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Review

The HDS Process: Origin, Process Evolution, Reaction Mechanisms, Process Units, Catalysts, and Health Risks

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Abstract

The sulfur content in crude oil varies between 1000 and 30,000 ppm (parts per million), meaning that its removal from fuels requires significant technical and economic effort. Growing concern about pollution, accompanied by stricter environmental regulations, have led to the development of strategies to mitigate the negative effects of sulfur-containing compounds in petroleum, which can cause malfunctions in manufacturing plants and refineries, such as causing catalyst poisoning in catalytic reforming equipment and sulfur dioxide emissions that have been generated through the use of fuels in vehicles, vessels, furnaces, etc. Sulfur is one of the main pollutants found in diesel and gasoline. The hydrodesulfurization method removes sulfur and nitrogen-containing compounds from diesel and gasoline, ensuring compliance with current environmental regulations established for the import and export of fuels. In addition, hydrodesulfurization contributes to reducing sulfur dioxide and nitrogen dioxide emissions into the environment and prevents corrosion, which increases safety for both manufacturing plants and end consumers. This situation is analyzed in this paper, considering Mexican legislation about fuels and their usage. Sulfur is an important pollutant contained in diesel and gasoline fuels; it exhibits lubricant properties, helping to reduce the maintenance intervals of the machines and increase engine life. Therefore, its removal from fuel blends is a topic of great scientific interest as researchers look for different lubricant alternatives, which are relevant to motor vehicle engines.

Keywords: hydrodesulfurization; sulfur compounds; environmental regulations; HDS process; automotive engines

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1. Introduction

1.1. Current Status of Development and Relationships with the Hydrodesulfurization Process

Today, there are two major simultaneous but contradictory concerns that should be addressed: energy and materials production versus climate change because of human activities. Efforts to address this mismatch have been under development since 1992, when speakers at the UN Conference on Environment and Development in Rio de Janeiro, Brazil, proposed an analysis of climate change. In 1995, the first Conference of the Parties (COP) took place in Berlin, Germany, where about 197 countries, plus the EU, started a discussion

of climate change and its causes. Some years later, in 1997, the famous Kyoto Protocol was proposed as a first attempt to diminish CO_2 emissions. About two decades later, the United Nations Framework Convention on Climate Change (UNFCCC) asked for proposals on how to address the ways in which humans are destroying the Earth, a challenge that is still open. Finally, at the COP28 conference in Dubai, the following agreement was signed: "The nearly 200 countries participating in the United Nations climate summit have decided to end their dependence on fossil fuels and begin the transition to clean, renewable energy to curb climate change". This agreement, reached after two weeks of deliberation, has since been hailed as "historic" by the conference organizers, as well as by representatives of the United States of America, the European Union, and the United Kingdom. Nevertheless, after 33 years of discussions and conferences, the conclusions of the last meeting, COP29, which took place at Bakú-Azerbaiyán on November 2024, were only that "... there is an Obligation for rich countries (23 + EU, excluding China) to finance the energy transition and climate adaptation of developing nations with $300 billion annually until 2035". The call for a "transition" away from fossil fuels, the major milestone of COP28 in Dubai, does not appear explicitly in the final texts of 2024; it only appears implicitly when the existence of the previous year's agreement is mentioned [1].

After this position was adopted by the world's governments, the only solution available was to develop palliative solutions, one of the most relevant being the production of "clean fuels". Among these technologies, the hydrodesulfurization (HDS) of mainly diesel and gasoline stands out as one of the more consistent and evolutionary solutions developed over approximately the last 60 years [2]. This brief review is intended to draw attention to the problem of petroleum dependence and the necessity for an urgent re-evaluation of manufacturing processes.

1.2. Structure of the Brief Review

This paper presents a literature review of works examining the hydrodesulfurization process of liquid fuels, beginning with searching for the origin of the contaminating heteroatoms, continuing with the evolution of the hydrodesulfurization process, the catalysts used for sulfur and nitrogen removal, and the health risks of these contaminants, and concluding with a brief review of the Mexican standards that regulate sulfur content in liquid fuels and the effect on the lubricating engines that use these fuels. Section 2 analyzes the origin of petroleum and, therefore, of sulfur content. Section 3 begins with an analysis of the hydrodesulfurization (HDS) process. Then, Section 4 looks for the different catalysts that have been produced and are available for the HDS processing of gasoline and diesel, supports, active species, regeneration, and disposal. Later, Section 5 analyzes Mexican legislation, the effect on engines of desulfurized fuels, and risks for human health as a consequence of SO_2 and SO_3 emissions during the combustion of fuels containing sulfur and nitrogen. Finally, Section 6 looks briefly at solutions that have been found for the lack of lubricity after the desulfurization of gasoline and diesel.

2. Origins

2.1. Petroleum

Petroleum is a fossil liquid mixture, the combustion of which contributes a high percentage of the total energy consumed worldwide and also constitutes a very important source of raw materials for the organic chemistry industry [3]. In this complex mixture of organic compounds, most of the petroleum compounds correspond to hydrocarbons, made up of carbon and hydrogen atoms, in addition to heterocompounds containing sulfur, nitrogen, and oxygen atoms, as well as some metals such as sodium, iron, nickel, and vanadium [4].

Unrefined petroleum is a dark brown, viscous liquid called crude oil. The composition of crude oil varies, depending on its origin. Sulfur is generally the most abundant heteroatom, and, according to the literature, the sulfur concentration is highest in younger crude oils [5,6].

In Mexico, crude oil that has been extracted for export is classified into three types, each with different characteristics. Table 1 shows some of the physical and chemical characteristics of these crude oils.

Table 1. Properties of oil types in Mexico [4].

Characteristics	Mayan	Istmo	Olmeca	Altamira
API Gravity	21.3	33.1	38.7	16.5
Elemental analysis (wt.%)				
Carbon	83.96	85.4	85.91	84.96
Hydrogen	1.8	12.68	12.8	1.7
Oxygen	0.35	0.33	0.23	0.36
Nitrogen	0.32	0.14	0.07	0.34
Sulfur	3.57	1.45	0.99	6.0
H/C Ratio	1.687	1.782	1.788	1.69
Metals (ppm)				
Nickel	53.4	10.2	1.6	53.9
Vanadium	298.1	52.7	8	299
Asphaltenes (wt.%)				
n-C_5	14.1	3.63	1.05	15
n-C_7	11.32	3.34	0.75	12

Mayan crude oil accounts for over 50% of Mexico's total crude oil production. It is characterized by its high viscosity, sulfur, metal, and asphaltene contents, and low yield of light fractions during distillation. Currently, Mexican refineries operate using blends of crude oil (55–60 wt.% Isthmus + 45–40 wt.% Mayan) [3].

2.2. Oil Distillation

Crude oil is separated using two distillation towers. The first distillation tower distills at atmospheric pressure (Figure 1), meaning that only hydrocarbons (HC), which contain up to 20 carbon atoms, can be separated without decomposition. As the temperature rises, those compounds with fewer carbon atoms in their molecules are the first to be released; subsequently, the liquid compounds vaporize and are also separated, a process that is repeated to obtain different fractions. The first vapors to liquefy are gasoline and fuel gases. This fraction is sent to another distillation tower, where the gases are separated from the gasoline. Kerosene liquefies at 175° C, light diesel at approximately 200° C, and finally, heavy diesel at approximately 300° C [4].

In the atmospheric distillation tower, light primary gas oil (LPG) is distilled by boiling between 250 °C and 310 °C. LPG contains paraffinic, naphthenic, and aromatic molecules with 15 to 18 carbon atoms.

To recover more fuel from the atmospheric distillation residues, it is necessary to pass them through a vacuum distillation tower to avoid thermal decomposition. Table 2 shows the distillation cuts of hydrocarbons obtained by vacuum distillation.

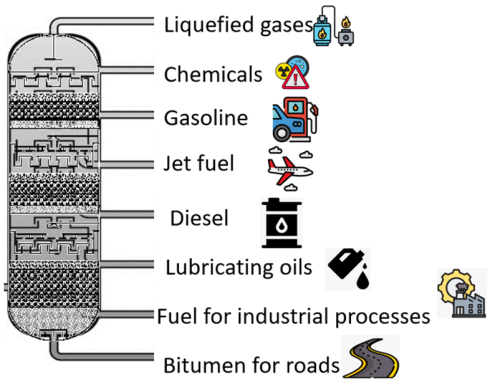


Figure 1. Atmospheric distillation tower.

Table 2. Mixtures of hydrocarbons obtained by vacuum distillation [4].

Fraction	Number of Carbon Atoms per Molecule
Non-condensable gas	C_1–C_2
Liquefied gas (LPG)	C_3–C_4
Gasoline	C_5–C_9
Kerosene	C_{10}–C_{14}
Diesel	C_{15}–C_{23}
Lubricants and paraffins	C_{20}–C_{35}
Heavy fuel oil	C_{25}–C_{35}
Asphalts	>C_{39}

2.3. Heteroatoms in Petroleum

Oil, after water, is the most important natural liquid on our planet; today, there is no other energy source on which humanity depends so much. However, calling it a non-renewable natural resource emphasizes that its existence is limited.

Currently, the amount of petroleum in oil fields is decreasing because of the growing global demand for its products. Furthermore, the quantity of light crude oil is decreasing, and the oil refining industry is being forced to use heavy crude oil, which, by its nature, contains a greater number of "impurities".

Among the main impurities are various heterocyclic compounds of nitrogen and sulfur, which make oil refining more difficult, cause poisoning and the deactivation of catalysts, and corrode equipment; during the combustion reaction, they will also be converted into polluting gases (NOx, SOx), thereby causing environmental damage.

Today, urban air quality is directly related to the quality of the fuels used in transportation. For this reason, environmental regulatory agencies frequently set minimum fuel quality specifications by law or resolution to maintain or improve air quality.

It is important to highlight that Mexican oil fields primarily produce heavy crude oil with a high content of sulfur compounds. Furthermore, Mexican environmental regulations regarding fuels have drastically reduced the allowable limit for sulfur in gasoline and diesel, requiring the implementation of more efficient sulfur removal processes [7–9].

Air quality standards refer to maximum acceptable concentrations of nitrogen oxides (NOx), sulfur oxides (SOx), particulate matter, carbon monoxide (CO), and photochemical oxidants (ozone) [10]. Such standards contribute to reducing sulfur dioxide and nitrogen dioxide emissions into the environment and prevent corrosion, which increases the safety of both manufacturing plants and end consumers.

3. The Hydrodesulfurization Process

3.1. Hydrotreating Processes

Among the various processes for obtaining petroleum products free of undesirable heteroatoms are operations of great importance for petroleum refining, known as hydrotreating (HDT) processes. HDT can be applied to a wide variety of petroleum fractions: solvents, distillates (light, middle, and heavy), residues, and fuels [11].

During HDT, hydrogenation reactions (HID) of unsaturated compounds and hydrogenolysis reactions of carbon–heteroatom bonds (sulfur, metals or metalloids, nitrogen, and oxygen) mainly occur. All reactions are exothermic; therefore, temperature control in the reactor, especially in the catalytic bed, is very important during operations. HDT consists primarily of certain reactions (HDS, HDN, HDO, and HDM), which are briefly described below [4]:

- Hydrodesulfurization (HDS): This leads to the removal of sulfur from petroleum compounds by converting them to H_2S and products in the form of hydrocarbons with lower molecular weight and boiling points.
- Hydrodenitrogenation (HDN): Nitrogen removal is performed to minimize catalyst poisoning in subsequent processes as they are a source of coke formation during catalytic cracking and inhibit reactions by adsorption on acid sites.
- Hydrodeoxygenation (HDO): Oxygenated compounds are present at low concentrations in petroleum, increasing with the boiling point. A process to remove the oxygen that is present is also carried out.
- Hydrodemetallization (HDM): Traces of nickel and vanadium (330 ppm Ni + V in Maya crude) are present in petroleum, generally in the form of porphyrins or chelating compounds. These compounds can be deposited on catalysts during the conversion process in the form of transition metal sulfides (Ni_3S_2, V_3S_4, and V_2S_3). This deposition poisons the catalytic material, reducing the number of active sites (the area where the substrate binds in catalysis) and impeding the transportation of reactants due to potential blockage of the pores [12,13].

The hydrodesulfurization process eliminates sulfur-containing compounds and, simultaneously, nitrogen-containing compounds, ensuring compliance with the various environmental regulations established for the import, export, and use of fuels.

Sulfur is one of the main pollutants found in diesel and gasoline. Sulfur content in crude oil varies between 1000 and 30,000 ppm, meaning that removing it from fuel requires significant economic effort. Growing environmental concern, accompanied by stricter environmental regulations, has led to the development of strategies to mitigate the negative effects of sulfur-containing compounds in oil, which can cause malfunctions in plants and refineries, such as catalyst poisoning in catalytic reforming equipment and sulfur dioxide emissions generated by fuel use in vehicles, vessels, furnaces, etc.

Sulfur content in fuels is a matter for concern because, during combustion, it is converted into SOx, which contributes to acid rain; therefore, as sulfur levels decrease beyond a certain point, the health and environmental benefits increase considerably [4].

In this regard, the NOM-086-SEMARNAT-SENER-SCFI-2011 [14] regulation "Specifications of fossil fuels for environmental protection" establishes the maximum allowable sulfur content in fuels for motor transport, which must not exceed 15 ppm by weight. Consequently, improved processes and more active catalysts are required to reduce the heteroatom content in fuels. Internationally, the rules concerning the sulfur levels permitted in diesel are quite stringent, as shown in Figure 2.

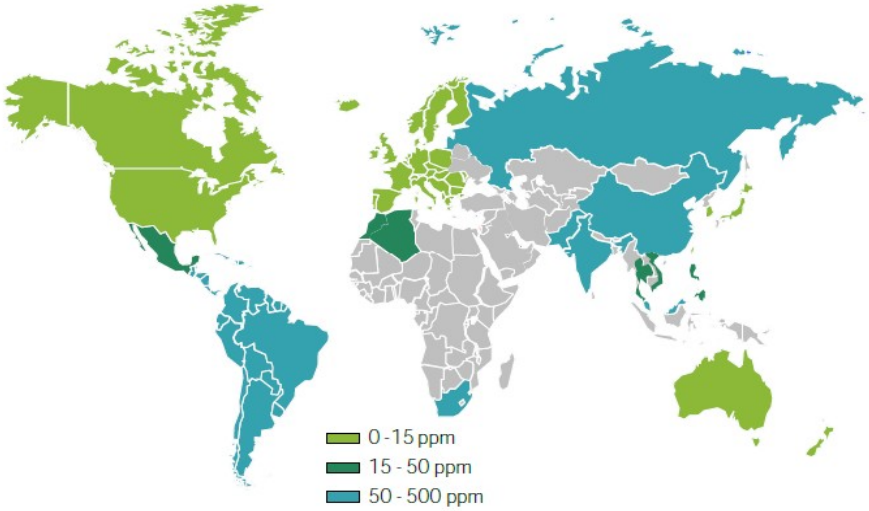


Figure 2. Permitted sulfur levels in diesel worldwide (Petroleum Products Outlook 2010–2025, SENER).

Currently, there are four commonly used hydrodesulfurization processes (Table 3).

Table 3. Main heteroatom removal processes [4,5,7].

Process	Function
Hydrocracking	Converts diesel fuel to gasoline and eliminate heterocompounds
Hydrodesulfurization of gasoline	Eliminates undesirable products such as sulfur and nitrogen from gasoline
Catalytic naphtha hydrodesulfurization	Reduces the sulfur content to below 15 ppm in gasoline
Hydrodesulfurization of cooking oil and vacuum gas oil	Reduces the sulfur content in diesel and gas oil products

Sulfur is a contaminant that can be removed to reach levels below 500 ppm with the aid of bifunctional catalysts such as NiMo/AlO and CoMo/AlO. Above this value, the remaining sulfur content in the middle distillates represents very stable sulfur compounds with dibenzothiophene-type di-aromatic structures [15,16].

Deep hydrodesulfurization requires catalysts with higher sulfur removal activity. The active phase of conventional hydrodesulfurization catalysts is composed of sulfide species such as MoS or WS, which are promoted with metals such as Co, Ni, and in some cases, both. Efficient formation of the effective active phase is achieved when the promoter is located at the edges and corners of the MoS crystallites. Therefore, the catalyst preparation and activation method are crucial for obtaining more active catalysts [17].

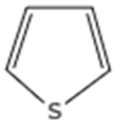
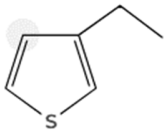
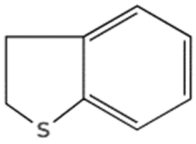
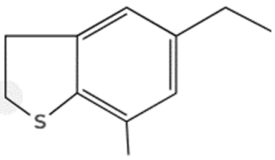
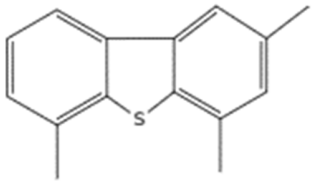
Hydrodesulfurization (HDS) is a process designed to reduce the percentage of sulfur found in petroleum fractions. It is carried out in the presence of hydrogen and a catalyst. Environmental regulations in many countries require more "friendly" transportation fuels with lower sulfur contents (10 ppm in ultra-low sulfur diesel) [18,19].

3.2. Mechanisms of Hydrodesulfuration Reactions

In petroleum fractions, sulfur-containing compounds (Table 4) are generally classified into two types:

- Non-heterocyclic: thiols (mercaptans, SSR), sulfides (RSR), and disulfides (RSSR).
- Heterocyclic: compounds containing several thiophenes (one or more rings), sometimes with alkyl or aryl substituents.

Table 4. Compounds containing sulfur that are present in petroleum.

Sulfur Compounds	**Structure**		
Thiols (mercaptans)	R-SH	R-S-R	R-S-S-R′
Thiophenes			
Sulfides			
Dibenzothiophenes			

The nitrogen compounds found in petroleum derivatives (fuels or lubricating oils) are classified into two types: heterocyclic and non-heterocyclic. The latter type includes anilines and aliphatic amines. Heterocyclic nitrogen compounds are usually divided into two groups: those with six-membered pyridine rings and those with five-membered pyrrole rings [20] (some examples are shown in Table 5).

Nitrogen, along with sulfur, is the most prevalent element in Maya crude oil. Most of the sulfur is organically bound, and very little is found as hydrogen sulfide and elemental sulfur. The sulfur species commonly found in crude oils are alkyl benzothiophene derivatives, dibenzothiophene (DBT), benzonaphthiophene, and penthiophene. Because these compounds are less reactive, they are more difficult to transform with HDT. Therefore, the DBT compound is considered a model molecule for studying the HDS process.

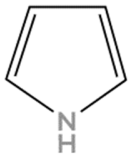
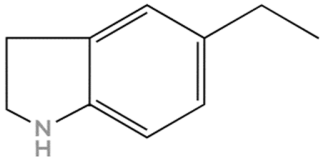
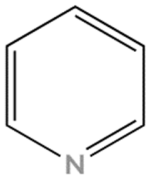
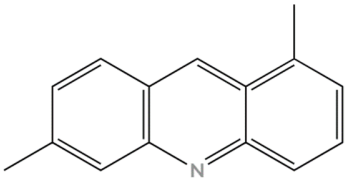
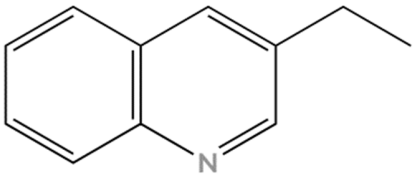
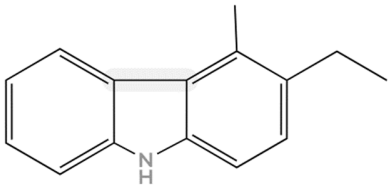
In 1980, Houlla et al. [21] described in detail the routes followed by the HDS reactions of DBT (Figure 3), which are currently the basis for the study of these reactions. It was observed that the conversion of DBT can be carried out through two parallel routes: first, by direct hydrodesulfurization (DSD), producing biphenyl (BF), and second, by hydrogenation (HID), initially producing tetrahydrodibenzothiophene (THDBT) and hexahydrodibenzothiophene (HHDBT), followed by desulfurization to form cyclohexylbenzene (CHB) and, subsequently, bicyclohexyl (BCH).

Nitrogen compounds are naturally present in atmospheric diesel fuel and the light cycle oil used as feedstock for diesel fuel production. These compounds have been identified as strong inhibitors of hydrodesulfurization reactions, even when present at very low concentrations [22,23]. These nitrogen compounds are also of great importance due to their tendency to strongly adsorb to the catalytic sites of HDS catalysts, especially pyridines and pyrroles, the heterocyclic nitrogen compounds, causing deactivation and hindering the hydrodesulfurization rate.

Unlike sulfur compounds, the lone pair belonging to nitrogen in six-membered heteroaromatic rings is not involved in the π electron cloud, allowing it to be shared with acids. These compounds act as strong bases; due to the electronegative property of nitrogen in the pyridine ring, six-membered heteroaromatic rings exhibit a lower electron deficiency (π-deficiency) compared to their benzene counterparts. These compounds likely prefer to use

nitrogen to make the first contact with the catalyst surface, provided that the heteroatom is not affected by steric hindrance.

Table 5. Compounds containing nitrogen present in petroleum.

Nitrogen Compounds	Structure
Pyrroles	
Indoles	
Pyridine	
Acridines	
Quinolines	
Carbazols	

The basic capacity of these nitrogen-containing compounds allows them to interact with acidic active sites on the catalyst surface in two ways: they can either receive protons from the surface (Brönsted acid sites) or they can provide unpaired electron pairs to electron-deficient areas on the same surface (Lewis acid sites).

The higher the pKa value, the more basic the compound. The saturated nitrogen of a heterocycle can lead to a higher value of pKa than the corresponding unsaturated nitrogen. It is important to note that, in terms of pKa, indoline and tetrahydroquinoline behave like substituted anilines.

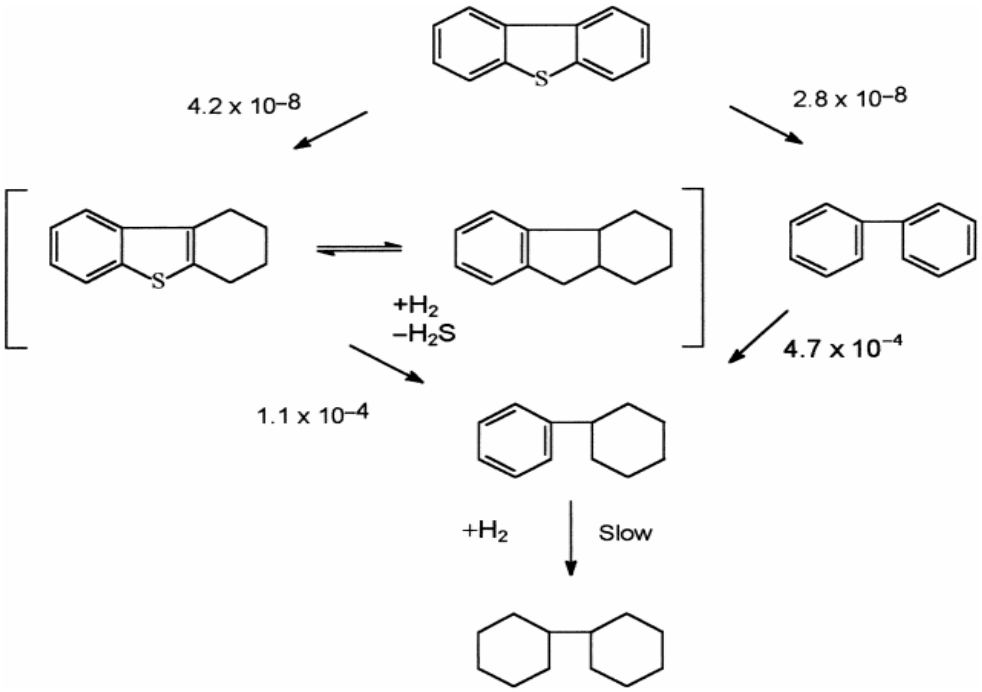


Figure 3. Proposed reaction pathways for DBT HDS. The numbers shown correspond to pseudo-first-order rate constants at 300 °C [L/(g) of catalyst].

Catalytic hydrodenitrogenation (HDN) is coupled with hydrodesulfuration during hydrotreating. Although it has long been recognized that HDN is more difficult than HDS, refiners have considered it of little importance due to the comparatively small amounts of nitrogenous compounds present in conventional petroleum sources and a lack of awareness of the negative effects of these compounds on product stability. This situation, however, is changing, primarily due to the need to process heavy or low-quality crude oils, which are rich in nitrogenous compounds. Currently, conventional HDS technology has been adapted to carry out HDN [23–26], even though it is often not the most suitable choice for nitrogen removal.

3.3. Hydrodesulfurization Units

In recent years, catalytic hydrodesulfurization (HDS) has become more important due to stringent environmental restrictions and the lower quality of available crude oil. In this context, new specifications for sulfur in diesel have been established in different countries, for example, sulfur concentrations are limited to less than 0.0015 wt.% (ultra-low-sulfur diesel) in the United States and Canada, while in Japan and Europe, sulfur concentrations have been projected below 0.0010–0.0015 wt.%. Hydrodesulfurization is the most widely recognized physicochemical technique for the removal of sulfur-containing compounds [27]. In this process, both light and heavy petroleum fractions containing sulfur compounds undergo a reaction with hydrogen in the presence of a bifunctional catalyst. This reaction generates hydrocarbons that have lost their sulfur content, along with hydrogen sulfide (H_2S). It is crucial to note that H_2S is continuously removed as it acts as an inhibitor in HDS reactions and deactivates the catalyst.

Worldwide, experience and research have shown that using current technology, developing low-sulfur fuels can be achieved economically. Incentives, increased regulations, and taxes have facilitated the full implementation of low- and ultra-low-sulfur fuels faster than anticipated in the United States, Europe, Japan, and Hong Kong. Low-sulfur fuels (50 ppm) offer greater advantages by integrating advanced control technologies for diesel engine vehicles. Diesel particulate filters can be used with these fuels but only achieve approximately

50% control efficiency. In this case, selective catalytic reduction can be applied to achieve NOx emission control greater than 80% [4]. Ultra-low-sulfur fuels (10 ppm) allow for the use of NOx absorption equipment, raising NOx control to more than 90% in both diesel and gasoline vehicles. This enables the design of more efficient engines, which are incompatible with current emission control systems. Particulate filters reach their maximum efficiency with ultra-low-sulfur fuels, with a reduction of nearly 100%.

The level of desulfurization depends on several factors, including the nature of the oil fraction to be treated (composition and types of sulfur compounds present), the selectivity and activity of the catalyst used (active site concentration and support properties, etc.), the reaction conditions (pressure, temperature, hydrogen/hydrocarbon ratio, and LHSV), and the process design. This process is divided into three main sections, as seen in any typical hydrodesulfurization unit (Figure 4):

- Reactor section or reaction section.
- Recycle gas section.
- Product recovery section.

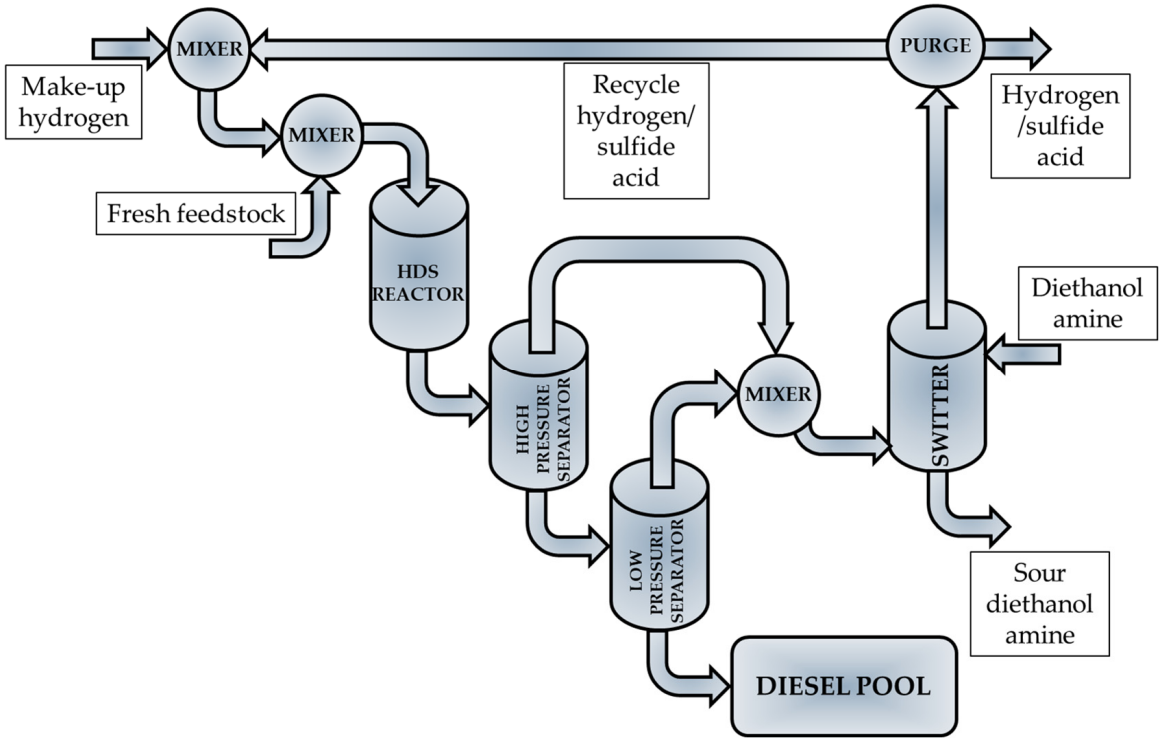


Figure 4. Diagram of a typical hydrodesulfurization unit (modified from [17]).

3.4. Three-Phase Reactors

The "trickle-bed" reactor can be considered a type of fixed-bed reactor operating in three phases: solid (catalyst), liquid, and gas.

Uses of "trickle-bed" reactors:

- HDT (Hydrotreating of naphtha and heavy gas oils).
- Hydrocracking.
- "Hydrorefining" of lubricating oils.

In HDT reactors, the high-pressure conditions keep part of the feed in a liquid state while the gas phase is produced, which is composed of hydrogen and the light oil fraction. The catalyst is in a fixed-bed structure. Solid–liquid–gas reactor systems are used in reactions that occur at relatively low rates and require a considerable amount of catalyst.

There are many interesting aspects of reactor–catalyst feedstock interactions. Consider the following questions:

(1) What are the main reaction types that occur during hydrotreating, and how do they relate to sulfur and nitrogen removal?

As in any other reaction, these pathways can be interpreted in different ways. One of the most accepted interpretations is that proposed by Houlla et al. [21], illustrated in Figure 3 in the manuscript. This mechanism considers a dual site surface (σ, τ), differentiating each reaction pathway according to the adsorption site. However, there are other proposals, such as the single event and LHHW mechanisms described by Prof. G. Froment's research group at the French Institute of Petroleum, i.e., lumping, functional group lumping, and other mechanisms from the Mobil group. All of them, however, are purely theoretical.

(2) How does the direct desulfurization (DDS) pathway differ from the hydrogenation (HYD) route in the HDS processing of dibenzothiophene?

The DDS path, as its name indicates, removes the -S- bond preferentially, prior to the hydrogenation of the aromatic rings. In contrast, the HYD path starts with the hydrogenation of some aromatic rings and later removes the -S- bond. This is illustrated using the model compound dibenzo thiophene developed by Houlla et al. [21], shown in Figure 3.

(3) What roles do nitrogen compounds play in inhibiting HDS activity, and how do their structures affect catalyst adsorption?

Nitrogen compounds are known for their basicity, and some nitrogen compounds are especially basic. These strongly adsorb active sites, provoking fouling and poisoning the catalyst.

(4) Why are CoMo and NiMo sulfides commonly used in HDS catalysts, and how do their promoters influence catalytic activity?

In fact, the sulfides of Mo are the active sites, and Co and Ni are the promoters. There are several explanations for the action of promoters, some more widely accepted than others, such as that suggested by Prof. Chianelli's group, i.e., that since Co and Ni are transition metals, there are interactions between free orbitals of the promoter and those of the Mo, provoking the formation of Ru-like atomic clouds that promote catalytic activity. Also, and no less importantly, Ni is a very good catalyst when used to dissociate and reassociate hydrogen, which also favors these reactions.

(5) What structural features of γ-Al_2O_3 make it suitable as a catalyst in HDS processes?

First, it is one of the cheapest mesoporous materials available on the market. Additionally, alumina combines mechanical strength with resistance to temperatures in the operating region and are easy to configure as spheres, cylinders, flower-like solids, etc. Finally, the surface acidity favors the interaction of metals (Co, Ni, Mo, and W) with alumina and interactions between them all.

(6) How do metal–support interactions affect the activity and selectivity of MoS_2-based catalysts?

These interactions are due to their dual functionality, giving rise to acidity plus metallic activity.

(7) What are the main causes of deactivation in hydrodesulfurization catalysts, particularly during the treatment of heavy feeds?

The main cause is catalyst fouling because of coke formation, followed by metal poisoning of the active sites.

(8) How does coke formation and metal deposition affect catalyst lifespan and regeneration potential?

Coke formation could be reversed; however, metallic poisoning destroys the active sites in the catalyst. Therefore, a coked catalyst is regenerable.

(9) What are the differences between in situ and ex situ regeneration methods, and which is more effective for restoring catalytic activity?

In situ regeneration occurs without the removal of the catalyst from the reactor; these methods attempt to regenerate the catalyst active sites, provoking other kinds of reactions such as coke combustion and vapor lixiviation. Ex situ methods, although similar in terms of reactions, involve the catalyst's removal from the reactor. Therefore, the variety of regeneration reactions increases, for example, by chelating reactions. These situations are described in Sections 4.10 and 4.11 of this manuscript.

(10) How do operating variables such as temperature, pressure, LHSV, and the hydrogen-to-hydrocarbon ratio influence HDS efficiency?

These operating variables are described in Section 3.5 of this manuscript.

(11) What is the significance of using trickle-bed reactors in industrial HDS applications?

These reactors are three-phase reactors. Hydrogen and hydrogen sulfide are supplied as gases, the fuel is used as a liquid, and the catalyst is in a solid fixed bed. Managing the pressure is also easy, and the only problem is controlling the temperature since HDS reactions are mainly exothermic.

(12) What are the health and environmental risks associated with sulfur oxides from fuel combustion?

The main risk is acid rain, causing forest devastation and agronomic damage. Additionally, there are many lateral reactions that are catalyzed by the nitrogen oxides in the atmosphere, as pointed out below in Section 5.2 of this paper.

3.5. Reactor Operating Variables

HDS reactors are designed to remove sulfur and other contaminants from feed gas oils and supply low-sulfur components for fuel oil blending. Depending on the operating conditions of the process, various degrees of hydrogenation can be achieved. The main operating variables that allow for proper plant operation are as follows:

- Liquid hourly space velocity (LHSV)

LHSV is an estimation of the residence time of the reacting mixture in the reactor. In industrial installations, this measurement ranges between 1 and 10 Vol h^{-1}. Because the catalyst volume remains constant in the system, the only way to decrease the space velocity is by reducing the inlet flow. Reducing the LHSV improves impurity removal, due to the increased time spent in the reactor, and favors hydrogenation. Increasing the space velocity decreases the conversion rate, hydrogen utilization, and coke production.

- Temperature

Increasing the temperature and hydrogen partial pressure improves sulfur and nitrogen removal, as well as hydrogen utilization. Although increasing the temperature improves sulfur and nitrogen removal, excessively high temperatures should be avoided due to increased coke formation. The severity of the treatment increases linearly with temperature as reaction rates increase; this causes an increase in coke accumulation on the catalyst, reducing its useful life and effectiveness. Hydrogen consumption rises to a peak and then decreases due to the initiation of dehydrogenation and decomposition reactions. The temperature is kept as low as possible to meet the required activity level, thereby minimizing coke consumption and preventing catalyst inactivation. However, the temperature gradually increased to counteract the decrease in activity caused by catalyst aging. The operating temperature ranges between 260 °C and 380 °C.

- Pressure

Increasing pressure also promotes hydrogen saturation and limits coke generation. The influence of pressure is directly related to the impact of recirculation gas concentration

and the hydrogen-to-hydrocarbon ratio. Increasing pressure improves the removal of sulfur, nitrogen, and oxygen and the conversion of aromatic compounds, in addition to having a positive effect on carbon deposition reduction. The operating pressure can vary between 10 bar and 70 bar.

- Hydrogen-to-hydrocarbon ratio

It should be noted that an increase in this value results in a reduction in coke deposition on the catalyst, which prolongs its useful life. Its range varies between 250 ft^3/bbl and 4000 ft^3/bbl.

3.6. Nature of the Feed

The selection of the correct intensity depends on the type of cut to be hydrogenated. Generally, less stringent conditions are used for distillates; in contrast, more stringent conditions are applied for residues and decomposition products.

4. Catalysts

Catalysts are materials that facilitate the acceleration of a chemical reaction and are not modified during the reaction. The process by which a chemical transformation occurs with the help of a catalyst is called catalysis [28]. The basic components of catalysts and the different types that exist can be classified as follows:

- Active agent: This is the primary constituent responsible for catalytic function and includes metals, semiconductors, and insulators.
- Support: Materials frequently used as catalytic supports are porous solids with a high specific surface area, which are classified as follows:
  - Inert supports, such as silica (SiO_2).
  - Supports with catalytic activity, such as alumina (Al_2O_3), aluminosilicates, and zeolites.
  - Supports that influence the catalytic activity of the active phase, such as titania (TiO_2).
- Promoter: Substances added to enhance the physical and chemical functions of the catalyst are known as promoters. Their purpose is to improve catalytic properties, increasing their activity, selectivity, and resistance to deactivation. Although promoters are added in relatively small quantities, their selection is often decisive regarding the catalyst's properties. Promoters can be incorporated into the catalyst at some stage in the chemical processing of the catalyst components. In some cases, promoters are added during the reaction. There are two types of promoters:
  - Textural promoters, which give greater stability to the active phase.
  - Electronic promoters, which increase activity.

The presence of Ni or Co promoters in Mo or W sulfides improves the catalyst's resistance to poisoning. These types of promoters are widely used for a wide variety of feedstocks but are primarily employed in the treatment of heavy crude oils and vacuum residues. NiMo-based catalysts are more active in hydrogenation reactions than CoMo-based catalysts and consume a greater amount of hydrogen per mole of sulfur removed. NiMo-based catalysts are more selective for nitrogen removal and are more tolerant of nitrogen content in streams than CoMo-based catalysts.

As a result, research related to the production of ultra-low sulfur diesel (ULSD) has garnered interest from the scientific community worldwide [25]. This renewed interest in ULSD research is related to the need for a better understanding of the factors that affect deep diesel HDS, down to low sulfur levels. The challenges of producing fuels with ultra-low sulfur contents in an economically feasible manner are among the main goals of refiners in improving existing technologies and developing new technologies, including

catalysts, processes, and reactors. The development and application of more active and stable catalysts are among the most desirable options, as they can improve productivity and increase product quality without a negative impact on investment capital. One of the HDS procedures on which this research project proposal is based is the increase in catalytic activity through the formulation of better catalysts. In the synthesis of a heterogeneous catalyst, it is important to define the type and characteristics of the support material, along with the active phases to be incorporated.

4.1. Transition Metal Sulfides (TMS)

Transition metal sulfides play an important role in the petroleum industry. Due to their resistance to poisoning, TMS are unique catalysts for the removal of heteroatoms (S, N, O) in the presence of large amounts of hydrogen. The HDS processing of organic molecules, such as those types mentioned above, is generally carried out with Mo and W sulfides and promoted by Group VIII elements such as Ni and Co [5]. The catalytic activity of TMS has been systematically studied based on the position of the metal in the periodic table [29]. DBT was used as a model molecule at 400° C and at high pressures, obtaining a variation curve of DBT HDS activity for different transition metal sulfides. The results indicated that the second and third rows (4d and 5d, respectively) of the SMTs were much more active, with a maximum for Group VIII metal sulfide systems. However, the first row (3d) did not show a clear pattern of behavior; they were less active, showing the lowest activity for manganese. A similar behavior was observed in the HDS processing of thiophene with SMT [12,28]. The order of activity observed was as follows:

- Third row: $RuS_2 > Rh_2S_3 > PdS > MoS_2 > NbS_2 > ZrS_2$.
- Second row: $OsSx > IrSx > ReS_2 > PtS > WS_2 > TaS_2$.

The selection of a catalyst for specific processes is based on activity, selectivity, and durability analyses. This process is often lengthy and complicated. Once a satisfactory catalyst that offers the required product quality at an acceptable price has been identified, the search for a superior option immediately begins [30].

In hydroprocessing, the catalyst selection is primarily based on the conversion required and the characteristics of the feedstock being processed. As noted above, feedstock properties can vary significantly, and the presence of impurities and physical characteristics influences catalyst selection. This indicates that there is no single catalyst or catalytic system that is suitable for the hydroprocessing of different petroleum feedstocks. Regarding physical and chemical properties, a wide variety of hydroprocessing catalysts have been developed for commercial use [31].

4.2. Supported Catalysts for HDS: The Role of the Support in Active Sulfide Phases

The nature of the support material is often critical to the shape, distribution, and ultimately catalytic function of the catalysts produced. Furthermore, it has been shown that the standard alumina does not act as a completely passive carrier under reaction conditions, as it can facilitate the displacement of active promoters, such as Ni or Co, toward its external surface, leading to the formation of spinels in subsurface layers or it may even promote isomerization reactions, depending on the acidity of these ions. In previous studies reported that, if the interaction between the Co-MoS phases and the alumina support could be eliminated or at least minimized, the new sulfided structures would display higher intrinsic activity. This led them to suggest the existence of a distinct structure with lower levels of interaction with the support, which they named the CoMoS-type II phase. Since then, numerous investigations have been carried out to fine-tune the interaction between the support and the active phases. It is now widely understood that the catalysts used for various petroleum fractions exhibit slight variations in the interactions between the metal

and the support. Therefore, regulating the dispersion of the active phase in the alumina is the crucial factor determining activity, selectivity, and stability (Figure 5).

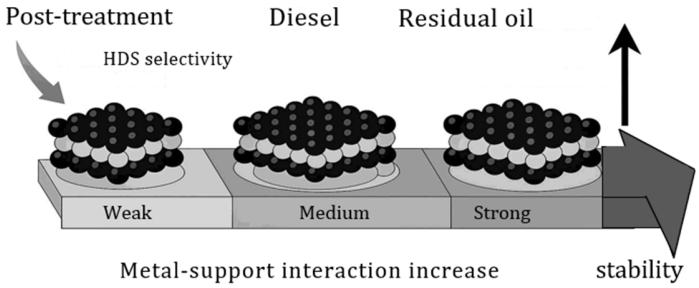


Figure 5. Metal–support interactions in hydrotreating catalysts, depending on use.

In this context, an in-depth study has been conducted on the influence of the support itself. The distribution, stacking ratio, and length of the MoS_2 or WS_2 layers, as well as the way in which the metal sulfides attach to the support surface, are under different research guidelines. Initial reports indicated that the catalytic performance of MoS_2-containing catalysts depends largely on their structure, but also on their arrangement, since the layers can be connected by edges or by flat faces, depending on the support (Figure 6).

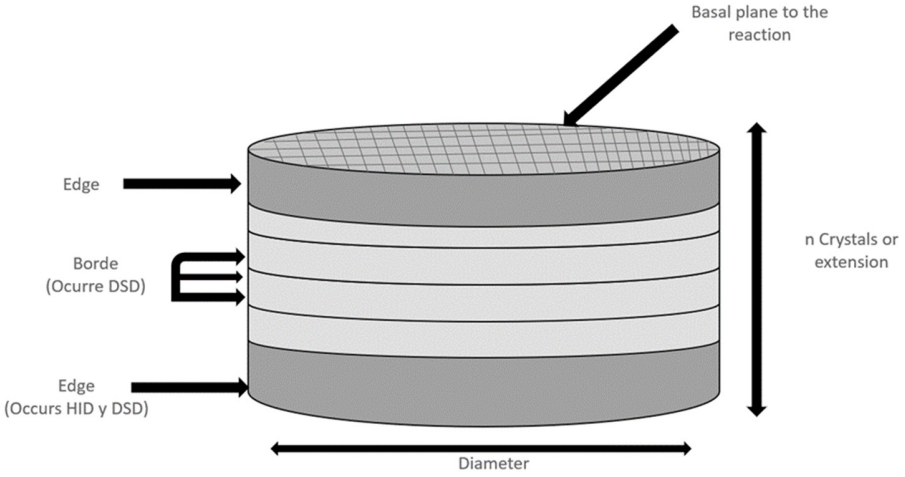


Figure 6. "Edge–edge" model for unpromoted transition metal sulfides.

Typically, in gamma-alumina, the preferential connection occurs through the basal (111) and (100) planes since these present rather soft and moderate interactions with the MoS_2 structures. In contrast, the (110) plane revealed remarkably dispersed and aligned oxide particles, with strong metal–support interactions. Therefore, the authors related this plane to small and weakly stacked MoS_2 sheets, in addition to a very low level of sulfidation.

4.3. Al_2O_3 Supports

Alumina is one of the most widely used supports in the refining industry due to its surface physicochemical properties, which can be regulated by the degree of dehydration. These properties, in turn, are modified by the calcination temperature. Among aluminas, the gamma phase is very important due to certain characteristics, namely, specific surface areas (180 to 320 m^2/g), pore volume, and pore diameters, among others—that make it suitable for use as a support for active substances in HDT catalysts.

Aluminas are readily found in nature as aluminum hydroxides; these are gibbite (γ-$Al_2O_3 \bullet 3H_2O$), boehmite (γ-$Al_2O_3 \bullet H_2O$), and diaspore (β-$Al_2O_3 \bullet H_2O$). Bauxite is composed of three main aluminum hydroxides. Another phase, although rare in nature, is

bayerite (β-$Al_2O_3 \bullet 3H_2O$), which is easily prepared using various methods with other aluminum compounds.

The dehydration of aluminum hydroxides produces a series of transition aluminas, known as oxides, with diverse properties and applications depending on the remaining hydroxyl (OH) groups in the structure. The dehydration achieved by the heat treatment of these aluminas is irreversible; complete dehydration of aluminum hydroxides (T > 1373 K) results in the most stable known phase: crystalline α-Al_2O_3, with very low specific areas of 1 to 5 m^2/g. The phase is thermally stable from absolute zero to its melting point (2273 K) [32].

The alumina phases obtained by dehydration with heating in the presence of air are schematized below (Figure 7). The phase transition depends on the starting material, its crystallinity, the heating rate, and any impurities [21]. In this way, alumina with very specific characteristics can be obtained; for example, to obtain alumina with large crystal sizes (100 μm), route b can be followed, which is favored by humidity and alkalinity. The first route (called "a") produces alumina with very small crystal sizes (less than 10 μm). The alumina phase used as the catalyst support is the gamma alumina (γ-Al_2O_3) because it calcines at around 773 K. Therefore, it is the most likely to be a material that initiates the phase change (boehmite to gamma), which is why it is believed to have small crystals on its surface. The dehydration or elimination of hydroxyl groups causes the formation of cavities or holes that give this material a high specific surface area (180 m^2/g to 500 m^2/g), making it very useful for dispersing catalytic substances, lowering the cost of using metals (or active phases) that require maximum dispersion over the support surface.

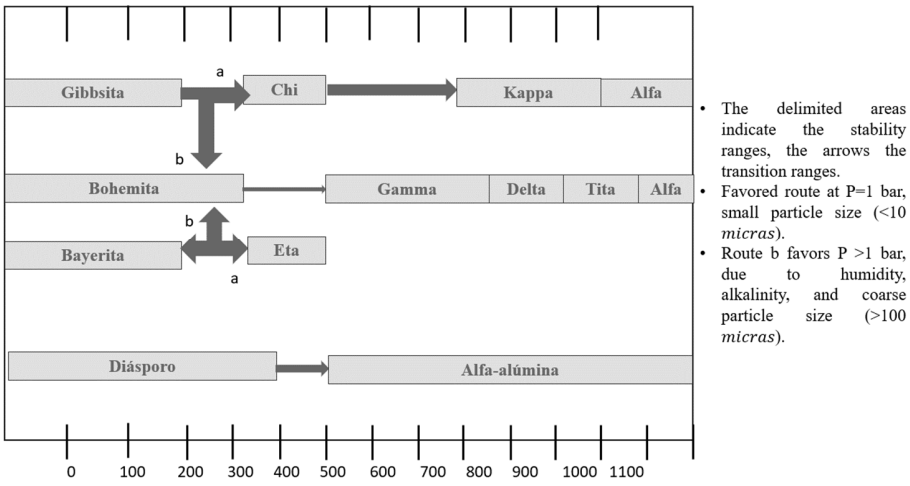


Figure 7. Phases of alumina, obtained by the dehydration of aluminum hydroxides.

4.4. Structure of γ-Al_2O_3

According to the literature, this phase of alumina exhibits a characteristic structure called a spinel (or spinel defect). Many binary or ternary oxides that are frequently used in catalysis crystallize in structures like this. The figure shows the spinel structure, which presents tightly packed cells of oxygen ions and aluminum ions (Al^{3+}) in octahedral and tetrahedral positions, which differ sequentially with superimposed oxygen-packed layers. In this structure, tetrahedra and octahedra are observed, where some oxygen atoms are shared between these tetrahedra and octahedra that make up the cell.

There are many ways in which spinel defects can form in the structure, depending on the cation vacancies in the cell in the tetrahedra and octahedra. In this structure, only 1/8 of the tetrahedral sites and 1/2 of the octahedral sites are occupied, so the solubility of cations in the spinel structure is apparently due to the occupation of cations in the interstices of the

tetrahedra and octahedra or their substitution by atoms (unit cells). Many other cations can be occluded in the interstitial vacancies, depending on their properties or characteristics, e.g., both physical and chemical properties, atomic size, valences, and electronegativity. Consequently, many multicomponent systems can be obtained, and their properties can be regulated by the addition of suitable cations and their appropriate composition, since they are believed to influence the catalytic activity of these oxides (binary or ternary).

4.5. Incorporation of Metal Ions into γ-Al_2O_3

Currently, catalysts are being developed that can maintain their catalytic properties (activity, selectivity, and stability) for longer periods of time and target a specific reaction. For example, in the case of CoMo/γ-Al_2O_3 catalysts in the sulfide state [9], the goal is to maintain high hydrodesulfurization activity and controlled hydrogenation by controlling the catalyst's acidic properties (number and type of acid or base sites) through the incorporation of certain metal ions, alkaline ions, alkaline earth ions, and even some rare earth ions, especially those from the lanthanide series.

Alumina-supported Co(Ni)Mo(W) catalysts are typically used in HDS reactions. The use of alumina supports is due to their remarkable mechanical and textural properties and relatively low cost.

The addition of ions to the catalyst support aims to modify the surface physicochemical (acidity and number of acid sites) and textural properties (pore volume, pore diameter, surface area, etc.), as well as the thermal and mechanical properties of the catalyst. The interaction of these modifying ions with the support is analyzed using the atomic properties of these ions and the Hume–Rothery rules for solid solutions. These rules typically conform to two models: substitutional solid solution or interstitial solid solution. In contrast, the Hume–Rothery rules are not absolute, but they can serve as a guide to factors that favor broad, solid solubility. These factors are as follows:

1. **Solid substitution solution**
    - A. Atomic size: The relative difference between the atomic diameters of the two species must be less than 15%; otherwise, the solubility is very limited.
    - B. Crystal structure: The solvent and solute atoms must crystallize in the same structure, e.g., face-centered cubic, hexagonal, etc.
    - C. Valence: The solute and solvent atoms must have the same valency.
    - D. Reactivity: The two species must be chemically similar and must be close in the electrochemical series. Chemical reactions between species tend to favor the formation of stable compounds before forming solid solutions.
2. **Interstitial solid solution**
    - A. Atomic size: The diameters of the solute atom must be small compared to the solvent atom (diameter ratio of less than 0.59).
    - B. Crystal structure: The structure of the solvent and solute atoms does not matter.
    - C. Solubility in metals: Solute atoms dissolve much more easily in transition metals than in other metals due to their electron configuration (d and f orbitals, free).

4.6. Acidity of the Alumina-Based Support

Alumina is characterized by naturally containing essential water in its structure (OH groups) and by hydration during synthesis processes. When hydrated, it forms a monolayer of OH^{-1} ions, which are responsible for its physicochemical properties, especially the acidity of the support. During calcination, adjacent hydroxyl ions (OH^{-1}) combine randomly to form a water molecule (evacuated by temperature) and an oxygen ion (O^{-2}), reducing the presence of acid sites. The complete calcination of alumina results in a

structure free of OH^{-1} groups. The hydroxyl groups (OH) remaining from calcination and the release of water cause some disorder in the alumina structure, which exhibits different types of sites depending on the OH groups present and the nearby O^{2-} ions. The random distribution of these sites throughout the alumina matrix results in surface heterogeneity, with up to five types of sites with four or no oxide ions nearby.

4.7. Catalysts Supported on SBA-15

Zhao et al. [33] synthesized a mesoporous material called SBA-15 in an acidic medium, producing a two-dimensional hexagonally ordered material. The result was a structure with large tunable pore sizes greater than 30 nm, obtained using amphiphilic copolymer blocks.

Gutiérrez et al. [23] prepared a series of Mo and NiMo catalysts supported on SBA-15, modified with different ZrO loadings using the chemical grafting method, with the aim of studying the effect of ZrO on the hydrodesulfurization of 4,6-dimethyldibenzothiophene. The results showed that the incorporation of ZrO led to improved dispersion of the Mo species and improved the catalyst activity. The addition of Ni also improved the dispersion of Mo species and led to a tendency toward the direct hydrodesulfurization route.

Escobar et al. [34] used EDTA and citric acid as chelating agents during the preparation of NiMo catalysts supported on TiO_2-ZrO_2 mixed oxides. A clear benefit of the chelating agent was evident when the sulfided catalysts were tested in dibenzothiophene. The authors concluded that the concentration of EDTA and citric acid needed to maximize activity was different for each one (Ni/EDTA = 1; Ni/citric acid = 1:2). These molar ratios appear to correspond to complete nickel impregnation.

Gutiérrez et al. [35] synthesized NiMo catalysts supported on ZrO_2-SBA-15 by varying the Mo loading and tested them in a deep hydrodesulfurization reaction (4,6-dimethyldibenzothiophene). The results showed that the addition of ZrO improved the dispersion of the metals. In terms of activity, the catalysts showed an increase of almost double the activity obtained with a reference NiMo/γ-AlO catalyst. It was also concluded that the optimal metal loading was 18 wt.% MoO and 4.5 wt.% NiO.

Klimova et al. [36] conducted a study comparing the benefits of adding TiO_2 and ZrO_2 in SBA-15 instead of using pure supports from these oxides and γ-alumina in catalysts for hydrodesulfurization. The materials were tested in the hydrodesulfurization of dibenzothiophene. The results showed that the catalysts supported on TiO_2-SBA-15 and ZrO_2-SBA-15 exhibited higher activity than the other materials, including the reference γ-alumina catalyst.

Chandra et al. [13] prepared a series of NiMo catalysts supported on SBA-15, doping the support with Ti or Zr, and studied the effect of the heteroatom on the catalyst. The catalysts were tested in HDS and HDN reactions. The results showed that the catalysts doped with only one element, either Zr or Ti, achieved better activity than the catalyst doped with both elements and the undoped material.

The development of desulfurization processes has been reported using solvents, zeolites, and catalytic methods, the latter being the main driver of catalytic hydrotreatment with transition metal formulations such as molybdenum (Mo), tungsten (W), cobalt (Co), nickel (Ni), and iron (Fe), which exhibit high activity compared to other elements.

Peña et al. [37] developed a series of CoMo catalysts supported on SBA-15 prepared with citric acid and EDTA as chelating agents, with MoO_3 loadings of 6.12 and 18% by weight. Catalysts prepared without chelating agents showed a crystalline phase (β-$CoMoO_4$), with the lowest metal loading detected by XRD. The addition of chelating agents to the impregnation solution prevented the precipitation of this crystalline phase on

the SBA-15 surface. Catalytic activity showed a significant improvement when the metal species were impregnated in the presence of EDTA or citric acid.

Several methods have been developed to prepare more active phases. In this context, improving the degree of dispersion of the active phases is of great importance to increasing the activity of HDS catalysts.

Viera et al. [38] prepared a series of NiMo catalysts supported on Ti- and Zr-modified SiO_2 using the hydrothermal and sol–gel methods, and these were tested in thiophene hydrodesulfurization. The results showed that the Zr-modified catalysts were more active in thiophene hydrodesulfurization than the Ti-modified catalysts because Ti interacts more strongly with Mo, and this does not allow for good dispersion and formation of the MoS_2 species. Furthermore, it was found that the sol–gel preparation method is faster than the traditional method, leading to a reduction in catalyst manufacturing costs.

Conversely, it is well known that the presence of nitrogen-containing compounds such as carbazole and quinoline inhibits deep HDS reactions, due to the competitive adsorption of sulfur and nitrogen compounds onto the catalyst's active sites.

4.8. Deactivation of HDT Catalysts

The loss of efficiency becomes apparent during operation, as the rate of hydrotreating reactions decreases over time. In practice, within a refinery, this reduction in activity is counteracted by raising the temperature [19,39]. Therefore, efforts are being made to develop more efficient and stable catalysts to minimize activity loss. This reduces catalyst usage and the need to regenerate spent catalysts. Deactivation assessment depends on multiple factors, including feedstock characteristics, operating conditions, and catalyst configuration, among others. It is important to note that there is a significant difference in catalyst deactivation in the hydrotreating of heavy versus light materials; in the case of heavy catalysts, the process is more complicated.

Most catalysts cannot maintain constant efficiency throughout their entire service life. These catalysts are prone to deactivation, which means that their performance decreases over time.

Catalyst deactivation is a key element in the planning and operation of catalytic processes. As indicated in Table 6, in hydrotreating, the three main reasons for deactivation are the plugging of the porous structure due to the accumulation of coke or metal sulfides, also known as fouling [9], which occurs during the first few days of operation; the sintering of the active phase and distribution, where the deactivation rate varies depending on process conditions, the feed, the catalyst itself, and the deactivation mechanism; and finally, the poisoning of the catalyst's active sites by the strong adsorption of molecules such as nitrogen compounds or coke.

Table 6. Main causes of deactivation in hydrotreating catalysts.

Catalytic Process	Catalyst	Cause of Deactivation		
		Coke Deposits	Sintering of the Active Phase	Poisoning
Diesel hydrodesulfurization	CoMo-NiMo/Al_2O_3	+++	++	+ [a]
Hydrotreatment of waste	NiMo-CoMo/Al_2O_3	+++	+	+++ [b]

[a]—Contamination by sodium, silicon, arsenic, and nitrogen. [b]—Contamination by vanadium, nickel, iron, sodium, silicon, arsenic, and nitrogen.

The useful life of HDS catalysts is generally determined by the degree of activity that meets product requirements, but it can also be curtailed by a malfunction in the unit (such

as a pressure increase, compressor failure, or a lack of hydrogen) or by a scheduled plant shutdown. Therefore, some catalysts are not considered spent when they are removed from the reactor and are sent for regeneration, while others reach their limit, meaning that they experience high temperatures at the end of their cycle, thereby accumulating a considerable amount of coke. For this reason, the percentage of coke over the HDS catalysts used varies significantly, ranging from 5 wt.% to 25 wt.%, with the average in diesel units being between 10 wt.% and 15 wt.%. Catalyst life cycles in atmospheric oil processing systems (ULSD) or vacuum gas oils range between 1 and 2 years; for waste treatment plants, the cycle is 0.5 to 1 year, and for naphtha hydrotreating, this can extend to 5 years or more.

4.9. Catalytic Reactivation

Meena Marafi et al. [19] define catalytic reactivation as the method of removing accumulated coke from the catalyst surface in order to restore its initial catalytic activity to its maximum potential, recovering both the active surface and the porosity. Generally, for effective regeneration, the level of metallic contaminants (Ni and V) in the catalyst used must be less than 5 wt.%. Otherwise, at least 80 wt.% of the original activity recovery cannot be achieved during the reactivation process. This level of recovery of catalyst activity is easy to achieve with catalysts used in the hydrotreating of light atmospheric distillates. Achieving this level of recovery is complicated when the catalyst surface contains both coke and metals deposited from the feedstock. The procedure that restores activity by removing coke and metals is also called catalyst rejuvenation.

4.10. Ex-Situ Reactivation

This oxidative regeneration method has been in commercial use for several decades. The most used method for ex-situ activity recovery is coke removal through an oxidative regeneration process, using diluted air or a combination of air and steam at 400 °C to 500 °C. Other oxidizing agents can also be used, such as steam and carbon dioxide; therefore, ex situ regeneration is more effective as it is carried out outside the reactor, thereby preventing corrosion problems. Some researchers indicate that this technique can produce highly active catalysts, achieving 94 wt.% recovery in HDS activity and 89 wt.% recovery in a specific surface area. Another available method is coke removal through reductive regeneration using H_2. However, this procedure has not yet been developed commercially.

This method is also known as catalyst revitalization. It usually employs non-oxidative approaches that focus on the selective leaching of contaminating metals from catalysts that have lost their effectiveness, using organic acids.

4.11. In-Situ Reactivation

In-situ reactivation is carried out within the reactor to remove buildup on the catalyst surface using various solvents. However, the effect of this alternative is limited; therefore, after heating, exerting the necessary mechanical strength, and removing the solvent from the catalyst, greater dispersion of the active metals is achieved using chelating agents (compounds that form complexes with heavy metal ions). This same method is also applied to regenerated catalysts.

4.12. Industrial Regeneration

In the early 1970s, most refineries regenerated their catalysts on site, using fixed-bed reactors. This process requires the provision of air and contact systems to incinerate the coke from the spent catalyst, as well as the provision of scrubbing facilities to prevent environmental problems related to the emission of gases generated during regeneration, which include sulfur, nitrogen, and carbon oxides. Both temperature and oxygen concentration

are monitored during coke combustion to prevent sintering of the active phase and its loss due to reactions with the support. Hot spots and temperature variations occur during the in-situ regeneration process. Furthermore, catalyst fines remaining in bed can cause reactor fouling and poor reactor distribution upon restart. Currently, more than 90 wt.% of refineries opted for off-site hydrotreating catalyst regeneration services.

Off-site hydrotreating catalyst regeneration processes achieve improved activity recovery thanks to rigorous temperature control during regeneration, more accurate evaluation for catalyst reuse through characterization, and quality control testing to remove fines and chips that can cause pressure-drop issues. Globally, three main companies offer this off-site regeneration service, namely, Eurecat™, Porocel™, and Tricat™, each employing their own technology, including a rotary kiln, a belt kiln, and a fluidized bed kiln, respectively.

4.13. Spent Catalysts and Management Alternatives

Furimsky et al. [27] reviewed the published research on the environmental management, disposal, and utilization of spent catalysts in refineries. Refineries have several alternatives, such as reducing the production of spent catalyst recycling waste through metal recovery and treating discarded catalysts for safe disposal and reintegration to manufacture new catalysts and other valuable materials.

Catalysts play a role in various processes and have specific life cycles that allow them to be used effectively for various purposes. A simplified diagram of a catalyst's life cycle begins with its production and storage (Figure 8). Depending on the process needs, it is then transported to the industrial plant and introduced into the appropriate reactors. It is then activated through a pre-sulfurization process, which involves converting the metal oxides into their sulfide form (active phase) using sulfurizing agents containing sulfur, such as hydrogen sulfide (H_2S). Occasionally, the catalyst is pre-sulfurized outside the reactor.

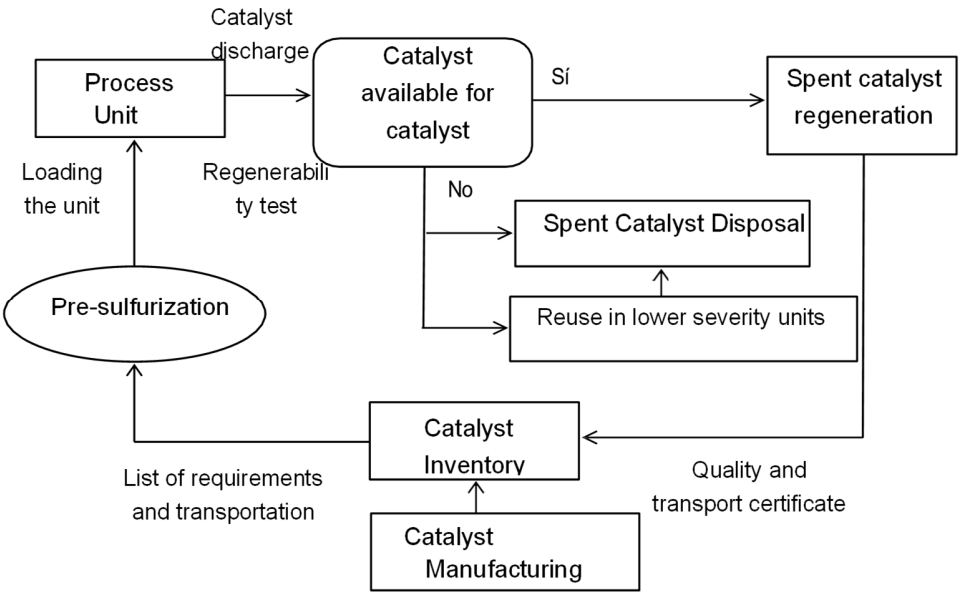


Figure 8. Life cycle of a catalyst.

Once the industrial plant has been in operation for a certain period, the catalyst is removed and a decision is made as to whether it is regenerated or stored in the catalyst inventory for later use in the same process or in other less intensive processes, or whether it is disposed of as industrial waste. Catalysts used in hydrotreating are based on γ-alumina and generally include molybdenum or tungsten oxides, combined with nickel or cobalt oxides. Catalysts used for hydrotreating heavy petroleum fractions lose their effectiveness

due to the accumulation of coke and metals on their surfaces, substances that are inherent to the nature of the hydrocarbons they process [26,40]. These catalysts undergo rapid initial deactivation by coke formation. Over time, coke formation decreases, but the catalyst continues to deactivate, mainly due to the accumulation of metals on its surface. At the end of the process, this catalyst is called a spent catalyst [27].

Spent catalysts can contain between 5 wt.% and 25 wt.% by weight of carbon (sometimes even more) and sulfur. The number of accumulated metals depends largely on the concentration of metals such as vanadium and nickel in the mixture. Other common contaminants include iron from the corrosion of tanks, pipes, and heat exchangers, as well as silica, resulting from the decomposition of antifoam additives, etc.

Furthermore, although catalyst recycling and regeneration capacities are likely to increase, the demand for new catalysts will not decrease due to the increase in their use, driven by stricter regulations on pollutant emissions. Large quantities of these catalysts are required in the hydrotreating process of heavy fractions, resulting in the accumulation of large inventories of spent catalysts. These catalysts are a significant source for metal recovery, generating both economic and environmental benefits.

5. Risks to Human Health, Environmental Issues, and Mexican Standards

5.1. Risks to Human Health

Studies by the World Health Organization show that approximately 1.3 million people die prematurely each year because of urban air pollution. In Spain, the Spanish Society of Pulmonology and Thoracic Surgery estimated the number of victims in 2019 at 16,000, almost 11 times more than the 1480 deaths recorded in 2011 [15].

Due to this significant health impact, there is great interest in the development and commercialization of catalytic technologies for HDS [28]. These include conventional hydrotreating, advanced catalyst hydrotreating, and/or reactor design, and the combination of HDT with some additional processes to meet fuel specifications. HDS processing of crude oil at the refinery, conducted at elevated temperatures and hydrogen partial pressure in the presence of a catalyst, converts organic sulfur compounds to hydrogen sulfide and hydrocarbons.

5.2. Environmental Damage

Additionally, sulfur oxides are damaging to human health; NOx (a generic term for all nitrogen oxides) provokes a variety of environmental damage types. NO_2 and NO_3 are highly reactive gases that can react with various volatile organic substances that are only found in the atmosphere in the presence of sunlight and heat. Their reaction results in what is known as tropospheric ozone (O_3). Although ozone is not considered a pollutant as it is part of the natural composition of the atmosphere and is primarily responsible for blocking UV rays from the sun, its presence at low altitudes is harmful to humans. In this condition, it causes respiratory irritation, the aggravation of respiratory allergies, and various chronic diseases. Additionally, nitrogen oxides actively contribute to the acidification of water in the process known as acid rain, which has the ability to react with atmospheric compounds and leads to the generation of numerous mutagenic and carcinogenic agents that are present in the air we breathe every day [17]. The composition of the atmosphere is changing continuously because of a collection of factors, some of which are anthropogenic. Molecular nitrogen has become the principal constituent of the atmosphere because it is relatively inert and, consequently, has accumulated. In contrast, oxygen in the atmosphere results, in part, from two main pathways: (1) the photo-dissociation of water vapor (Equation (1)), associated with hydrogen escaping into space; and (2) photosynthesis (Equation (2)), which, in the past, has been associated with the accumulation of organic fossil carbon [41,42].

Additionally, ozone formation and depletion in the lower atmosphere [43] also change oxygen concentration; this process follows several steps that require light (3a, 3c) and nitrogen oxides (Equations (3d)–(3f)):

$$2H_2O + 4h\nu \rightarrow 2H_2 + O_2 \quad (1)$$

$$6CO_2 + 12H_2O \rightarrow C_6H_{12}O_6 + 6H_2O + 6O_2 \quad (2)$$

$$O_2 + h\nu \rightarrow O + O \quad (3a)$$

$$O_2 + O \rightarrow O_3 \quad (3b)$$

$$O_3 + h\nu \rightarrow O_2 + O \quad (3c)$$

$$NO_3 + h\nu \rightarrow NO + O_2 \quad (3d)$$

$$NO_3 + h\nu \rightarrow NO_2 + O \quad (3e)$$

$$NO_2 + h\nu \rightarrow NO + O \quad (3f)$$

$$O + O_3 \rightarrow 2O_2 \quad (3g)$$

Finally, if fuel combustion temperatures become higher than 876 °C, the formation of nitrous oxide (N_2O) is observed (Figure 9). This situation is rare in vehicle engines; however, it is very common in carbo- and thermoelectric (even using VGO) generation plants. N_2O is the strongest agent of climate change, being about 212 times more prominent than CO_2 (Figure 10), and its longevity in the atmosphere is longer than 6 times that of CO_2 (Figure 11). Therefore, along with HDS processes, there are many parallel problems that should urgently be addressed.

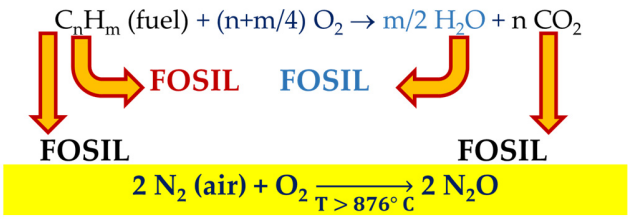


Figure 9. Schematics of the formation of nitrous oxide.

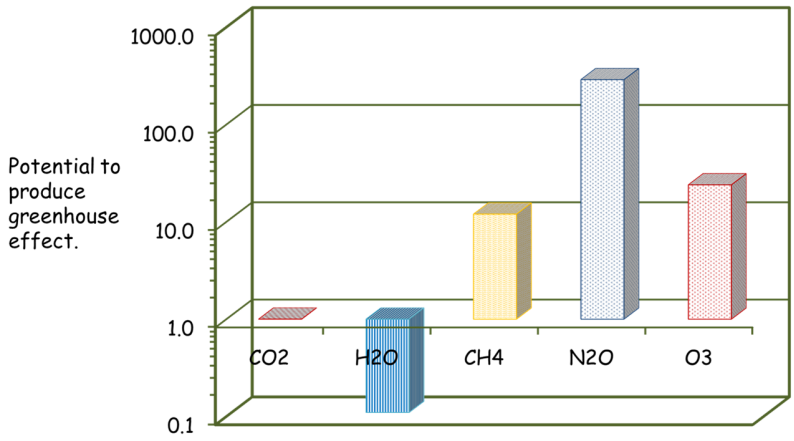


Figure 10. Schematics of climate change from nitrous oxide and other common molecules in the atmosphere.

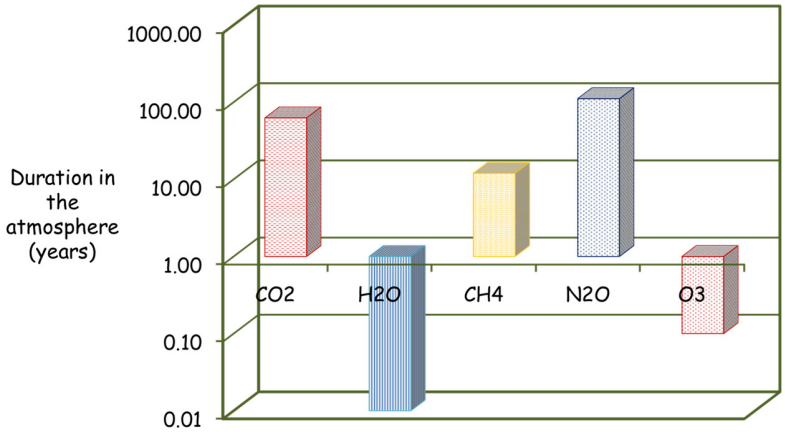


Figure 11. Schematics of the longevity of nitrous oxide and other common molecules in the atmosphere.

5.3. Mexican Regulations

Due to the existence and seriousness of the problem of contaminants in fuels, as a starting point in solving this problem, several laws have been created and amended to establish the maximum limits for toxic agents allowed in fuels. In Mexico, the official Mexican standard (NOM-086-SEMARNAT-2011 [14]) establishes the maximum permissible emission levels from vehicles powered by engines that use gasoline and liquefied petroleum gas (Table 7). This standard is mandatory for the manufacturers, importers, and assemblers of new engines who wish to enter the market in Mexico.

Table 7. Maximum permissible limits of sulfur in fuels according to the Mexican official standard (NOM-086-SEMARNAT-SENER-SCFI-2011).

Product	Sulfur Content (ppm S Weight)
Premium gasoline	October 2011: 80
MAGNA gasoline	January 2011: 500 October 2011: 80 January 2009 30
PEMEX diesel	January 2011: 500 January 2011: 15 January 2011: 10
Agricultural and marine diesel	5000
Industrial diesel	500
Jet fuel	3000
LP gas	140
Domestic diesel	500

Because of the growing demand for clean fuels with lower sulfur content, significant investment in refining will be necessary. The availability of facilities to produce low- and ultra-low-sulfur gasoline and diesel will be essential for those countries wishing to participate in the global petroleum market. Research into catalysts that meet environmental specifications will also be essential [17]. The post-treatment units in Mexican refineries are described below (Table 8).

Table 8. Post-treatment construction in Mexico's refineries.

Refinery	Construction
Cadereyta	A 42,500-barrel-per-day catalytic gasoline desulfurization plant, with an amine regeneration unit, elevated burner, pumping equipment for hydrocarbons and sour water, complementary facilities, and integrations
Madero	Two catalytic gasoline desulfurization plants with a capacity of 20,000 barrels per day, two amine regeneration units, an elevated burner, pumping equipment for hydrocarbons and bitter waters, complementary facilities, and integrations
Minatitlán	A 25,000-barrel-per-day catalytic gasoline desulfurization plant, an amine regeneration plant, complementary auxiliary service systems, and their integration into the refinery
Salina Cruz	Two catalytic gasoline desulfurization plants with a capacity of 25,000 barrels per day, two amine regeneration plants, complementary auxiliary service systems, and their integration into the refinery
Tula	A 30,000-barrel-per-day catalytic gasoline desulfurization plant, an amine regeneration plant, complementary auxiliary service systems, and their integration into the refinery
Salamanca	A 25,000-barrel-per-day catalytic gasoline desulfurization plant, an amine regeneration plant, complementary auxiliary service systems, and their integration into the refinery

6. Effects of Desulfurized Fuels on Motor Engines

Although sulfur is an important pollutant in diesel and gasoline fuels, its lubricant properties in particular help to reduce the maintenance intervals of engines and increase an engine's life. This section looks briefly at those solutions that are given for the lack of lubricity after the desulfurization of gasoline and diesel.

Originally, the lead played this lubricating role; tetra-ethyl lead was the molecule that helped to protect cylinders, pistons, valves, etc., in diesel and gasoline engines [39]. Later, lead was discovered to be highly toxic to living entities. Also, lead, sulfur, and some carbon compounds, such as CaS_2 [44], which form during fuel combustion, caused corrosion on concrete, destroying important buildings around the world. To address these problems, it was declared by environmentalists and, consequently, by governmental laws that fuel must be "cleaned" prior to being used in engines.

Currently, the search for lubricant substitutes is another research field in a state of continuous growth, as is that for methods for better managing oils and their residues [10,45–47]. Among the vast variety of additives on the market, there are two important families of additives used to reduce wear and shear: the first family consists of zinc dialkyl-dithiophosphates, also known as ZDDPs ($Zn((RS)_2PO_2)$); the second family is used to reduce shear stress and consists of molybdenum dithio-carbamates, also known as MoDTCs ($Mo_2O_2S_2(OSNR_2)_2$) [13,35,36]. For further insight into this topic, there are a number of papers are available in the specialized literature [13,35,36].

7. Conclusions

This literature review, which has mainly focused on the HDS process for gasoline and diesel, has revisited several important aspects of this technology. Its development is an example of the parallel evolution of petroleum refining and human growth, although it is also illustrative of the great dependence that humans have on fossil resources, especially petroleum. Currently, there are a number of initiatives to identify substitutes for fossil-derived products; however, the complete decarbonization of human life is still far off. Therefore, processes associated with petroleum refining, such as HDS, must be improved as much as possible by using more active catalysts, enhancing pretreatment units, and changing the production objectives to achieve better process integration of industry and nature in the future.

The authors have greatly enjoyed writing this brief review and hope that it will prove useful for both newcomers to this topic and professionals in the field.

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Abbreviations

Al^{3+}	Aluminum (III) ions
Al_2O_3	Alumina
BCH	Bicyclohexyl
BF	Biphenyl
CHB	Cyclohexylbenzene
Co	Cobalt
CO	Carbon monoxide
CoMoS	Cobalt and molybdenum sulfur
COP	Conference of the Parties
CS_2	Carbon disulfide
DBT	Dibenzothiophene
DSD	Direct desulfurization reactions
HC	Hydrocarbons
HHDBT	Hexahydrodibenzothiophene
HDM	Hydrodemetallization reactions
HDN	Hydrodenitrogenation reactions
HDO	Hydrodeoxygenation reactions
HDS	Hydrodesulfurization reactions
HDT	Hydrotreatment processes
HYD	Hydrogenation reactions
IUPAC	International Union of Pure and Applied Chemistry
LHSV	Liquid hourly space velocity, h^{-1}
MoDTCs	Molybdenum di-thio-carbamates, $(Mo_2O_2S_2(OSNR_2)_2)$-type compounds
MoS_2	Molybdenum disulfide
Ni	Nickel
N_2O	Nitrous oxide
NO_X	Nitrogen oxides, (X = {either 2 or 3 or both})
O^{2-}	Oxygen ions
-OH	Hydroxyl substituent
OH^{-1}	Hydroxyl ion
R or -R	Alquil substituent group
SO_X	Sulfur oxides, (X = {either 2 or 3 or both})
THDBT	Tetrahydrodibenzothiophene
UNFCCC	United Nations Framework Convention on Climate Change
VGO	Vacuum gas oil
WS_2	Tungsten disulfide
ZDDPs	Zinc dialkyl-dithio-phosphates, $(Zn((RS)_2PO_2))$-type compounds.

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