Chromatography). It also describes the equipment and devices used to conduct the extraction process under the influence of a magnetic field.

The third chapter presents the results of the research aimed at determining the optimal parameters for both conventional and magnetic field-based purification methods of the diesel fraction. It includes studies on the use of N-methylpyrrolidone and its mixtures with acids as solvents under the effect of the magnetic field.

Additionally, a mathematical model of the cleaning process under the influence of the magnetic field is discussed in this chapter.

The fourth chapter provides the block diagram and principle technological scheme for the extraction purification process under the influence of a magnetic field, along with calculations reflecting its technical and economic indicators.

The dissertation concludes with a summary of the results obtained, followed by the list of references utilized throughout the study.

KEY CONTENT OF THE STUDY

The purification process of the diesel fraction obtained from the primary refining of oil, focusing on the removal of aromatic hydrocarbons and sulfur compounds, was conducted. A thorough review of existing literature revealed that the use of N-methylpyrrolidone (NMP), which is commonly utilized as an extractant in the petrochemical industry, yields even more effective results when combined with other solvents. Moreover, the application of a magnetic field was employed to enhance the efficiency of the process.

The experiments were performed under standard conditions as well as under the influence of a magnetic field. Extractants composed of N-methylpyrrolidone and its mixtures with various acids were used. Specifically, the solvents included N-methylpyrrolidone (CAS 872-50 (STP-TU-COMP-2-207-10) standard), orthophosphoric acid (GOST 6552-80), sulfuric acid (GOST 4204-77), and acetic acid (GOST 61-75).

To generate the magnetic field, an electromagnet was utilized. The electromagnet was constructed with a wire wound around a ferromagnetic core, employing a specially designed electrotechnical iron alloy. The magnetic moment and the strength of the magnetic field were found to be directly proportional to the number of wire turns, the cross-sectional area of each turn, and the current passing through the wire.

Experimental section and research methodology.

The experiments for purifying diesel distillate through extraction were conducted as follows: The diesel distillate was introduced into a flask, and the mixer was activated. Subsequently, the solvent was added to the mixture. The temperature within the flask was closely monitored using a thermometer. In experiments involving elevated temperatures, the vapor produced was directed into a condenser attached to the flask, where it was cooled, condensed, and returned to the process.

For single-step extraction, the extractant and raw material were simultaneously added to the flask, and the process proceeded with intensive mixing. After completion, the mixture was transferred to a separatory funnel, allowing the phases to settle. The raffinate phase was then separated from the extract solution. The experiments revealed that phase separation was achieved within 15 minutes.

The extraction process employed offers several notable advantages:

- the process is conducted under milder conditions.
- there is no need for expensive catalysts or hydrogen.
- the boiling point of the diesel fraction does not need to be reduced, as sterically hindered di- and trialkyl derivatives of dibenzothiophene (DBT) are effectively removed during extraction, thereby expanding the available feedstock base.
- polycyclic aromatic hydrocarbons with low cetane numbers are easily removed, leading to an increase in the cetane index of the diesel fuel.
- nitrogen compounds, which are difficult to eliminate during hydrogenation, are efficiently removed.

The following quality indicators were evaluated for both the initial diesel fractions and the resulting products (raffinate and extract): sulfur content, aromatic hydrocarbons, and cetane number.

Analytical Methods.

The quantity of aromatic hydrocarbons was determined using the sulfuric acid absorption reaction and the iodine number method. In this study, infrared (IR) spectra were recorded with a BRUKER Research Spectrometer. Nuclear magnetic resonance (NMR) was

utilized to detect the resonant absorption of electromagnetic waves, which occurs when the orientation of atomic nuclei's angular momentum vectors (spins) changes.

Aromatic hydrocarbons in the distillates were quantified using Agilent 1260 Infinity II High Performance Liquid Chromatography (HPLC) with refractive index detection.

For the extraction method, the diesel fraction obtained from the primary refining of petroleum was selected as the object of study. The quality indicators of the diesel fraction are provided in Table 1.

Table 1.

Quality indicators of diesel fraction

S/S	Indicators	Qiymətlər
1	Density, at 20°C	0.8450
2	Total sulfur content, % (mass)	0.0895
3	Kinematic viscosity, mm ² /sec	6.2
4	Freezing temperature, °C	-36
5	Cloud point, °C	-25
6	Ignition temperature, °C	72
7	Iodine number	1.83
8	Acidity	57.7
9	Aromatic hydrocarbons, % (mass)	18.08
10	Real resin	3.4
11	Fractional composition, % (mass)	
	Boiling point °C	222
	50% boiling point °C	296
	96% boiling point °C	357
	Final boiling point, °C	367
12	Residue	3.8
13	Cetane number	46

The infrared (IR) spectra of the samples were obtained using a ZnSe crystal in the wavelength range of 600-4000 cm⁻¹, employing an ALPHA IR-Fourier spectrometer manufactured by the German company BRUKER (Figure 1).

The examination of various solvents as extractants and the discussion of the fundamental requirements for extractants in industrial applications were conducted. A review of the literature indicates that morpholine, sulfur dioxide, furfural, dimethylformamide (DMFA), and N-methylpyrrolidone are

commonly recommended for the selective purification of intermediate oil fractions. These solvents are favored due to their reasonable cost and availability in sufficient quantities for industrial use.

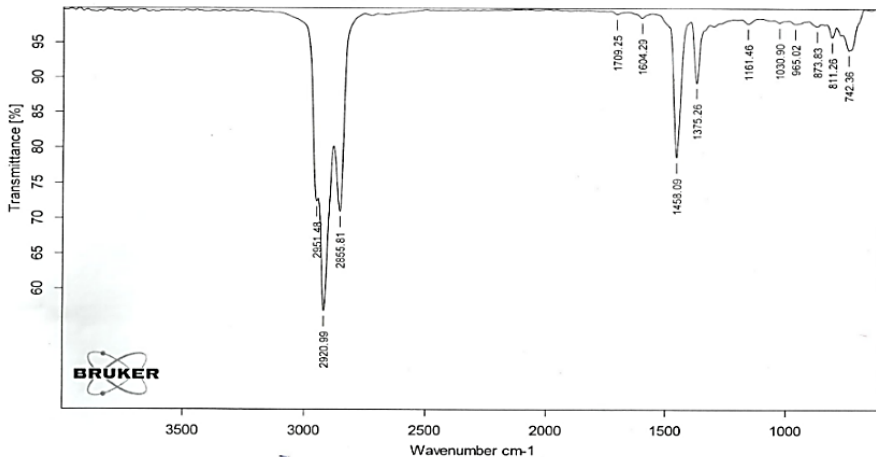


Figure 1. Infrared (IR) spectrum of the diesel fraction.

The application of nitrogen-containing solvents, particularly N-methylpyrrolidone, in the extraction process has demonstrated its effectiveness in reducing both sulfur and aromatic hydrocarbon content. N-methylpyrrolidone stands out for its lower toxicity compared to other solvents, as well as its high solubility, thermal and hydrolytic stability, low corrosion activity, and rapid phase separation due to its low viscosity. These favorable properties make N-methylpyrrolidone and its mixtures with various acids ideal candidates as extractants for the research.

Extraction of diesel distillate with N-methylpyrrolidone and identification of optimal parameters.

The optimal ratio was first established by performing extractions of N-methylpyrrolidone with diesel distillate in various proportions. The relationship between the extractant-to-crude material ratio and the level of purification is presented in Table 2.

Table 2.**Extractant-to-Raw Material Ratio and Purification Efficiency**

NMP: Diesel Distillate Ratio	Aromatic Hydrocarbon Content (% by mass)	Sulfur Content (% by mass)
0,25:1	14	0,085
0,5:1	13	0,081
1:1	10	0,075
2:1	10	0,078
3:1	10	0,076

As a result of the experiments, it was determined that the degree of purification of the diesel fraction from aromatic hydrocarbons and sulfur compounds was higher in 1:1, 2:1 and 3:1 ratio of N-methylpyrrolidone and diesel distillate. In this context, the optimum ratio is taken as 1:1.

After the optimum ratio was determined, studies on the effect of temperature were carried out. The results of the study are presented in Figure 2.

According to the experimental results, the optimum temperature for the extraction process was determined to be 20 °C.

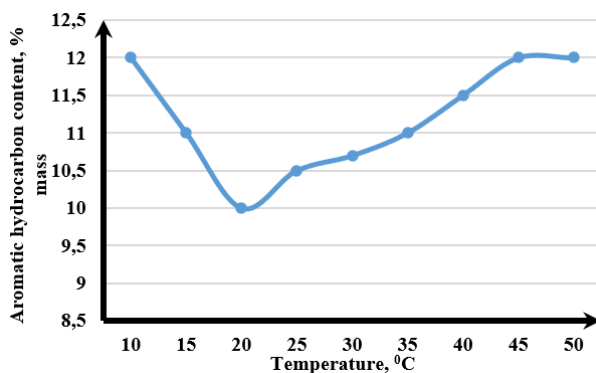


Figure 2. Impact of Temperature on the Extraction Process and Purification Efficiency.

One of the most important parameters affecting the extraction process is the speed of the mixing element in the extractor. Figure 3 shows the results of the effect of the number of cycles of the mixing element on extraction. As seen in Figure 3, the highest results are obtained at 70 rpm agitator speed provided that other parameters remain constant (N-methylpyrrolidone:diesel distillate, temperature).

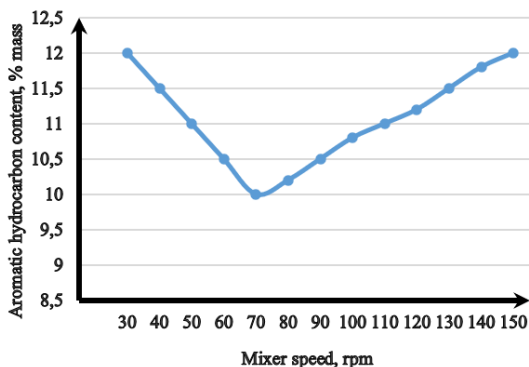


Figure 3. Effect of the number of agitator cycles on the raw material containing extractant and the degree of purification.

One of the factors determining the efficiency of the extraction process is the stirring time. The effect of stirring time on the process parameters is shown in Figure 4.

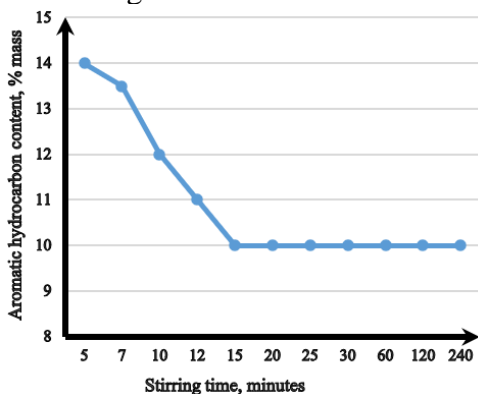


Figure 4. Effect of stirring time on the extraction process and degree of purification.

As illustrated in Figure 4, the optimal stirring time for the extraction process is 15 minutes. Under these conditions, the aromatic hydrocarbon content in the diesel fuel is reduced to 10% (by mass), and the sulfur content decreases to 0.075% (by mass).

An area of significant interest in this research involved exploring the use of N-methylpyrrolidone (NMP) combined with various acids as an extractant. The extractant mixtures tested included NMP-acetic acid, NMP-sulfuric acid, and NMP-phosphoric acid, which were evaluated separately for their effectiveness.

Once the optimum parameters were identified, the experiments were conducted under the influence of a magnetic field. The magnetic field was generated by passing an electric current through a copper wire wound around a specially designed iron core. This process induced a magnetic field within the iron core, which was divided into North and South poles based on the current's flow direction.

When current flows through the copper wire, the magnetic field generated around the wire penetrates the iron, causing the iron's electrons to align their spins and create a magnetic field parallel to the one induced by the wire. This alignment amplifies the magnetic field within the iron core, resulting in a strong and uniform magnetic field.

The experiments were conducted under varying magnetic field intensities and optimal conditions, including a 1:1 NMP-to-diesel distillate ratio, a temperature of 20°C, a stirrer rotation speed of 70 rpm, and a stirring time of 15 minutes.

The experiments were conducted using the setup depicted in Figure 5 below.

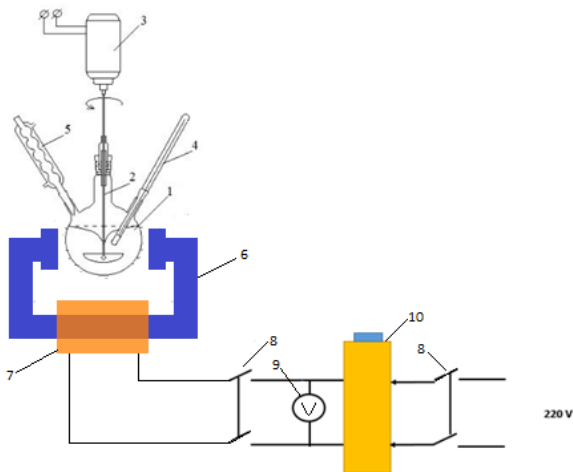


Figure 5. The apparatus used for experiments under the influence of a magnetic field: 1 - Three-neck round-bottom flask, 2 - Glass stirrer, 3 - Electric stirrer motor, 4 - Thermometer, 5 - Reflux condenser, 6 - Special metal core, 7 - Copper coil, 8 - Electric switch, 9 - Voltmeter, 10 - Rheostat (for voltage adjustment).

During the experiments, diesel distillate was poured into a flask, the stirrer was activated, and the magnetic field was switched on after the solvent was added. The intensity of the magnetic field was adjusted using a rheostat. The extraction process was conducted under magnetic fields of varying intensities (5-50 milliTesla (mT)). The removal rates corresponding to different magnetic field strengths are shown in Tab.3.

Table 3.

Effect of Magnetic Field on the Extraction Process

Magnetic Field Strength (mT)	Ratio (NMP:Diesel)	Aromatic Hydrocarbon Content (% mass)	Sulfur Content (% mass)
0	1:1	10	0,075
5	1:1	10	0,075
10	1:1	9	0,051
15	1:1	7	0,037
20	1:1	6	0,026
25	1:1	7	0,030
30	1:1	7	0,031
35	1:1	8	0,036
40	1:1	7	0,030
45	1:1	7	0,031
50	1:1	7	0,029

As illustrated in Table 3, the optimal extraction results were achieved at a magnetic field intensity of 20 mT.

The IR spectrum of the diesel distillate purified with N-methylpyrrolidone under different ratios and conditions following extraction is shown in Figure 6.

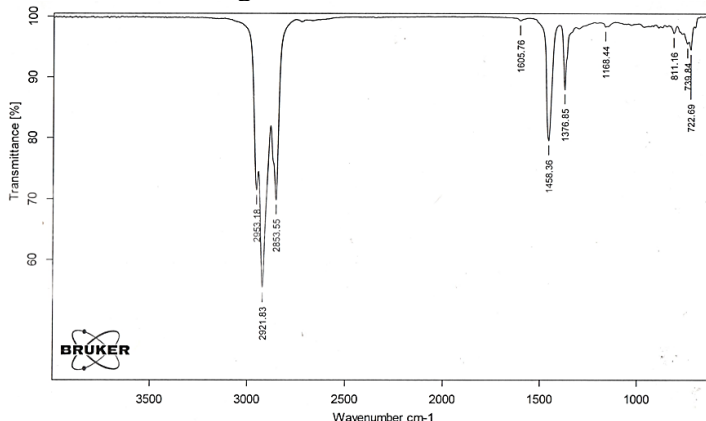


Figure 6. IR spectrum of a diesel fraction purified with N-methylpyrrolidone in a magnetic field.

Extraction of diesel distillate with a mixture of N-Methylpyrrolidone and sulfuric acid under the influence of a magnetic field

Under optimal conditions, the diesel distillate was treated using a purification process involving a mixture of N-methylpyrrolidone and sulfuric acid. The experiments were conducted under both standard conditions and in the presence of a magnetic field, employing various mixing ratios. The magnetic field intensity was maintained at 20 mT. The experimental outcomes are illustrated in Figure 7.

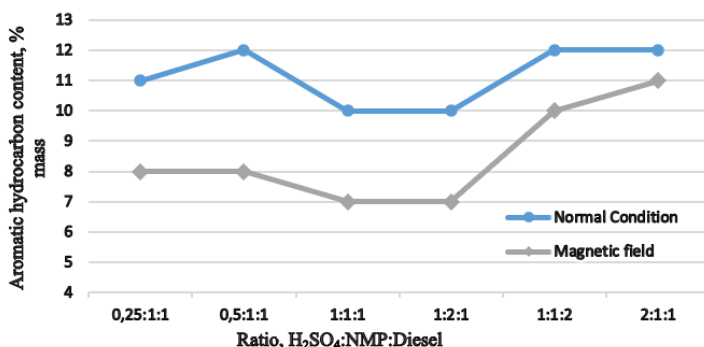


Figure 7. Influence of N-methylpyrrolidone-to-sulfuric acid mixture ratios on the purification process

As illustrated in Figure 7, the application of a magnetic field resulted in a reduction in the concentration of aromatic hydrocarbons. Under optimal conditions—comprising a 1:1:1 ratio of components, a temperature of 20°C, a stirrer rotation speed of 70 rpm, a stirring duration of 15 minutes, and a magnetic field intensity of 20 mT—the aromatic hydrocarbon content was determined to be 7% by mass.

The IR spectra of the diesel distillate subjected to extraction using a mixture of N-methylpyrrolidone and sulfuric acid in varying ratios, as well as under optimal conditions, were subsequently analyzed (Figure 8).

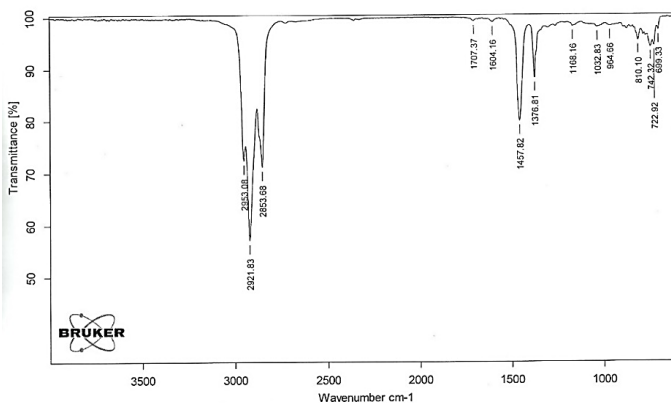


Figure 8. IR spectrum of the diesel fraction extracted using a 1:1:1 solvent mixture of N-methylpyrrolidone and sulfuric acid under the influence of a magnetic field.

Extraction of diesel distillate using a mixture of N-methylpyrrolidone and phosphoric acid under the influence of a magnetic field

Under the previously established optimal conditions, the purification of diesel distillate was conducted using a mixture of N-methylpyrrolidone and phosphoric acid as the extractant. The experiments were performed with varying mixture ratios under both standard conditions and the influence of a magnetic field, with the magnetic field intensity set at 20 mT. The experimental results are presented in Figure 9 for comparison.

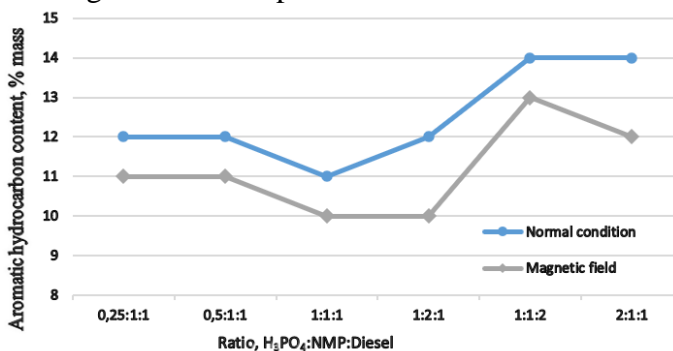


Figure 9. Influence of N-methylpyrrolidone-to-phosphoric acid mixture ratios on the purification process.

The IR spectrum of the diesel distillate purified using a mixture of N-methylpyrrolidone and phosphoric acid in different ratios and conditions following the extraction process is depicted in Figure 10.

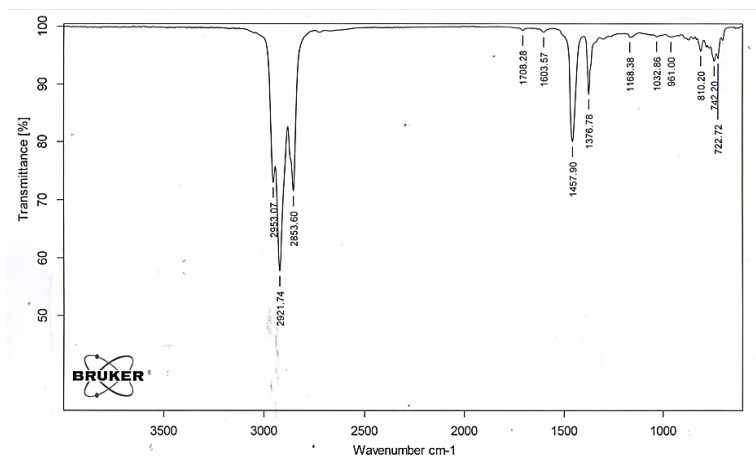


Figure 10. IR spectrum of the diesel fraction extracted using a 1:1:1 solvent mixture of N-methylpyrrolidone and phosphoric acid under the influence of a magnetic field.

Extraction of diesel distillate with a mixture of N-methylpyrrolidone and acetic acid under the influence of a magnetic field

The purification of diesel distillate using a mixture of N-methylpyrrolidone and acetic acid as the extractant was performed under optimal conditions. Experiments were conducted with varying mixture ratios under both standard conditions and the influence of a magnetic field with an intensity of 20 mT. The results are presented in Figure 11 for comparative analysis.

The IR spectra of diesel distillate purified using a mixture of N-methylpyrrolidone and acetic acid in varying ratios and under different conditions were analyzed following the extraction process. The IR spectrum for a representative sample is presented in Figure 12.

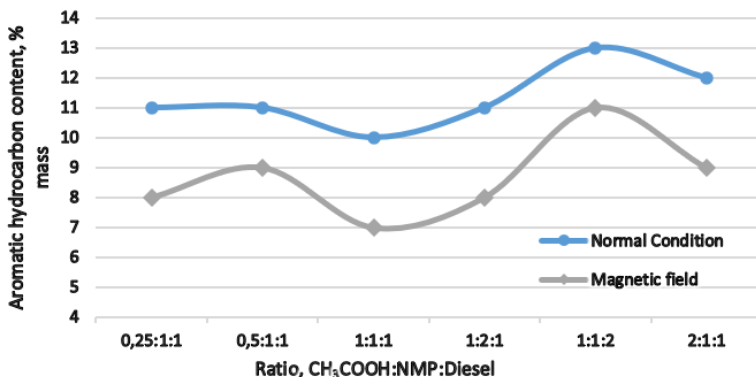


Figure 11. Influence of N-methylpyrrolidone-to-acetic acid mixture ratios on the purification process.

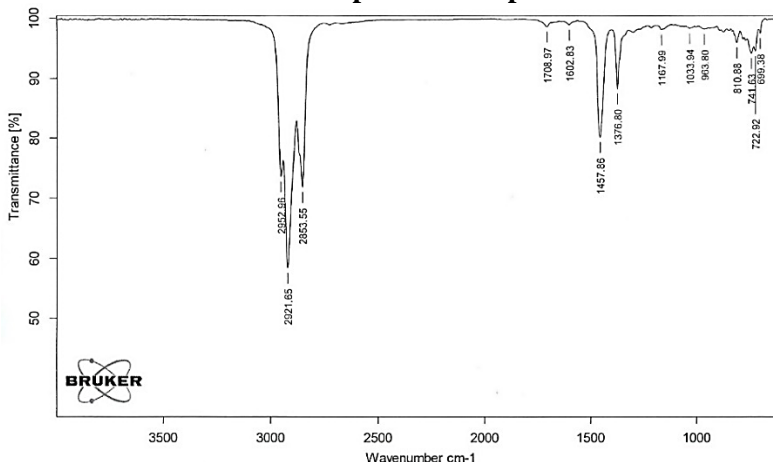


Figure 12. IR spectrum of the diesel fraction extracted using a 1:1:1 mixture of N-methylpyrrolidone and acetic acid under the influence of a magnetic field.

The quality indicators of diesel fuel purified through the extraction process under optimal conditions—using N-methylpyrrolidone (NMP), NMP under a magnetic field, NMP-sulfuric acid mixture, NMP-sulfuric acid mixture under a magnetic field, NMP-acetic acid mixture, NMP-acetic acid mixture under a magnetic field, NMP-phosphoric acid mixture, and NMP-phosphoric acid mixture under a magnetic field—are summarized in Table 4.

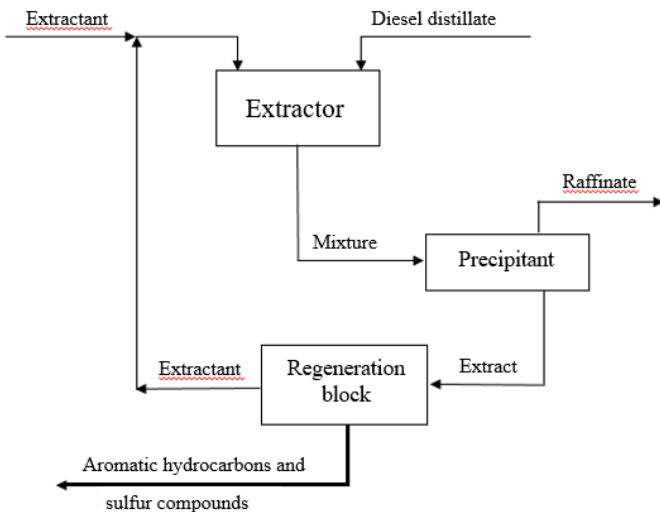
Table 4.**Quality Indicators of Diesel Fuel**

Indicators	Raw material	NMP	NMP in magnetic field	NMP Sulfate	NMP Sulfate in magnetic field	NMP Acetic acid	NMP Acetic acid in mag-field	NMP Phosphate	NMP Phosphate in mag-field
Density, at 20°C	0.8450	0.8425	0.8390	0.8460	0.8459	0.8439	0.8433	0.8449	0.8445
Total sulfur content, %	0.0895	0.075	0.026	0.047	0.028	0.068	0.031	0.058	0.026
Kinematic viscosity, mm ² /sec	6.2	4.8	4.5	4.8	4.9	4.8	4.6	5.2	5
Freezing point, °C	-36	-40	-42	-38	-40	-37	-39	-38	-39
Mist point, °C	-25	-27	-28	-26	-26	-26	-28	-26	-26
Ignition point, °C	72	67	62	64	65	66	64	65	66
Aromatic hydrocarbons, %	18.08	10	6	10	7	10	7	11	10
Boiling start, °C	222	173	175	177	179	183	181	176	178
50% boiling point, °C	296	275	275	276	280	276	276	277	275
96% boiling point, °C	357	347	345	347	350	350	350	351	350
Cetane number, minimum	46	52	55	51	52	52	53	53	52

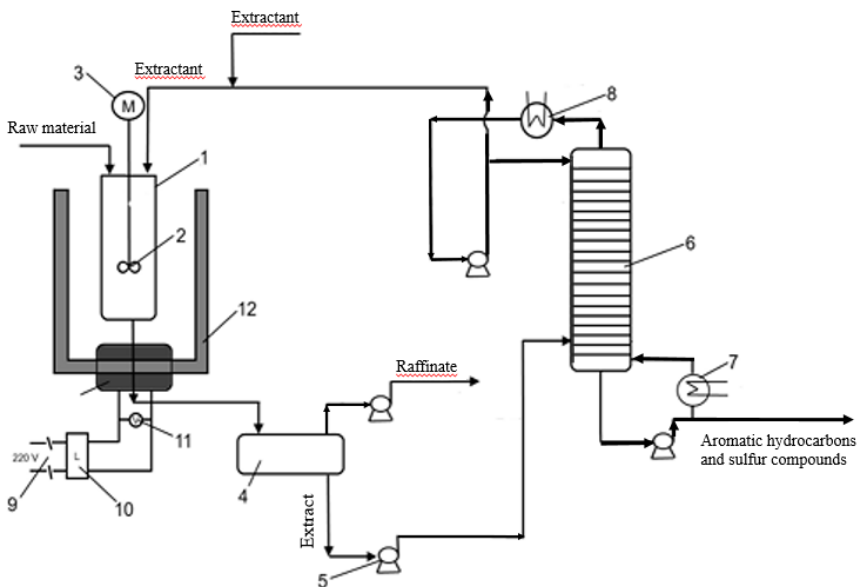
Regeneration of the solvent from the extract phase and its reintegration into the system

As previously noted, to enhance the economic efficiency of the process and develop a waste-free technology, the solvent was extracted from the extract phase and reintroduced into the system.

The block diagram illustrating the extraction and regeneration processes is presented below (Scheme 1).



Scheme 1. Block diagram of the extraction and regeneration processes. Once the block diagram of the extraction process was developed, the technological flow diagram of the process was also created (Scheme 2).



Scheme 2. Principal technological flow diagram of the diesel fraction purification process by extraction method.

The diesel fraction and extractant 1 are introduced into the extractor from the upper section. The mixture is intensively agitated by mechanical mixer 2 under the influence of a magnetic field. Once the extraction phase is completed, the mixture flows into the precipitator 4. In the precipitator, the raffinate and extract solution are separated, with the raffinate being directed from the upper section to the product pool via pump 5. The extract is taken from the lower section of the precipitator via pump 5 and transferred to the rectification column 6. Aromatic hydrocarbons are separated at the bottom of the rectification column. A portion of the solution extracted from the lower part is heated and sent to column 7 as steam for irrigation.

The remaining portion is pumped to the product pool. The purified extractant separated from the upper section of the column is cooled in heat exchanger 8 and recirculated back to the extractor, with part of it used as liquid irrigation at the top of the column. To generate the magnetic field, an electric switch 9 is connected, and the magnetic field is created within a specialized metal casing 12 by the current flowing through the copper coils. The magnetic field intensity is monitored with a teslameter, and the strength is adjusted by varying the voltage via 10.

The raffinate (extract), obtained after the regeneration of the expelled N-methylpyrrolidone, is weighed, and a material balance is established to calculate the product yield.

Mechanism and Mathematical Modeling of the Diesel Fraction Purification Process via Extraction with N-Methylpyrrolidone

Mechanism of the Process

The mechanism underlying the influence of a constant magnetic field on the complex systems formed during selective purification can be understood through the theory of oil disperse systems. When a diesel fraction is subjected to a magnetic field, the particles in the dispersed phase reorganize in a manner that redistributes the components of the complex structural unit. This redistribution is advantageous for enhancing the solubility of N-methylpyrrolidone

with respect to the undesirable polar components of the raw material. Concurrently, it reduces the solubility of the extractant concerning n- and cycloalkanes, thus increasing the solution's selectivity toward aromatic and polycyclic compounds during the purification with N-methylpyrrolidone.

As the magnetic field intensity increases, the intermolecular interactions between the aromatic components (core) and the N-methylpyrrolidone molecules on the particle surface (solvate layer) intensify. This results in a rapid transition of polycyclic aromatic compounds from the core to the solvate layer. The optimal outcome is observed at a magnetic intensity of 20 mT.

Further increments in magnetic field intensity do not significantly influence the extraction of aromatic hydrocarbons, suggesting that the magnetic field no longer impacts the interactions between the aromatic hydrocarbons and the solvent molecules on the particle surface. In this scenario, the system becomes more homogeneous, causing the solvent molecules to be surrounded by the molecules that constitute the core and solvate shell. As a result, the new complex structural unit formed from the solvent molecules is associated with the molecules that previously made up the solvate layer. Consequently, the absorption of aromatic hydrocarbons by the solvent after magnetic treatment becomes more efficient, and the selectivity of the process toward the absorption of these hydrocarbons is enhanced.

The magnetic field's effect on the diesel fraction causes the redistribution of the dispersed phase particles, leading to a shift in the molecular structure of the components. This results in an increase in the solubility of N-methylpyrrolidone towards aromatic hydrocarbons, while simultaneously reducing its solubility for normal and cycloalkanes, thus improving the selectivity of the process.

It has been determined that the application of a magnetic field to diesel fuel generates a new homogeneous, ordered, and low-viscosity structure. This structure facilitates the transfer of aromatic hydrocarbons into the solvent through both molecular and convective diffusion.

Kinetic Model of the Process

In the design of liquid-phase extraction processes, one of the primary requirements is to ascertain the kinetic characteristics of the exchange processes. These characteristics are essential for determining the mass flow rates and component distributions within the system.

The development of reliable mass transfer models facilitates the creation of a mathematical representation of mass exchange processes in two-phase systems. This approach is crucial for the design of mass transfer devices, enabling the use of minimal experimental data collected during laboratory-scale studies.

When applying extraction processes in industrial settings, it is considered practical to conduct studies using laboratory-scale mixer-type extractors. The mass transfer equation for the primary (overall) phase in column-type extractors can be expressed as follows:

$$(\vec{V}_V)\vec{V} = -\frac{1}{\rho_2}P + \nabla[(v + v_T)_2\nabla\vec{V}] + \vec{r}_p \quad (1)$$

$$\text{div } \vec{V} = 0 \quad (2)$$

$$(\vec{V}_V)C_2 = \nabla[(D + D_T)_2\nabla C_2] + r_0 \quad (3)$$

where : V – Volume of the entire phase;

ρ_2 – Density of the dispersed phase;

P – Pressure gradient;

v – Kinematic viscosity coefficient of the entire phase;

D and DT Molecular and turbulent diffusion coefficients, respectively;

∇C_2 – Concentration gradient of the distributed substance.

Considering the boundary conditions, the expressions (1) to (3) correspond to the material balance equation:

$$G_1 dC_1 = -G_2 dC_2 \quad (4)$$

Here G_1 –represents the mass of the phase,

dC_1 and dC_2 - denote the initial and final concentrations of the distributed substance in the main phase, respectively.

The relationship between the mass flows is given by the following equation:

$$\beta_2(C_{bd2} - C_2) = \beta_1(C_1 - C_{bd1}) \quad (5)$$

The equilibrium equation at the interface between the two phases is as follows:

$$C_{bd2} = m C_{bd1} + b \quad (6)$$

This equation provides a comprehensive mathematical description of mass exchange processes in two-phase systems, encompassing all exchange mechanisms.

To determine the mass transfer coefficient, a mathematical model was developed, drawing on the Chilton-Colborne hydrodynamic analogy and the generalization of the Landau-Levich boundary layer model for the flows involved in the process.

In this study, the laminar flow regime of dispersed particles ($Re < 200$, indicating laminar flow) was considered.

The following equation is proposed to calculate the mass transfer rate in a process where the mass transfer coefficient remains constant in both the bulk and dispersed phases:

$$\beta_1 = 0.62 \left(\frac{\tau v}{\delta_1} \right)^{1/3} Sc^{-\frac{n-1}{n}} \quad (7)$$

In the droplet δ_1 changes over time according to the following equation.

$$\delta_1 = \varphi \sqrt{D_1 t} \quad (8)$$

where δ_1 - is the effective thickness of the diffusion layer,
 τ - is the shear stress,
 ν - represents the kinematic viscosity coefficient,
 n - denotes the number of nuclei.

The primary resistance to mass transfer within both the bulk and dispersed phases is concentrated in the viscous layer. This is particularly the case when the Schmidt number $SC > 1$,

$$\frac{1}{\beta_1} = \int_0^{\delta_B} \frac{dy}{(B + D_T)_1} \quad (9)$$

By integrating equation (9), we obtain the equation used to calculate the mass transfer coefficient across the entire phase.

$$\beta_2 = \frac{u_2}{\arctg \sqrt{R_{\delta_2} Sc_2} \sqrt{R_{\delta_2} Sc_2}} \quad (10)$$

The mass transfer coefficient in the dispersed phase is

expressed as follows:

$$\beta_1 = u_1 \sqrt{\frac{u_1 \rho_1 D_1}{2\sigma}} \left[\operatorname{arctg} \sqrt{Sc_1 \frac{u_1 R_{\delta_1}^2 v_1 \rho_1}{2\sigma}} \right]^{-1} \quad (11)$$

It is important to note that the hydrodynamic behavior of two-phase flows differs from that of single-phase flows. In two-phase systems, the formation of a turbulent boundary layer occurs at lower Reynolds numbers compared to single-phase flows. Consequently, the boundary layer in the dispersed phase is considered pseudolaminar. Specifically, in the initial region, the boundary layer exhibits a laminar nature, while turbulence in the external flow induces the formation of the boundary layer.

The graphs below illustrate the calculated and experimental values of the mass transfer coefficients in the integral and dispersed phases, based on the aforementioned equations (10, 11). Figure 13 presents the relationship between the experimental and calculated values of the mass transfer coefficient in the integral phase and nd_q .

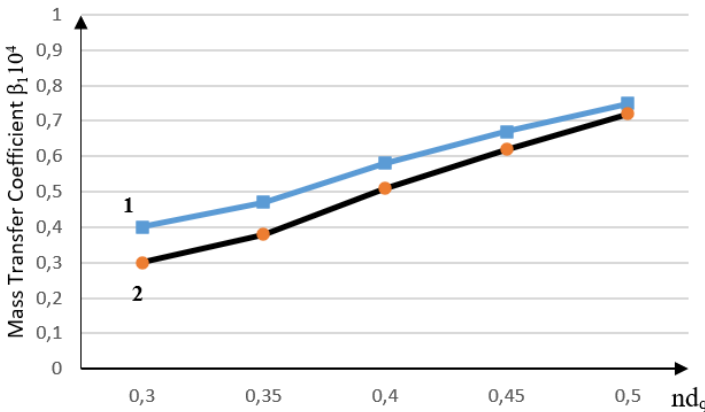


Figure 13. Relationship Between Experimental (1) and Calculated Values (2) of the Mass Transfer Coefficient in the Bulk Phase with Respect to nd_q .

The relationship between the experimental and calculated values of the mass transfer coefficient in the dispersed phase with respect to nd_q is illustrated in Fig. 14 below.

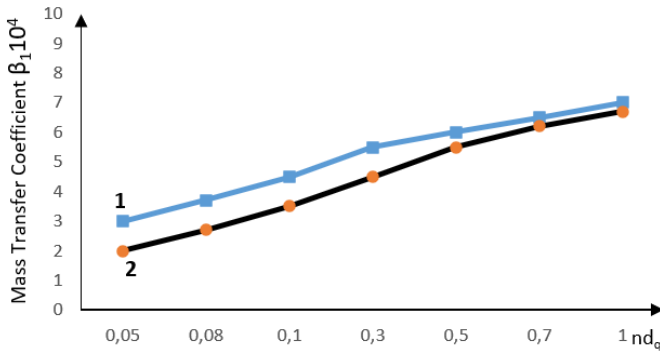


Figure 14. Relationship between experimental (1) and calculated values (2) of the mass transfer coefficient in the dispersed phase as a function of nd_q .

The developed computational algorithm for determining velocity and density fields within the mixer-extractor enables the calculation of separation efficiency and facilitates the selection of optimal design and operating parameters. Using equations (10) and (11), the calculated mass transfer coefficients for both the bulk and dispersed phases closely align with the experimental values, as demonstrated in Figs. 13 and 14.

The algorithm for calculating velocity and density fields enables the determination of effective solubility, optimal structural configuration, and operational parameters in mixer-type extractors.

The developed mathematical model provides a detailed description of mass transfer processes in both the bulk and dispersed phases, highlighting the driving force of the process and the characteristics of the interphase boundary layer.

Comprehensive technical and economic indicators of the process are detailed in the associated dissertation work. According to the report, the economic efficiency of the process was calculated at 291 AZN/t. Laboratory calculations indicate that the production cost of 1 g of diesel distillate is approximately 0.0292 coins, resulting in a target product cost of 292 AZN/t.

Given the wholesale price of diesel fuel in the country, currently 583 AZN/t, the process demonstrates notable economic viability.

It is important to emphasize that this study serves as a preliminary feasibility analysis. Further recalculations and

refinements will be undertaken upon the industrial implementation of the process, taking into account updated consumption rates and revised costs of raw materials and other inputs.

Table 5.

Economic Indicators of the Diesel Distillate Production Process

Obtained	Mass, gr	Intrinsic, kop/gr	Total quantity, units
Obtained:			
1. N-methylpyrrolidone	30,11	0,34	10,24
2. Diesel Distillate	29,9	0,018	0,55
Total:	60,01		10,79
Operating expenses:			
Electricity energy			0,18
Total:			10,97
Loss:	1,55		
Acquired:			
Non-calculated product:			
N-methylpyrrolidone	29,0	0,34	9,86
Extract	2,77	0,12	0,33
Total:	31,77		10,19
Calculated product:			
Refined:	26,69	0,0292	0,78

CONCLUSION

1. To produce high-quality diesel fuel meeting EURO-5 standards, the initial purification of the diesel fraction, directly obtained from distillation at the Oil Refinery named after H.Aliyev, was performed through an extraction method. This is a first time of process was conducted under the influence of a magnetic field, utilizing N-methylpyrrolidone as the extractant [1-3,9,11,18,19].
2. The optimal operational parameters for the extraction process, conducted in a mechanical mixer extractor, were identified as follows[17]:
 - temperature, 20°C
 - pressure, 760 mm.Hg
 - diesel fraction to N-methylpyrrolidone ratio: 1:1
 - mixer rotational speed: 70 stg/min
 - magnetic field intensity: 20 mT

Under these conditions, the concentration of aromatic hydrocarbons reduced from 18.08% to 10% (mass, %), while the sulfur content decreased from 0.0895% to 0.075% (mass, %). When subjected to a magnetic field, the values for aromatic hydrocarbons and sulfur further decreased to 6% and 0.026%, respectively [21].

3. The extraction process was performed with the inclusion of acetic, phosphoric, and sulfuric acids, yielding the following results [12,16]:
 - N-methylpyrrolidone: acetic acid: diesel distillate (1:1:1) [8,14,23]:
 - Aromatic hydrocarbons: 10%, sulfur: 0.068%
 - Under a magnetic field: aromatic hydrocarbons: 7%, sulfur: 0.031%
 - N-methylpyrrolidone: phosphoric acid: diesel distillate (1:1:1) [6]:
 - Aromatic hydrocarbons: 11%, sulfur: 0.058%
 - Under a magnetic field: aromatic hydrocarbons: 10%, sulfur: 0.026%
 - N-methylpyrrolidone: sulfuric acid: diesel distillate (1:1:1) [7,13]:
 - Aromatic hydrocarbons: 10%, sulfur: 0.047%
 - Under a magnetic field: aromatic hydrocarbons: 7%, sulfur: 0.028%.
4. The rectification process enabled the separation of the solvent from the extract phase and its subsequent recycling, establishing a waste-free technology [4,5].
5. The mechanism of the process has been investigated, and it has been determined that the application of a magnetic field to diesel fuel induces a novel homogeneous, structured, and low-viscosity configuration, facilitating the transfer of aromatic hydrocarbons to the solvent via molecular and convective diffusion [10,15,20].
6. A mathematical model of the process was developed and based on it, a detailed analysis of mass transfer in the integral and dispersed phases was conducted, highlighting the process's driving force and the characteristics of the interphase boundary layer [22].
7. The technical and economic parameters of the process were evaluated, revealing an economic efficiency of 291 AZN/ton [21].

8. A technological guidelines for its industrial implementation were developed.

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The defense will be held on 07 March 2025 at 10⁰⁰ at the meeting of the Dissertation council ED 1.17 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Institute of Petrochemical Processes named after academician Y.H.Mammadaliyev of Republic of Azerbaijan Ministry of Science and Education

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Abstract was sent to the required addresses on 06 February 2025.

Signed for print: 31.01.2025

Paper format: A5

Volume: 38015

Number of hard copies: 20