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MODERN APPROACHES TO THE STUDY OF SULFUR-CONTAINING COMPOUNDS IN PETROLEUM AND METHODS FOR THEIR CONTROL AND REMOVAL

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Abstract: *Sulfur-containing compounds are among the most significant impurities in crude oil, determining the quality of motor fuels, the efficiency of petroleum refining, and the environmental characteristics of final products. This paper summarizes current views on the origin, composition, and distribution of sulfur compounds in different petroleum fractions. A comparative analysis of analytical methods for sulfur determination is presented, including X-ray fluorescence spectrometry, ultraviolet fluorescence, chromatographic, and electrochemical methods. The technological and environmental consequences of the presence of sulfur compounds in crude oil and petroleum products are considered. Modern approaches to desulfurization are compared, including hydrodesulfurization, oxidative, adsorption, extraction, and biotechnological desulfurization. It is shown that the most promising strategies are combined methods for deep purification of heavy petroleum fractions, based on the integration of selective catalytic systems, energy-efficient processes, and modern analytical platforms that provide rapid control of sulfur content directly within the technological cycle.*

Keywords: *petroleum, petroleum products, sulfur-containing compounds, desulfurization, hydrodesulfurization, analytical control.*

NEFT TARKIBIDAGI OLTINGUGURTLI BIRIKMALARNI TADQIQ ETISH VA ULARNI NAZORAT QILISH HAMDA YO‘ QOTISHNING Z AMONAVIY YONDASHUVLARI

Annotatsiya: *Oltingugurt saqlovchi birikmalar neft xomashyosidagi eng muhim qo‘ shimchalardan biri bo‘ lib, motor yoqilg‘ ilarining sifati, neftni qayta ishlash samaradorligi va yakuniy mahsulotlarning ekologik xususiyatlarini belgilaydi. Ushbu ishda turli neft fraksiyalaridagi oltingugurt birikmalarining kelib chiqishi, tarkibi va taqsimlanishi haqidagi zamonaviy qarashlar umumlashtirilgan. Oltingugurtni aniqlashning analitik usullari, jumladan rentgen-fluorestsent spektrometriya, ultrabinafsha fluorestsensiya, xromatografik va elektrokimyoviy usullar qiyosiy tahlil qilingan. Neft va neft mahsulotlarida oltingugurtli birikmalar mavjudligining texnologik hamda ekologik oqibatlari ko‘ rib chiqilgan. Gidrotozalash, oksidlovchi, sorbsion, ekstraksion va biotexnologik desulfurizatsiyani o‘ z ichiga olgan zamonaviy oltingugurtni yo‘ qotish usullari taqqoslangan. Og‘ ir neft fraksiyalarini chuqur tozalashning eng istiqbolli yo‘ nalishlari selektiv katalitik tizimlar, energiya tejamkor jarayonlar hamda texnologik sikl davomida oltingugurt miqdorini tezkor nazorat qilish imkonini beruvchi zamonaviy analitik platformalarni birlashtiruvchi kompleks usullar ekanligi ko‘ rsatildi.*

Kalit so‘ zlar: *neft, neft mahsulotlari, oltingugurtli birikmalar, desulfurizatsiya, gidrotozalash, analitik nazorat.*

СОВРЕМЕННЫЕ ПОДХОДЫ К ИССЛЕДОВАНИЮ СЕРОСОДЕРЖАЩИХ СОЕДИНЕНИЙ НЕФТИ И МЕТОДАМ ИХ КОНТРОЛЯ И УДАЛЕНИЯ

Аннотация: *Серосодержащие соединения относятся к числу наиболее значимых примесей нефтяного сырья, определяющих качество моторных топлив, эффективность нефтепереработки и экологические характеристики конечной продукции. В работе обобщены современные представления о происхождении, составе и распределении соединений серы в нефтяных фракциях различного типа. Проведён сравнительный анализ методов аналитического определения серы, включая рентгенофлуоресцентную спектрометрию, ультрафиолетовую флуоресценцию, хроматографические и*

электрохимические методы. Рассмотрены технологические и экологические последствия присутствия сернистых соединений в нефти и нефтепродуктах. Выполнено сопоставление современных подходов к десульфуризации, включающих гидроочистку, окислительное, сорбционное, экстракционное и биотехнологическое обессеривание. Показано, что наиболее перспективными являются комбинированные методы глубокой очистки тяжёлых нефтяных фракций, основанные на сочетании селективных каталитических систем, энергоэффективных процессов и современных аналитических платформ, обеспечивающих оперативный контроль содержания серы непосредственно в технологическом цикле.

Ключевые слова: *нефть, нефтепродукты, серосодержащие соединения, десульфуризация, гидроочистка, аналитический контроль.*

Introduction

Crude oil is a complex multicomponent system composed of a wide variety of hydrocarbon and heteroatomic compounds. In addition to hydrocarbons, petroleum contains oxygen-, nitrogen-, metal-, and sulfur-containing compounds that significantly affect the physicochemical properties of crude oil and the characteristics of its processing [1,2]. Among these heteroatomic constituents, sulfur-containing compounds are of particular importance because they largely determine the quality of petroleum products, the stability of process equipment, and the environmental characteristics of fuels [3].

Depending on sulfur content, crude oils are classified as low-sulfur, sulfurous, and high-sulfur. An increase in the concentration of sulfur compounds complicates the transportation and refining of crude oil, promotes equipment corrosion, and necessitates additional purification stages [4,5].

The composition of sulfur-containing compounds in petroleum systems is highly diverse. Crude oil contains mercaptans, sulfides, disulfides, thiophenes, benzothiophenes, and dibenzothiophenes [2]. Among them, alkyl-substituted dibenzothiophenes present the greatest technological challenge because of their high chemical stability and low reactivity under conventional hydrodesulfurization conditions [6,7].

The growing interest in sulfur removal is associated with increasingly stringent environmental regulations governing the quality of motor fuels. Current international standards limit sulfur content in gasoline and diesel fuels to approximately 10 mg/kg [8]. Compliance with these requirements has stimulated the development of highly efficient desulfurization technologies and the improvement of analytical methods for determining ultralow sulfur concentrations [9,10].

Sulfur compounds adversely affect most petroleum refining processes. Under high-temperature conditions, they accelerate corrosion, cause catalyst deactivation, and contribute to the formation of resinous and coke deposits [11,12]. During fuel combustion, sulfur compounds are converted into sulfur oxides, which participate in the formation of acid precipitation and atmospheric pollution [13].

At present, sulfur in crude oil and petroleum products is determined using X-ray fluorescence [14,17], fluorescence [15], chromatographic, and electrochemical analytical methods [16,17]. Particular attention is being paid to electroanalytical systems that combine high sensitivity, the possibility of miniaturization, and rapid measurement capabilities [18–20].

Despite advances in deep purification technologies, the effective removal of refractory organosulfur compounds remains an important challenge [5,21–23]. Consequently, combined catalytic [21,24], oxidative [22,25], sorption-based [26,27], and biotechnological approaches [28,29] aimed at achieving deeper desulfurization of heavy petroleum fractions are being actively investigated.

The aim of this study was to systematize current data on the composition and distribution of sulfur-containing compounds in crude oil and to comparatively analyze methods for their analytical determination as well as technologies for sulfur removal from petroleum feedstocks and petroleum products.

Materials and Methods

The informational basis of the study consisted of publications from leading international peer-reviewed journals and specialized industrial editions published between 2023 and 2026, focusing on the analytical determination of sulfur, petroleum product quality monitoring, and modern desulfurization technologies [9,30].

The selection of literature sources was based on the relevance of the studies, the reliability of experimental data, the reproducibility of analytical procedures, and the practical significance of the reported results for the petroleum refining industry. The review included studies containing data on the quantitative determination of sulfur, comparative evaluations of analytical techniques, and the efficiency of sulfur removal processes.

The methodological framework of the study was based on a comparative analytical approach involving the systematization of published data and the comparison of results obtained by different research groups. The sensitivity, selectivity, limits of detection, analysis time, and sample preparation requirements of various sulfur determination methods were comparatively evaluated.

In addition, a comparative assessment of current technologies for reducing sulfur content in petroleum feedstocks was performed, including catalytic hydrodesulfurization, oxidative desulfurization, sorption and extraction processes, as well as biotechnological methods for the removal of organosulfur compounds.

Results and Discussion

Origin and Distribution of Sulfur-Containing Compounds in Petroleum Feedstocks

The presence of sulfur in crude oil is associated with a combination of geochemical and biochemical processes occurring in sedimentary basins during the transformation of organic matter [1–3]. Anaerobic microorganisms play a significant role in this process by reducing sulfates to hydrogen sulfide, which subsequently participates in reactions leading to the formation of organosulfur compounds [28,29].

Sulfur-containing components in petroleum occur in both inorganic and organic forms. The most common species include hydrogen sulfide, mercaptans, sulfides, disulfides, thiophenes, benzothiophenes, and dibenzothiophenes. Their quantitative distribution depends on the origin of the crude oil, the degree of its thermal maturation, and its fractional composition.

Light petroleum fractions are characterized predominantly by low-molecular-weight mercaptans and sulfides, whereas heavy distillates contain increased amounts of polycyclic aromatic sulfur compounds [1,2]. Among these compounds, alkyl-substituted dibenzothiophenes are considered the most refractory because the sulfur atom is sterically shielded by hydrocarbon substituents, significantly hindering hydrodesulfurization processes [22].

Figure 1 presents a generalized scheme illustrating the distribution of the major classes of sulfur-containing compounds among petroleum fractions as a function of boiling point and molecular weight.

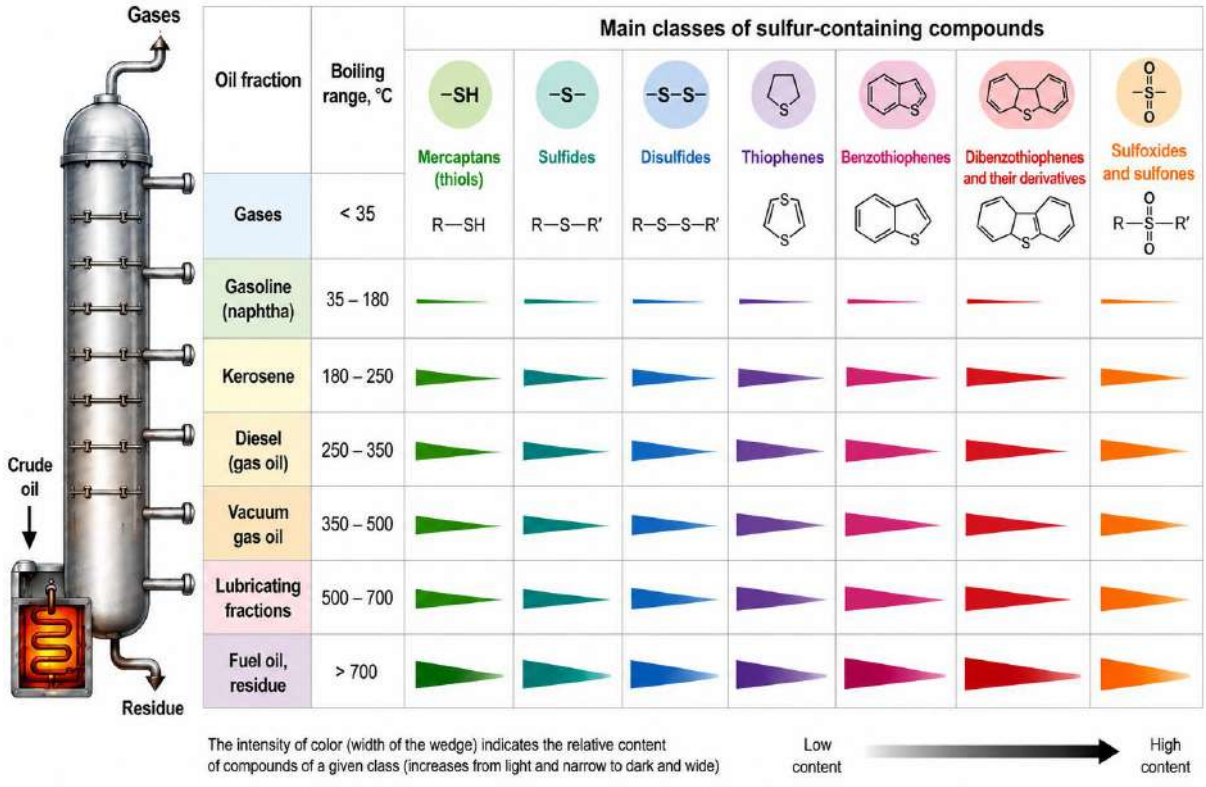


Figure 1. Distribution of the Main Classes of Sulfur-Containing Compounds in Petroleum Fractions

Influence of Sulfur-Containing Compounds on the Properties of Crude Oil and Petroleum Products

Sulfur-containing compounds exert a negative impact on petroleum refining processes, the performance characteristics of fuels, and the environmental safety of petroleum products. The most reactive sulfur species cause intensive corrosion of processing equipment, particularly in the presence of moisture and at elevated temperatures [11,12].

High-molecular-weight heterocyclic sulfur compounds are capable of participating in thermal condensation reactions leading to the formation of resinous substances and coke deposits [5]. This results in catalyst deactivation and deterioration of the operational efficiency of refining units [3,24].

The environmental consequences associated with the use of high-sulfur fuels are primarily related to the formation of sulfur oxides during fuel combustion. These compounds contribute to acid precipitation and the generation of toxic atmospheric aerosols, thereby adversely affecting environmental quality [13].

To systematize the major consequences associated with the presence of sulfur in crude oil and petroleum products, Table 1 summarizes the most characteristic effects of different classes of sulfur-containing compounds on the technological and environmental properties of petroleum products.

The obtained data indicate that the chemical nature and distribution of sulfur-containing compounds directly determine both the technological complexity of petroleum refining and the environmental characteristics of final petroleum products. This necessitates the development of highly efficient analytical control methods and the improvement of deep desulfurization technologies.

Table 1. Influence of the Main Classes of Sulfur-Containing Compounds on the Technological and Environmental Characteristics of Petroleum Products

Sulfur-Containing Compound	Characteristic Impact
Hydrogen sulfide	High toxicity and accelerated equipment corrosion
Mercaptans	Strong unpleasant odor, susceptibility to oxidation and corrosion
Sulfides and disulfides	Formation of resins and carbonaceous deposits
Thiophenes	Catalyst deactivation and reduced catalytic activity
Dibenzothiophenes	Resistance to hydrodesulfurization and accumulation in heavy fractions

Modern Methods for Analytical Determination of Sulfur

At present, a wide range of methods for sulfur determination in crude oil and petroleum products has been developed, including spectroscopic, chromatographic, and electrochemical approaches [9,10].

One of the most widely used techniques for total sulfur determination is ultraviolet fluorescence analysis, which is based on sample combustion followed by the determination of SO_2 according to fluorescence intensity [17]. This method is characterized by high sensitivity and good reproducibility of results.

X-ray fluorescence analysis is distinguished by its high measurement speed and minimal sample preparation requirements. Modern wavelength-dispersive systems allow sulfur determination at concentrations below 0.2 ppm [14].

Ion chromatography methods combined with thermal decomposition are employed for the analysis of heavy petroleum fractions and enable the simultaneous determination of sulfur and halogen-containing compounds.

In recent years, electrochemical analytical methods based on modified screen-printed electrodes have been actively developed [18,19]. Such systems provide high sensitivity, compact instrumentation, and the possibility of rapid on-site analysis directly at sampling locations.

Table 2 summarizes modern analytical methods used for sulfur determination in crude oil and petroleum products.

Table 2. Modern Analytical Methods for Sulfur Determination in Crude Oil and Petroleum Products

Method	Determined Sulfur Forms	Advantages	Limitations
UV fluorescence analysis	Total sulfur	High sensitivity	Requires sample combustion
X-ray fluorescence analysis	Total sulfur	No sample preparation required	Matrix effects
Ion chromatography	Sulfates and oxidation products	High selectivity	Complex sample preparation
Potentiometric titration	Active sulfur	Simplicity	Limited sensitivity
Electrochemical methods	Hydrogen sulfide, mercaptans	Rapid analysis	Electrode modification required

Technological Approaches to Reducing Sulfur Content in Petroleum Feedstocks

The principal industrial method for removing sulfur-containing compounds remains catalytic hydrodesulfurization, which is based on the interaction of organosulfur compounds with hydrogen in the presence of heterogeneous catalysts. The process is carried out at elevated temperatures and pressures using molybdenum-based catalysts promoted with nickel or cobalt [24].

Despite its high industrial efficiency, conventional hydrodesulfurization is insufficiently effective for the removal of alkyl-substituted dibenzothiophenes [4,5]. Steric shielding of the sulfur atom decreases the accessibility of active molecular sites for catalytic interaction.

As alternative approaches, oxidative desulfurization methods are being extensively investigated. In these processes, sulfur-containing compounds are converted into more polar sulfoxides and sulfones, which can subsequently be removed by extraction or sorption techniques.

Considerable interest has also been directed toward sorption technologies employing zeolites, carbon-based materials, metal–organic frameworks, and nanostructured adsorbents. The main advantages of these methods include mild operating conditions and environmental safety; however, their relatively limited sorption capacity still restricts large-scale industrial application.

Extraction methods are based on the use of polar solvents and ionic liquids for the selective removal of organosulfur compounds. These processes are characterized by comparatively simple process design, although subsequent regeneration of the extractants is required.

A separate research direction involves biodesulfurization, which is based on the ability of microorganisms to cleave carbon–sulfur bonds in organic molecules [31]. Biocatalytic processes proceed under mild conditions and are characterized by reduced energy consumption; however, their practical application is limited by the relatively low rate of biochemical transformations.

Figure 2 illustrates the principal desulfurization methods currently employed in the petroleum industry.

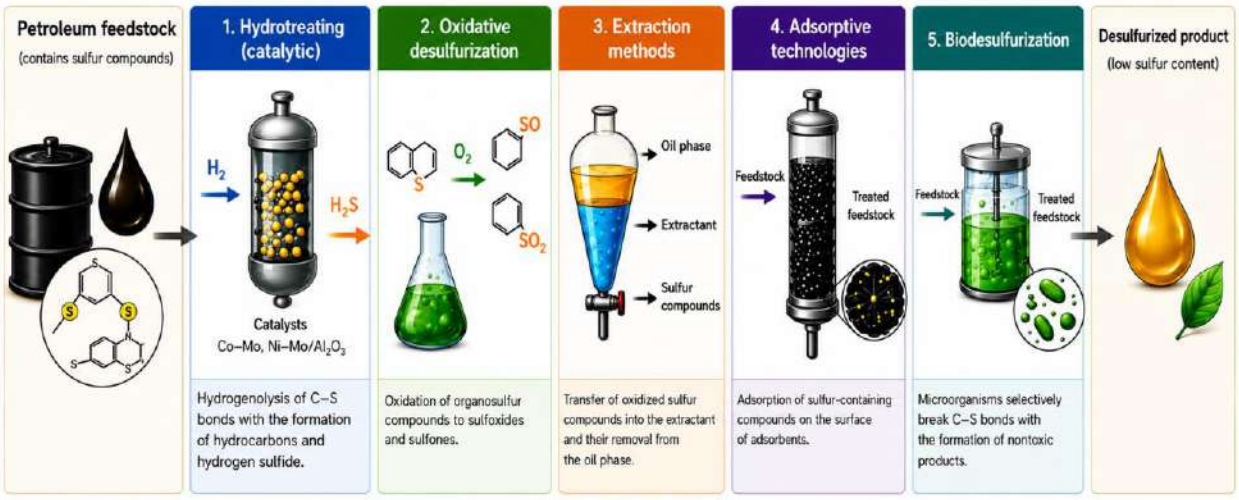


Figure 2. Modern Methods of Petroleum Desulfurization

To compare the principal advantages and limitations of current purification technologies, Table 3 presents a comparative characterization of the most widely used desulfurization methods.

Table 3. Comparative Characteristics of Technologies for Sulfur Removal from Petroleum Feedstocks

Desulfurization Method	Main Advantages	Main Limitations
Catalytic hydrodesulfurization	High productivity and well-established industrial implementation	High energy consumption and incomplete removal of refractory thiophenes
Oxidative desulfurization	Enhanced selectivity toward aromatic sulfur compounds	Requirement for oxidizing agents and additional purification stages
Extraction methods	Simple process design and equipment configuration	Limited efficiency of sulfur compound extraction
Sorption technologies	Environmental safety and mild operating conditions	Relatively low sorption capacity of adsorbent materials
Biodesulfurization	Energy efficiency and selective cleavage of C–S bonds	Low rate of biochemical transformations

Conclusion

The conducted analysis demonstrated that sulfur-containing compounds exert a significant influence on petroleum refining processes, the quality of motor fuels, and the environmental characteristics of petroleum products. It was established that light petroleum fractions predominantly contain low-molecular-weight sulfur compounds, whereas heavy distillates are characterized by increased concentrations of refractory polycyclic thiophenic structures.

Sulfur compounds were shown to promote equipment corrosion, catalyst deactivation, the formation of resinous and coke deposits, and increased emissions of sulfur oxides into the atmosphere. These factors highlight the necessity for improving both analytical control methods and deep desulfurization technologies.

A comparison of modern sulfur determination techniques indicates the high efficiency of X-ray fluorescence, fluorescence, and chromatographic analytical methods. Electrochemical sensor systems based on modified screen-printed electrodes remain a particularly promising direction due to their capability for rapid and sensitive on-site monitoring under industrial conditions.

It was also established that conventional hydrodesulfurization is insufficiently effective for the removal of refractory aromatic sulfur compounds. Therefore, combined desulfurization technologies integrating catalytic, oxidative, sorption-based, and biotechnological approaches appear to be the most перспективными for achieving deeper sulfur removal from petroleum feedstocks and petroleum products.

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