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STRATEGIC ROLE OF THE OIL AND GAS INDUSTRY IN THE ECONOMY OF UZBEKISTAN AND SCIENTIFIC-TECHNOLOGICAL PRINCIPLES OF DIESEL FUEL HYDROTREATING PROCESSES

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Abstract

This paper analyzes the role of Uzbekistan's oil and gas processing industry in ensuring the country's economic, social, and environmental stability. Using the Bukhara oil refinery as a case study, the dynamics of diesel fuel production and modernization processes within the sector are examined. Furthermore, the chemical mechanism of the hydrotreating process for diesel fractions, as well as hydrogenation reactions of organic sulfur, nitrogen, and oxygen compounds, are detailed.

Keywords: Oil and gas industry, economy of Uzbekistan, Bukhara oil refinery, Euro-5, hydrotreating, catalyst, sulfur compounds, hydrogenation, mass transfer, environmental sustainability.

Introduction The oil and gas industry serves as a strategic "locomotive" of Uzbekistan's economy, contributing a significant portion of the country's GDP. The primary objective of the sector is to produce high-value-added products (gasoline, diesel, polymers) through deep processing of raw materials and to enhance export potential. Additionally, the industry plays a central role in creating hundreds of thousands of jobs and transitioning toward a "green economy."

Main Part As a result of tightening global environmental requirements and "Euro" standards, diesel fuel production quality at the Bukhara Oil Refinery has undergone three main stages of technological transformation. In the first stage (1997–2010), the primary focus was on ensuring stable domestic supply, producing L-0.5 and L-0.2 grade fuels with high sulfur content (2000–5000 ppm). In the second stage (2010–2020), this figure was reduced to 350–500 ppm (Euro-2, 3) through the modernization of hydrotreating units. In the modern stage, which began in 2020, the production of premium-class Euro-4, 5, and 6 standard fuels with a sulfur content of only 10–50 ppm was established.

This was achieved through the utilization of new-generation cobalt-molybdenum catalysts and integration with synthetic components from the Shurtan GTL plant. Such a systemic evolution has not only increased the international competitiveness of the product but also significantly reduced toxic gas emissions into the atmosphere, serving as a crucial factor in implementing Uzbekistan's "green economy" strategy.

The evolution of diesel fuel over the years is inextricably linked with the tightening of environmental requirements in Uzbekistan.

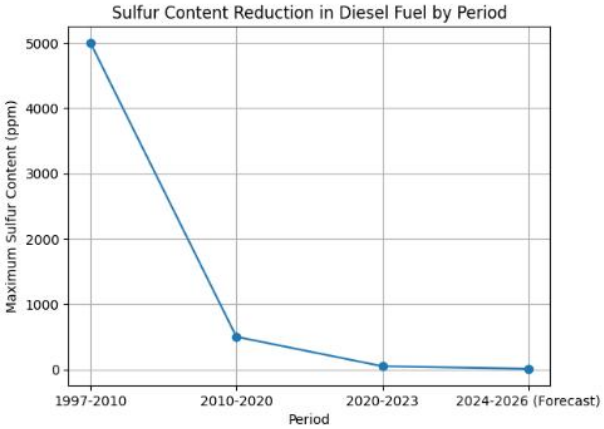


Figure 1. Dynamics of Sulfur Content Reduction

Table 1 below presents the dynamics of diesel fuel production at the Bukhara oil refinery.

Table 1. Dynamics of diesel fuel production at the bukhara oil refinery

Period	Grades	Sulfur Content (S)	Average Annual Volume (thousand tons)	Remarks
1997 –2010 yy.	L-0,5 and L-0,2	2000 – 5000 ppm	800 – 1000	Designed for older generation diesel engines
2010 –2020 yy.	Evro-2, Evro-3	350 – 500 ppm	1000 – 1100	First stage of refinery modernization
2020 –2023 yy.	Yевро-4, Евро-5	10 – 50 ppm	1000 – 1100	Stable industrial-scale production established
2024 –2026 йй.	Евро-5, Евро-6	< 10 ppm	1100 – 1300	Euro-6 samples obtained based on GTL components

Chemical characterization of the process. The hydrotreating process is fundamentally based on catalytic hydrogenation, where organic sulfur (sulfides, thiophenes, disulfides, mercaptans), nitrogen (pyridine, pyrrole), and oxygenated compounds (phenols) are converted into hydrocarbons in the presence of a catalyst and hydrogen. This transformation yields hydrogen sulfide (H_2S), ammonia (NH_3), and water (H_2O) as by-products. Alongside the primary hydrogenation of heteroatomic and organometallic compounds, several parallel reactions occur, including the saturation of unsaturated hydrocarbons, isomerization of naphthenes and paraffins, hydrogeneration of organochlorine compounds, and hydrocracking. At elevated temperatures, partial dehydrogenation of naphthenic hydrocarbons and the formation of ammonium chloride or coke may also be observed. Furthermore, organometallic compounds undergo transformation, with metallic components adsorbing onto the catalyst surface. The overall depth and kinetics of these reactions are governed by the catalyst's properties, process parameters, and the physicochemical characteristics of the feedstock.

During hydrotreating, organic sulfur compounds are converted into hydrogen sulfide (H_2S) and hydrocarbons, the structure of which directly depends on the initial sulfuric precursors. As the molecular weight of petroleum fractions increases, the rate of hydrodesulfurization (HDS) generally declines. Among these, acyclic sulfides react with hydrogen to form corresponding alkanes and H_2S through a two-stage mechanism involving the sequential cleavage of carbon-sulfur (C-S) bonds. While increased branching and molecular weight slightly reduce reaction

kinetics, acyclic sulfides remain significantly more reactive and easier to decompose compared to more stable structures such as thiophenes.

Reactions of organic sulfur compounds. During the hydrotreating process, organic sulfur compounds are converted into hydrogen sulfide (H_2S) and hydrocarbons. The structure of the resulting hydrocarbons is directly determined by the composition of the initial sulfur-containing precursors. As the molecular weight of petroleum fractions increases, the rate of hydrodesulfurization (HDS) tends to decrease.

Sulfides. Acyclic sulfides react with hydrogen during hydrotreating to form corresponding alkanes and H_2S. This reaction typically occurs in two stages: first, one of the carbon-sulfur (C-S) bonds is cleaved, followed by the hydrogenation of the second bond. This sequence ensures the complete removal of sulfur from the feedstock.

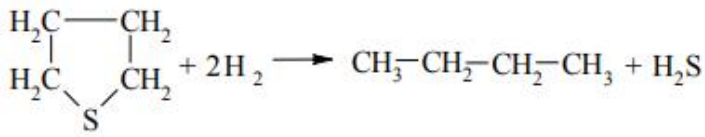
The hydrogenation rate of sulfides depends significantly on their chemical structure. While increased chain branching and higher molecular weight lead to a slight reduction in reaction velocity, acyclic sulfides are decomposed much more easily and rapidly compared to other organosulfur compounds, such as thiophenes.

$$RSR' + 2H_2 \rightarrow RH + R'H + H_2S$$

Monocyclic Sulfides (Thiophanes). During the hydrotreating process, monocyclic sulfides undergo ring-opening reactions in the presence of hydrogen. This process results in the formation of corresponding saturated hydrocarbons (alkanes) and hydrogen sulfide (H_2S).

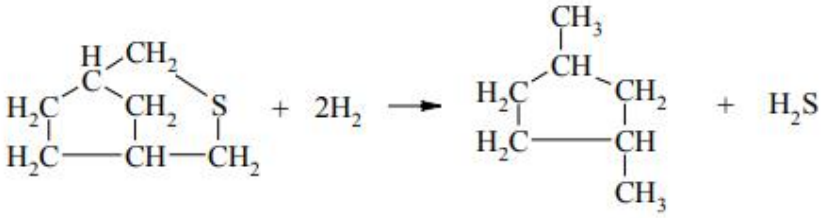
The reaction mechanism typically proceeds as follows: initially, one of the carbon-sulfur (C-S) bonds is cleaved to form a mercaptan as an intermediate product. Subsequently, the second C-S bond is broken, leading to the complete elimination of sulfur and the formation of an open-chain saturated hydrocarbon.

The hydrogenation rate of monocyclic sulfides is slightly lower than that of acyclic sulfides but remains significantly higher than that of thiophenic compounds. However, the presence of substituents (alkyl groups) on the ring typically reduces the reaction velocity due to steric hindrance, which obstructs the access of the sulfur atom to the active sites of the catalyst.



*Bicyclic sulfides.*Bicyclic sulfides exhibit lower reactivity during hydrotreating compared to monocyclic analogs. Their hydrogenation involves the cleavage of rings, leading to the formation of monocyclic hydrocarbons or open-chain alkanes. The process begins with the cleavage of carbon-sulfur (C-S) bonds; specifically, if the sulfur atom is shared between two rings, the bicyclic system decomposes to yield alkylnaphthenes and H_2S.

The hydrogenation rate of bicyclic sulfides is strictly governed by their molecular architecture and ring dimensions. Increased structural complexity and a higher number of substituents impede the adsorption of the molecule onto the catalyst surface, thereby significantly reducing the overall reaction velocity.



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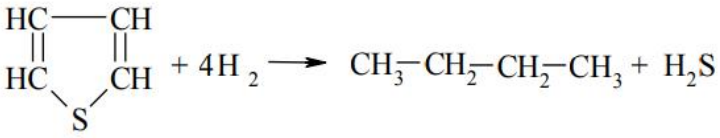
Disulfides. Disulfides undergo hydrogenation very easily during the hydrotreating process. The reaction proceeds in two distinct stages: initially, the sulfur-sulfur (S-S) bond is cleaved to form two mercaptan molecules; subsequently, these mercaptans decompose into hydrocarbons and hydrogen sulfide (H_2S).

$$RSSR' + 3H_2 \rightarrow RH + R'H + 2H_2S$$

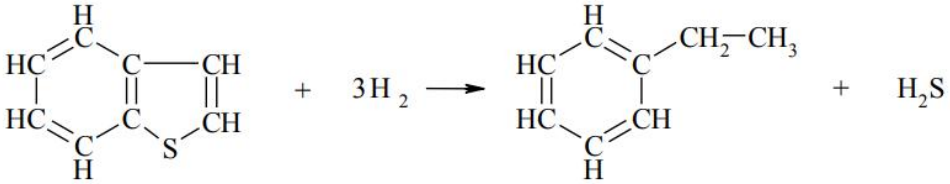
Mercaptans (Thiols). Among organosulfur compounds, mercaptans (thiols) exhibit the highest reactivity. Their hydrogenation results in the formation of corresponding alkanes and hydrogen sulfide (H_2S). While the reaction rate slightly decreases as the molecular weight increases, it remains consistently high compared to other sulfur species.

$$RSH + H_2 \rightarrow RH + H_2S$$

Thiophenes. Thiophenes and their derivatives are among the most refractory compounds to decompose during hydrotreating. The reaction process involves the initial saturation of the thiophene ring to form tetrahydrothiophene, followed by ring-opening to yield saturated hydrocarbons (butane or its derivatives) and hydrogen sulfide (H_2S).



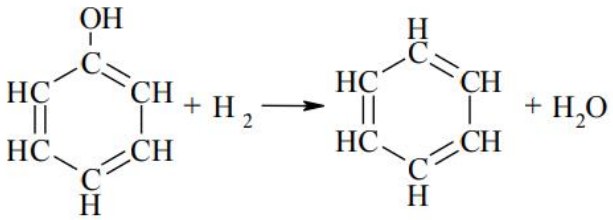
Dibenzothiophenes. Dibenzothiophenes, characterized by two benzene rings fused to a central thiophene ring, represent the most refractory sulfur species in heavy diesel fractions. Their hydrodesulfurization (HDS) occurs through two parallel pathways: direct desulfurization and pre-hydrogenation of the aromatic rings. Due to significant steric hindrance, particularly in 4,6-substituted derivatives, their removal requires highly active catalysts and severe process conditions.



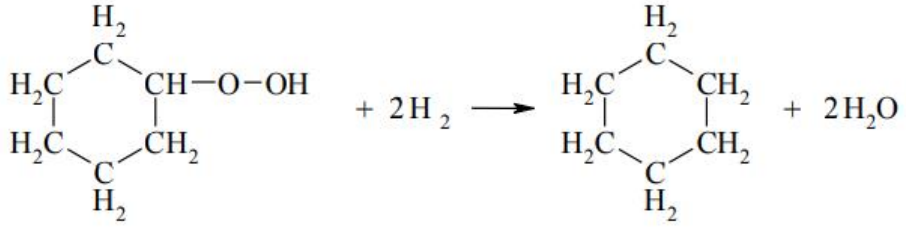
Among organosulfur compounds, mercaptans and sulfides exhibit the highest susceptibility to hydrogenation. In contrast, thiophenes and benzothiophenes are characterized by their high resistance to hydrodesulfurization (HDS). Under identical process conditions, mercaptans and sulfides achieve conversion rates of up to 95%, whereas the hydrogenation yields for thiophenes and benzothiophenes remain limited to approximately 40–50%.

Furthermore, temperature variations significantly impact the chemical equilibrium of these reactions. As the temperature rises, the equilibrium constants for the hydrogenation of mercaptans, disulfides, and sulfides increase; conversely, a decline in the equilibrium constant is observed for thiophenic compounds.

Reactions of oxygen-containing compounds. In petroleum fractions with medium boiling ranges, oxygen is primarily found within compounds such as alcohols, ethers, phenols, and naphthenic acids. During the hydrotreating process, phenols react with hydrogen to yield aromatic hydrocarbons (e.g., benzene) and water. This hydrodeoxygenation (HDO) mechanism involves the substitution of the hydroxyl group (-OH) with hydrogen, resulting in the elimination of water from the system.



*Cyclic Hydroperoxides.*During hydrogenation, cyclic hydroperoxides are converted into the corresponding cyclanes (saturated cyclic hydrocarbons).



This reaction is accompanied by the elimination of two molecules of water (H_2O) for each molecule of hydroperoxide processed.

Heptane hydroperoxide. Under hydrotreating conditions, heptane hydroperoxide undergoes complete reduction in the presence of hydrogen. This process results in the formation of n-heptane and water (H_2O).

$$C_7H_{15}OOH + 2H_2 \longrightarrow C_7H_{16} + 2H_2O$$

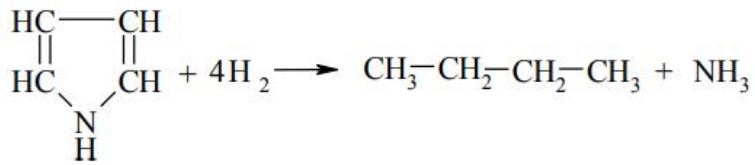
Reactions of nitrogen-containing compounds. In petroleum fractions, nitrogen is primarily present in the form of heterocyclic compounds, such as pyrrole and pyridine derivatives. Among these, amines are considered the most readily hydrogenated nitrogenous species:

$$C_6H_5CH_2NH_2 + H_2 \rightarrow C_6H_5CH_3 + NH_3$$

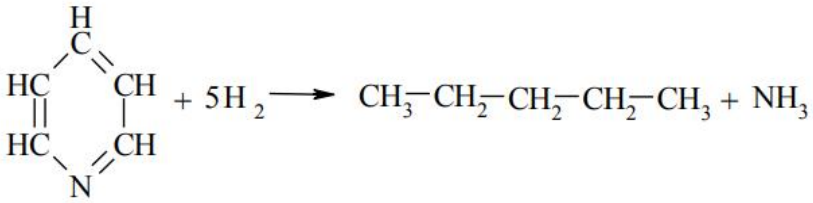
Aniline exhibits greater resistance to hydrogenation compared to simpler aliphatic amines:

$$C_6H_5NH_2 + H_2 \rightarrow C_6H_6 + NH_3$$

*Pyrrole.*The cleavage of the pyrrole ring during hydrotreating results in the formation of saturated hydrocarbons and ammonia (NH_3).



Pyridine. During the hydrogenation process, the pyridine ring undergoes ring-opening to yield pentane and ammonia (NH_3).



Comparative reactivity in hydrodenitrogenation (HDN). Compounds such as pyridine, pyrrole, and piperidine exhibit relatively high reactivity in hydrogenation reactions. In contrast, aniline, m-cresol, and quinoline are significantly more stable and refractory, necessitating more severe process conditions for their complete decomposition.

The overall hydrodenitrogenation process proceeds at a slower rate compared to hydrodesulfurization. This kinetic difference is primarily attributed to the higher bond dissociation energy of the carbon-nitrogen (C-N) bond relative to the carbon-sulfur (C-S) bond, making the former more resistant to catalytic cleavage.

Metal-containing compounds. The nature and reaction mechanisms of organometallic compounds during the hydrotreating process remain partially understood. It is established that these compounds decompose on the active sites of the catalyst, leading to the deposition of free

metals onto the catalyst surface. This phenomenon causes catalyst "poisoning," significantly reducing its catalytic activity. Consequently, metal-containing compounds act as potent inhibitors and permanent poisons for hydrotreating catalysts.

Hydrogenation of chlorine-containing compounds. During hydrotreating, organochlorine compounds (such as chlorinated alkanes or aromatic chlorides) react with hydrogen on the catalyst surface. In this process, the chlorine atom is replaced by hydrogen, resulting in the formation of hydrocarbons and hydrogen chloride (HCl). The general reaction is represented as follows:

$$R - Cl + H_2 \rightarrow R - H + HCl$$

During the hydrotreating process, ammonia (NH_3) released from the denitrogenation of nitrogenous compounds reacts with hydrogen chloride (HCl) generated from the hydrodechlorination of organochlorine species. This interaction leads to the formation of solid ammonium chloride (NH_4Cl):

$$NH_3 + HCl \rightarrow NH_4Cl$$

Ammonium chloride (NH_4Cl) tends to form solid deposits in low-temperature zones, such as heat exchangers and condensers. These precipitates can lead to severe equipment fouling and the eventual plugging of pipelines, disrupting the continuous flow of the process.

Furthermore, in the presence of water vapor, hydrogen chloride (HCl) transforms into a highly aggressive acid, triggering intense localized corrosion on the metallic surfaces of vessels and piping systems. Excessive chlorine concentrations also significantly impact the catalyst's acid sites. This interference can alter the catalyst's selectivity or induce undesired hydrocracking reactions, leading to an over-acceleration of the cracking process and a shift in product distribution.

Reactions of Hydrocarbon Compounds. In the hydrotreating process, various chemical transformations involving hydrocarbons occur in parallel with the removal of sulfur, nitrogen, and oxygen-containing compounds:

Saturation of unsaturated hydrocarbons. The saturation of aromatic and olefinic hydrocarbons is among the most critical secondary reactions accompanying hydrodesulfurization. At relatively low hydrogen partial pressures and temperatures ranging from 350 to 500 °C, nearly complete saturation of unsaturated species is achieved.

Hydrocracking. The intensity of hydrocracking reactions increases significantly with rising temperature and pressure. During this process, high-molecular-weight molecules undergo catalytic cleavage to form lower-molecular-weight hydrocarbons.

Isomerization of naphthenes and paraffins. Isomerization occurs under typical hydrorefining conditions suitable for sulfur removal. This reaction leads to structural rearrangements, resulting in the formation of branched-chain hydrocarbons from straight-chain precursors.

Hydrogenation of aromatic hydrocarbons. The hydrogenation of monocyclic aromatic hydrocarbons, such as benzene and its homologs, requires more severe conditions (hydrogen partial pressures of 20 MPa or higher) compared to polycyclic aromatic hydrocarbons. Conversely, the partial hydrogenation of condensed multi-ring aromatics can proceed even under standard hydrotreating conditions.

Conclusion. The technological evolution of Uzbekistan's oil and gas industry, particularly at the Bukhara Refinery, holds strategic importance in the nation's transition toward a "green economy." Achieving Euro-5 standards through the catalytic hydrotreating of diesel fractions remains the most effective chemical-engineering solution, enabling a reduction of sulfur and nitrogenous compounds by up to 95%.

Looking ahead, the integration of "digital twin" technologies and the localization of catalyst production are set to elevate the industry's economic independence and technological stability to a new level. These advancements will ensure a sustainable balance between industrial growth and environmental stewardship in the region.

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