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Diesel Hydrodesulfurization and its Impact on the Fuel Market in Ecuador: A Review

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Abstract

This article examines the hydrodesulfurization process used to produce diesel with low sulfur content in Ecuador. The analysis covers the level of processing in the country, the quality of domestic diesel compared to other nations, and the technical and economic requirements of the process. It also explores the need to modify or upgrade catalysts to achieve deep hydrodesulfurization.. Unfortunately, the review found that sulfur content in Ecuadorian deposits is very high, with 3.53 MMkg produced in 2018. Despite improvements in the country's refineries, diesel sulfur content has only been reduced to 110 ppm.. Ecuador regulates sulfur emissions through the Ecuadorian standard NTE INEN-1489 (2012). This norm classifies the fuel into three types, diesel #1 (3000 ppm), diesel #2 (7000 ppm), and premium diesel (500 ppm), following the use of diesel both in the industrial and transportation sectors. However, Ecuador seeks to adjust to countries with stricter regulations, such as the European Union. The standard that regulates sulfur emissions in this community is Euro VI, which limits the concentration to 10 ppm. One of the challenges in achieving international standards in the hydrodesulfurization units of the Ecuadorian refineries is to modify or improve the catalytic systems. Trimetallic catalysts, both supported and unsupported, can help overcome this challenge by decomposing the refractory molecules (e.g., dibenzothiophene and 4,6-dimethyldibenzothiophene) found in deep hydrodesulfurization. These catalysts can handle molecules that commonly used catalysts such as CoMo or MoW cannot. Therefore, proposals such as using trimetallic catalysts to achieve deep hydrodesulfurization levels are techno-economic options for Ecuador.

Keywords: diesel, sulfur, Ecuador, hydrodesulfurization, refineries, catalyst.

1. Introduction

Humanity has depended on using energy resources since it found a way to control, produce and manipulate fire. Through time, this dependence on energy resources has increased for several reasons, the increase in population, the development of industries, and transportation. Oil and its derivatives are the primary energy sources since they are liquids with high energy content. The derivative of greater demand is diesel, mainly used as fuel [1-3]. Although there are new energy options, diesel remains profitable and efficient as a fuel [1]. Consequently, diesel has a significant role in the economic system



worldwide. For this reason, we should keep the attention on diesel and thus be able to meet the market's needs. Diesel combustion produces nitrogen oxides (NO_x) and carbon oxides (CO_x). In addition, as diesel also has sulfur in its chemical composition, they produce sulfur oxides (SO_x); in the same that in contact with water vapor in the atmosphere, it produces sulfuric acid (H_2SO_4), coming back to the surface and gives rise to acid rain [4, 5]. Additionally, they cause operational problems, such as corrosion or the poisoning of catalysts [6, 7]. Consequently, the processes to remove sulfur in a refinery are very necessary. Among the hydrotreatment (HDT) processes used to reduce sulfur content in a refinery, hydrodesulfurization (HDS) is the most important. This is a procedure in which a hydrogen treatment is given to the different crude oil fractions. Furthermore, modified catalysts are applied, supported or unsupported to achieve deep desulfurization when obtaining diesel. The level of desulfurization required depends on the nature of the oil fraction, selectivity and activity of the catalyst, operating conditions, and process design.

The refinery with the largest crude processing capacity in Ecuador is the Refinería Estatal de Esmeraldas (REE) (110,000 bbl/d), designed and constructed between 1975 and 1977 [8]. The national oil production for 2021 was 377,011 bbl/d. A fraction of crude oil production was subjected to refining operations to obtain derivatives; such production was approximately 206,960 /d, showing an increase of 20.1% compared to 2020 [9]. Likewise, there was an increase in the national demand for derivatives (27.89%) compared to 2020 [10]. In this work, of the derivatives produced, we will highlight diesel as the fuel with the highest demand in the nation (36.52% of the total) and one of the leading emitters of sulfur in the environment and other pollutants. National diesel can be found in three types: diesel #1, diesel #2, and premium diesel. These three types of diesel represent a significant percentage of the national production of derivatives, with 22,685 bbl/d [10]. The automotive sector uses a great portion of the diesel produced at the domestic level, followed by the industrial and shipping industries. Ecuadorian oil is considered a medium to heavy oil with high sulfur content. The premium diesel (higher demand) produced in the country has 500 ppm of sulfur, which complies with national regulations but not with European and other international regulations [11]. Hence the importance of the hydrodesulfurization process in refineries. To comply with the latter, the national oil company —EP Petroecuador — imports diesel and other derivatives, which is not feasible for the country's economy [12].

The development of this work centers on analyzing the impact of the hydrodesulfurization process of diesel in the Ecuadorian market and the potential alternatives that can be carried out to reduce its sulfur content. The diesel hydrodesulfurization unit of the REE had improvements. These improvements achieved positive results, so since 2018,



the REE has produced a premium diesel with 110 ppm sulfur content [13]. Nevertheless, this concentration of sulfur in premium diesel is not yet within European and other international regulations, which require an amount of 10 ppm. On the other hand, it is important to visualize what would happen to production if the sulfur were removed entirely. In addition, consider whether the country's refineries, with their infrastructure, could produce ultra-low-sulfur diesel [14]. So, this study proposes to analyze a potential improvement in the diesel hydrodesulfurization process.

As diesel is the derivative with the highest demand in Ecuador, its most important aspect is the quality of sulfur content. Even with high sulfur content, the raw material that leaves the refineries goes through the hydrodesulfurizer that produces diesel that has not yet reached the specifications. It is for this cause that the import of diesel represents more than double the national production. Ecuador currently needs 90,600 bbl/d of diesel, which imports 65,200 bbl/d. This is because diesel production needs to mix with diesel that delivers less sulfur to commercialize it in the domestic marketplace. The primary air pollutants are sulfur compounds in exhaust emissions from diesel combustion processes. Consequently, emissions of polluting gases in Ecuador have increased because the desired diesel quality is not yet achieved. Refining heavier crude oil with a higher content of sulfur compounds in Ecuador requires more sophisticated active catalysts in the HDS process because these poisoning and deactivation are more easily. Besides, this causes operating costs to increase and, consequently, the price of diesel to the public. Therefore, NiMoW trimetallic catalysts are an excellent option for achieving deep hydrodesulfurization levels. In this way, a cost-benefit analysis is necessary to utilize this technology.

2. Methods

Figure 1 shows the methodology developed in this work. Initially, an extensive review was carried out on diesel as a petroleum derivative, the quality specifications emphasizing sulfur content, and HDS as a technological alternative for reducing sulfur in diesel and gasoline. Then, the study focused on the Ecuadorian market. The first step consisted of identifying the status of diesel production in Ecuador. It identified the refinery facilities and the companies in charge of all operations from extraction to production, including the production figures and the units that process diesel. Fuel quality aspects were also reviewed. It is essential to note that national and international regulations or standards are of the utmost importance because they establish diesel quality for industrial and transportation purposes. Therefore, refineries are obliged to produce diesel according to specifications. This way, the technology challenges in the refineries, specifically in the

hydrodesulfurization units, were identified, observing the necessary public and private investments. Furthermore, the adaptation or change of commonly used catalysts was emphasized.

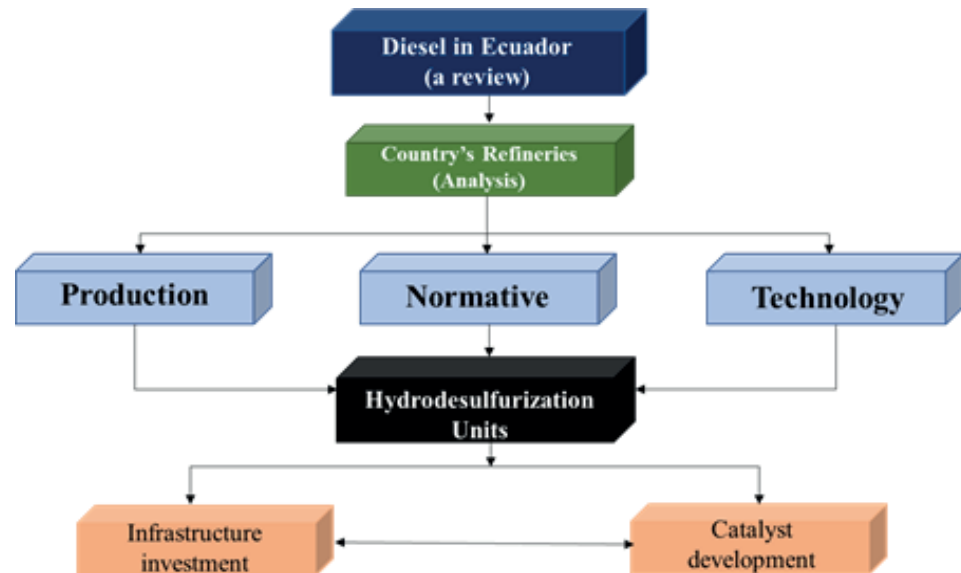


Figure 1

Methodology diagram.

The search base was essentially on the public and available information from (i) the national oil company EP Petroecuador, (ii) international databanks, (iii) product quality specifications based on national and international regulations, and (iv) scientific databases.

2.1. Diesel fuel and hydrodesulfurization

An exhaustive bibliographic search was carried out on the characteristics of diesel to be marketed in Ecuador. In this way, the hydrodesulfurization process for obtaining low-sulfur diesel was analyzed. The diesel quality in the domestic market was evaluated and compared with the United States of America and Europe standards. Although Ecuador has its own regulations governing the sulfur content of diesel, the country seeks to align itself with countries with stricter regulations, such as the European Union, which regulates sulfur emissions with the Euro VI standard, limiting the concentration to 10 ppm. On the other hand, in Ecuador, the standard NTE INEN-1489 (2012) regulates sulfur emissions and classifies the fuel into three types, diesel #1 (3000 ppm), diesel #2 (7000 ppm), and premium Diesel (500 ppm). In the United States of America, the American Society for Testing and Materials (ASTM) stipulates that the use of diesel is the ASTM-D975 standard, which extends over seven grades of diesel. Finally, an analysis was



made of the catalysts that can be improved in the country to obtain a low sulfur content that complies with international standards.

2.2. Hydrodesulfurization in Ecuador

The production of derivatives, especially diesel in Ecuador, is mainly in charge of the REE, which has a refining capacity of 110,000 bbl/d. This data is found in the academic thesis works from Ecuadorian Universities and in domestic reports on the oil sector. These reports are constructed by the Central Bank of Ecuador, which presents accumulated figures quarterly or annually. However, there are international agencies, such as the BP Statistical Review of World Energy or World Oil Outlook 2040 of the Organization of Petroleum Exporting Countries (OPEC), where a complete description of the oil status of each nation in the world is made. Based on this information, the feasibility of building new refineries or expanding existing ones can be projected.

2.3. Alternatives to improve the hydrodesulfurization process of diesel

It was found technologies to reach levels of ultra-deep hydrodesulfurization units (UDHDS) with the modification of catalysts, for this an in-depth review was conducted in scientific and academic databanks, among them Elsevier, Scopus, ACS publications, and Google Scholar, where the procedures were found. In addition, as it is known that other materials are used for hydrodesulfurization following another route, information regarding unconventional catalysts was searched in the same databanks, as well as the synthesis of trimetallic (supported and unsupported) catalysts.

2.4. Economic feasibility of the use of NiMoW trimetallic catalysts supported on alumina-gallium in Ecuadorian refineries

Some references and information sources have mentioned that Ecuador is searching for updating, improving, and building new hydrodesulfurization units. A thorough search was carried out on the official website of EP Petroecuador and the Central Bank of Ecuador to validate this information. Moreover, information was sought on the types of catalysts used by the REE and traced back to the supplier to analyze them and consider the possibility of modifying them to increase their performance and average lifetime.



3. Diesel fuel and hydrodesulfurization

In the petroleum industry, diesel is a complex mixture of hydrocarbons obtained by fractional distillation of crude oil at temperatures ranging from 200 °C to 350 °C and specially purified to remove sulfur. It is composed of 64wt.% of aliphatic hydrocarbons, that is to say, a number of carbons predominantly in the C₉ - C₂₀ range, 5 wt.% of aromatic hydrocarbons (including benzene and polycyclic aromatic hydrocarbons), and 1-2 wt.% of olefinic hydrocarbons [15]. Its production consists, in the first place, of the distillation of crude oil and its separation into different fractions of boiling ranges. After, this fraction is refined by cracking, branching/isomerization, and aromatization. As the last step, unwanted contents are removed; among the most important is sulfur [16]. The essential properties of diesel fuels are volatility, heating value, ignition quality/cetane number, viscosity, low-temperature flow, lubricity, storage stability, component compatibility, and sulfur content [1].

3.1. Uses and classification of diesel

Diesel as fuel is significant for the transport and electricity generation sector. It is mainly used as fuel in diesel engines. The primary diesel uses are road, rail, shipping industry, mining, construction and logging, electric power generation, and military transport. The use of diesel is categorized as follows [3]:

1. **Diesel A:** It is the most suitable for motor vehicles, the refinement is more significant, and it contains additives that prevent the paraffin solidification at low temperatures. In addition, they provide properties to reduce consumption and polluting emissions and protect the pump and the injection system.
2. **Diesel B:** It is used for agricultural machinery, fishing, boats, and authorized vehicles. It is less filtered and contains more paraffins than Diesel A, which can cause trouble when used in vehicles and trucks.
3. **Diesel C:** It is explicitly used for boilers or equipment that generate high temperatures due to its high paraffin content. It is forbidden for cars or boats; it delivers much more impurities than diesel A and B and is cheaper.

The diesel fuel classification in Ecuador is as follows [17].

1. **Diesel #1:** fuel used in industrial or domestic combustion appliances.
2. **Diesel #2:** fuel used in the following sectors: industrial, fishing, electrical, maritime transport, and so forth, except for automotive usage.



3. **Premium diesel:** fuel used in auto-ignition engines for propulsion vehicles in the automotive sector nationwide.

The importance of recognizing the different ways to classify the use of diesel lies in the minimum permissible limits of sulfur content because, based on this information, the different types of procedures for the elimination of sulfur are planned and thus carry out an economic study cost benefit in the development of new technologies.

3.2. Diesel quality specifications

In the 1960s, various social demonstrations were held in the United States of America to make environmental consciousness for solving climate problems because there was a boom in pollution generated mainly by industrial, marine, and automotive machinery. Consequently, the United States Environmental Protection Agency (US EPA) was created, the federal government's office responsible for protecting human health and the environment: air, water, and soil. The US EPA commenced with the implementation of regulations that limited pollutant emissions from the diverse sources mentioned. As of December 2010, all diesel fuel sold for 2007 and later model vehicles must be graded Ultra Low Sulfur Diesel (ULSD) in the United States. That is, a maximum sulfur emission of 15 ppm was allowed.

In the United States of America, the agency responsible for setting up the procedures and standardization of tests for petroleum derivatives is the American Society for Testing and Materials (ASTM). And since 2004, the standard that stipulates the use of diesel is D975, which spreads over seven grades of diesel (Table I).

Nonetheless, according to the EPA regulations in 2010, the sulfur content determined that for all automobiles in densely populated cities, their maximum allowed content is 15 ppm (w/w), corresponding to grade 1- D S15 for D975. For other cities, the ASTM D975-94 standard [18] still applies, which admits a maximum emission of 50 ppm of sulfur (Table II). This fuel is called Ultra Low Sulfur Diesel.

The quality of European diesel fuels is specified by the EN 590 standard [11]. Even though these specifications are non-obligatory, they must be complied with by all European fuel suppliers. Since the late 1990s, several diesel fuel properties, including cetane number, sulfur content, and Fatty Acid Methyl Esters (FAME) biodiesel, have been subject to environmental regulations. Whereas the EN 590 standard mainly focuses on on-road applications, many European Member Countries define the same fuel for nonroad mobile machinery, simply adding a marker or dye for taxation purposes. Other member countries accept a different standard for fuel for off-road mobile applications. Some of the critical observations of the EN 590 standard were:



Table 1

ASTM D975 standard: diesel fuel classification.

| Grade | Description | Max Sulfur |
|---------------|---|------------|
| No. 1-D S15 | A special-purpose, light middle distillate fuel for diesel engine applications with frequent and widely varying speeds and loads or when encountering abnormally low operating temperatures. Higher volatility than that provided by No. 2 -D fuels. | 15 ppm |
| No. 1-D S500 | | 500 ppm |
| No. 1-D S5000 | | 5000 ppm |
| No. 2-D S15 | A general-purpose, middle distillate fuel for use in diesel engines, especially in applications with relatively high loads and uniform speeds, or in diesel engines not requiring combustibles having higher volatility or other properties specified in Grade No. 1-D fuels. | 15 ppm |
| No. 2-DS500 | | 500 ppm |
| No. 2-D S5000 | | 5000 ppm |
| No. 4-D | A heavy distillate fuel, or a blend of distillate and residual oil, for low-and medium-speed diesel engines in applications involving predominantly constant speed and load. | >5000 ppm |

Table 2

Diesel properties according to ASTM D975-94 specification.

| Properties | Unit | 1-D Grade | 2-D Grade |
|---|-------|------------------------|------------------------|
| Sulfur | wt.% | 0.05 (max) | 0.05 (max) |
| Carbonaceous residue over 10% using Ramsbottom or Conradson apparatus | wt.% | 0.15 (max) | 0.35 (max) |
| Ashes | wt.% | 0.01 (max) | 0.01 (max) |
| Cloud point | °C | -15 to 15 ^a | -15 to 15 ^a |
| Cu foil corrosion | | N° 3 (max) | N°3 (max) |
| Distillation: Temperature at 90% | °C | 288 (max) ^b | 282-338 ^b |
| Cetane number | - | 40 (min) ^c | 40 (min) ^c |
| Cetane index | - | 40 (min) | 40 (min) |
| Flashpoint | °C | 38 (min) | 52 (min) |
| Total aromatics | vol.% | 35 (max) | 35 (max) |
| Kinematic viscosity @40 °C | cSt | 1.3 – 2.4 | 1.9 – 4.1 |

^a: Cloud Point must be 6 ° C above the 10th percentile of the room temperature minimum.

^b: If the cloud point is less than -12 ° C, the minimum viscosity should be 1.7 cSt, and 90% of the distillate must be adjusted.

^c: Low ambient temperature and operation at altitude require a higher cetane number.

(-): Data not reported.



1. **EN 590:1993**—The first EU diesel fuel specification. It established a sulfur limit of 0.2 wt.% and a cetane number of 49 in on-road and nonroad diesel fuels. Sometimes it is referred to as Euro 1 diesel fuel.
2. **EN 590:1996**—This standard reflected a new sulfur limit of 500 ppm. The cetane number remained at 49. Sometimes it is referred to as Euro 2 diesel fuel.
3. **EN 590:1999**—This standard reflected the sulfur (350 ppm) and cetane number (51) specifications by Directive 98/70/EC (so-called Euro 3 diesel).
4. **EN 590:2004**—Sulfur limits of 50 ppm (so-called Euro 4) and 10 ppm (Euro 5) as regulated by Directive 2003/17/EC. FAME content of 5 wt.%.
5. **EN 590:2009**—FAME content of 7 wt.% as regulated by Directive 2009/30/EC. This directive also adopts mandatory biofuel requirements for refiners and introduces a 10 ppm sulfur limit in nonroad fuels effective 2011.

In the European Union regulatory language, “gas oil” describes a broad class of fuels, including diesel for on-road vehicles, nonroad vehicles, and other distillate fuels. Within the gas oil classification, fuels for on-road vehicles (typically with sulfur content below 0.05 wt.%) are called “diesel fuel”. In comparison, fuels for nonroad mobile machinery (typically with sulfur content up to 0.2 wt.%) are denoted as “gas oils intended for utilization by nonroad mobile machinery (including inland waterway vessels), agricultural and forestry tractors, and recreational craft” [11]. These terms are used in the terminology of the EU Common Customs Tariff. Different goods are assigned unique CN (Combined Nomenclature) codes to identify the applicable tariffs. Diesel fuel for on-road applications has a CN code of 2710-19-41. Gas oils for nonroad mobile machinery can acquire a CN code of either 2710-19-41 or 2710-19-45, depending on sulfur level [11]. Table III summarizes the European diesel standards created from 1993 to 2009 [19]. We also see how, as time goes by, the euro standards become more rigid concerning the sulfur content, which ranges from 500 ppm in Euro II to 10 ppm in Euro V.

Agreeing with the Ecuadorian Technical Standard INEN (NTE INEN-1489, 2012), the minimum permissible requirements for using diesel in its different modalities are classified into three types: diesel #1, diesel # 2, and premium diesel. The importance of compliance with these standards is that every day there is an increase in diseases caused by gaseous emissions, deforestation, and the deterioration of infrastructures due to acid rain, among others. An example of this damage is that suffered by the metropolis of Quito; a study carried out by Flores and Bonilla [20] in 2010 identified that 50% of the surface of the city is affected by acid rain. The acid values of rainfall were lower at a pH of 5.6 because the atmosphere is polluted with sulfur and nitrogen



Table 3

Diesel quality specifications in the European Union.

| | Diesel | | | |
|-----------------------------------|--------------|---------------------------------|-----------------------------------|---|
| | EN 590: 1993 | FQD - Dir. 98/70/EC EN 590:1999 | FQD - Dir. 2003/17/EC EN 590:2004 | FQD - Dir. 2009/30/EC EN 590:2009: +A1:2010 |
| Poly Aromatics, vol%, max | N/A | 11,0 | 11,0 | 8,0 |
| Sulfur, ppm, max | 2000 | 350 | 50/10 | 10 |
| Cetane number, min | 49 | 51 | 51 | 51 |
| Density @ 15°C, kg/m ³ | 820 - 860 | 820 - 845 | 820 - 845 | 820 - 845 |
| Distillation, T95 °C, max | 370 | 360 | 360 | 360 |
| FAME content | - | - | 5 % | % |

(-) Data not reported.

oxides from Thermoelectric power plants and vehicular traffic, which by contact with humidity and rain, become sulfuric and nitric acid. Table IV shows the permissible limits of compounds considered pollutants in the environment for the different types of diesel used in Ecuador. In the case of sulfur, the range goes from 500 ppm to 7000 ppm.

Adequate knowledge of hydrodesulfurization processes is essential to provide the best proposals to achieve the minimum permitted levels of sulfur content in diesel. Understanding these aspects allows us to know the need for stricter regulations and significant investments in the country’s refining units. Therefore, in the following topics, the operation of a hydrodesulfurization unit and some essential aspects of catalytic systems will be described in a general way.

3.3. Hydrodesulfurization (HDS)

The hydrodesulfurization unit (HDS) is a fundamental process to remove the sulfur combined within the fuel molecules as an impurity. HDS is one of the most critical operations performed after crude oil fractionation in refining. The level of HDS depends on several factors, including the nature of the oil fraction, the selectivity and properties of the catalyst, the thermodynamic reaction conditions, the hydrocarbon/hydrogen ratio, and the design of the process. The heavier the crude, it will cause the higher non-volatile fraction. Therefore, there will be a higher sulfur content. In Ecuador, the sulfur content in crude oil varies between 2.1 to 2.35 wt.% [21]. In addition, there is catalyst poisoning when crude oil has a higher sulfur content. This likewise affects the quality of the diesel, reducing the yields of the process. In the end, the diesel consumed without treatment



Table 4

Requirements for three types of diesel.

| Requirements | Diesel #1 | | Diesel #2 | | Premium Diesel | |
|---|--------------------|---------|------------|---------------------------|----------------|-------------|
| | Unit | Minimum | Maximum | Unit | Minimum | Maximum |
| Flash point | °C | 40 | | °C | 40 | |
| Water volume and sediments | % | - | 0.005 | % | - | 0.05 |
| Carbonaceous residue over 10% of the distillation residue (w/w) | % | - | 0.15 | % | - | 0.15 |
| Ash content (w/w) | % | - | 0.01 | % | - | 0.01 |
| 90% distillation temperature | °C | - | 288 | °C | - | 360 |
| Kinematic viscosity (37.8°C) | mm ² /s | 1.3 | 3 | mm ² /s (40°C) | 2 | 5 |
| Sulfur content (w/w) | % | - | 0.3 | % | - | 0.05 |
| Copper corrosion grade | - | - | - | Classification | - | No. 3 |
| Cetane index calculated | - | 40 | - | - | 45 | - |
| Biodiesel content (w/w) | - | - | - | % | NOTE | 5 |

(-) Data not reported



causes severe environmental problems. It is significant to emphasize that in the HDS for obtaining diesel, H_2S is a by-product produced, which must be continuously removed because it is an inhibitor of some of the reactions of the process in addition to poisoning the catalyst (Figure 2).

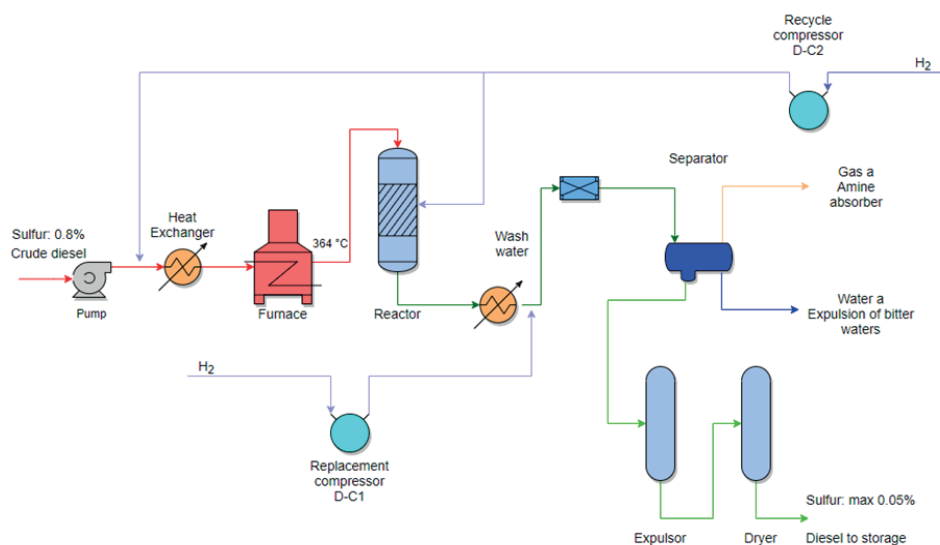


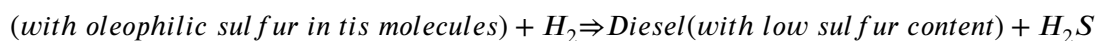
Figure 2

Diagram of the diesel hydrodesulfurization unit (HDS).

A representation of the chemical reaction of HDS from diesel is as follows:

Diesel fraction

(1)



(2)

The thermodynamic variables that control this reaction are temperature, pressure, and the amount of catalyst added for the optimal residence time in the reactor. However, it must be emphasized that even though there are various chemical transformations of the molecules linked to sulfur, the physicochemical properties of diesel fuel change, its cetane number, specific gravity, and distillation curve, among others.

In Ecuador, the diesel hydrodesulfurization unit is in the area of catalytic unit 3 of the REE, this unit possesses a reaction and separation section, and its processing capacity in 2011 was 24,500 Bls/d [21]. The diesel to purify comes from the fractional atmospheric distillation of the crude. This fraction generally reaches the HDS unit with an approximate content of 0.7 wt.% of sulfur. The final concentration of the diesel



purification will depend on the guideline according to its use. In Ecuador, according to the Ecuadorian Technical Standard INEN, its ranges go from 0.7 wt.% to 0.05 wt.% for diesel. In 2018, the national government, through the public company EP Petroecuador, made five temperature adjustments from 326 °C to 338 °C to increase the severity of the processing. The result obtained was obtaining a premium diesel with a concentration of sulfur of 0.011 wt.% [13]. Nevertheless, the goal is to continue reducing the sulfur concentration until reaching the strictest international standards. The HDS unit must have a Reaction Section and a Separation Section to obtain diesel with a lower sulfur content from the crude oil.

- 1. Reaction section:** The HDS unit receives a raw diesel feed load from a prime distillation plant, known as atmospheric distillation. The feed stream initially reaches a loaded tank, then passes to a pump to increase the pressure and mix it with a hydrogen flow. The diesel-hydrogen mixture enters a heat exchanger or preheater, then a second heater where the conditions are adjusted to enter the reactor. The optimal reactor for a pilot scale evaluation is one with a catalytic bed, for example, that of the Nitto Koatsu Company, where the primary catalyst is nickel-molybdenum (NiMo). The reaction system typically consists of three-phase packed reactors, where the liquid phase (diesel oil), the gas phase (H_2S and H_2), and the solid phase (catalyst) are present. The current operate these. In other words, the liquid and gas phases flow in the same direction, and the catalyst mass remains fixed. As seen previously, the chemical reaction in the reactor is between the organic sulfur compounds and the hydrogen feed. Organic compounds and hydrogen sulfide are the products obtained. The hot effluent from the reactor is used to exchange energy with the feed in the preheater; later, it goes to a cooler and introduces a high-pressure separator tank. In this tank, there is a separation of the gas phase and the liquid phase. The gas phase is mainly hydrogen that is recirculated to the initial process. When this operation ends, the liquid phase goes to the following division.
- 2. Separation section:** In this section, an exhausting tower performs the separation. The separated components are the desulfurized diesel and the sour gases (hydrogen sulfide, H_2 , and light hydrocarbons). The bottom product containing a minor sulfur composition passes to a fractionating tower, separating it into desulfurized diesel and bitter gasoline. The diesel obtained in the fractionating tower is the dry end product with lower sulfur content. In the end, the amine absorber treats the sour gas transforming it into sweet gas and removing the hydrogen sulfide. The diesel obtained in the crude units is subject to the hydrodesulfurization process, which produces diesel with low sulfur content (less than 0.05 wt.%) and is free



of nitrogen compounds. A principal component of the hydrodesulfurization units is solid catalysts. They accelerate reaction times, optimizing energy consumption and operating costs. It is necessary to know in-depth catalysis and its procedures to design the catalyst that manages to break up the refractory molecules; these molecules remain as a background after thermal hydrotreating and limit the capacities of the HDS units.

3.4. Characteristics that catalysts must-have for the HDS process

A catalyst can be composed of three parts that increase its rendering and effectiveness. The first is the site or active agent, the point where the reaction will take place, or the catalytic substance that causes the acceleration of the reaction. These substances can be dispersed or not on support-generating active sites. The second is the support, a system with high porosity and high specific area that allows the catalyst to be extended by increasing its reactive area, improves the stability of the catalyst and prevents sintering, improves mechanical properties, and facilitates energy transfer. The third component is the promoter, a chemical substance that improves catalytic properties, increases resistance to deactivation, and improves selectivity and performance [6]. The methods of preparing these supports are diverse: precipitation, gelatin (sol-gel), impregnation, melting, anchoring, and hydrothermal transformation. In these methods, templates are commonly used to guide the shape of the supports, giving different structural models. According to the flow dynamics, the type of catalytic reactor and the operating conditions of the systems will be the appropriate selection of the catalytic support, in addition to considering its performance capacity and costs.

The first catalysts in the HDS process were those used in hydrogenating liquids derived from coal with high sulfur content [22]. The catalysts used in the HDS process must have the ability to tolerate high pressures (150-2250 psi) and high temperatures (320-440 °C) to be able to remove sulfur impurities bound with carbon atoms (C-S). In addition to withstanding acidic conditions generated when hydrogen sulfide is produced as a by-product [6]. Sulfur is a heteroatom found in the derivatives of dibenzothiophene (DBT), benzothiophenes (BT), benzonaphthothiophenes (BNT), dinaphthothiophenes (DNT), thiols, thiophenes, and others. The processes and catalytic systems are designed for elimination in conformity with these properties. In the range of middle distillates, there are mainly derivatives of DBT and BT, increasing their concentration in heavier fractions such as vacuum gas oil (VGO) [23]. This suggests that the concentration of the alkyl-DBTs is found in crude fractions with boiling points above 300 °C. Furthermore, the fractions in the 300-340 °C contain a high concentration of C₁/C₂-DBT together with



C₅/C₆-BT, while at temperatures below 300 °C, alkyl-BT is present. However, it must be emphasized that the distribution of these compounds will also depend on the crude oil origin [7]. In the same way, benzothiophenes and dibenzothiophenes are found in intermediate sections. These molecules are refractory because they persist in much lower concentrations when there are fewer reagents in a conventional hydrotreating process. Therefore, these molecules are employed as the groundwork for modeling and designing catalysts for HDS processes [14].

The most common catalysts used in HDS are based on binary systems of molybdenum-cobalt oxides and nickel-molybdenum oxides dispersed on alumina support surfaces. Cobalt and nickel act as promoters to increase catalytic activity. The catalyst acquires the active form through its sulfidation process, mainly during the feeding stage and when it is treated before use. According to the type, the fuel load is the catalyst's preference. The most popular alternative is CoMo because it reacts with most sulfurized organic molecules in the presence of hydrogen gas. Even so, this catalyst type does not allow reaching all the desired levels in the oil fractions. For instance, when there is a very high saturation activity of aromatic compounds, and it is also necessary to remove nitrogen or refractory sulfur compounds, NiMo catalysts are a suitable option. The composition of the catalyst will depend on the desired activity. Table V presents the typical compositions of the most common catalysts used in diesel hydrodesulfurization [12].

Table 5

Commercial catalysts and their typical compositions.

| | CoMo | NiMo | NiW |
|-------------------|-------------|-------------|------------|
| Cobalt (wt.%) | 2.5 | - | - |
| Nickel (wt.%) | - | 2.5 | 4 |
| Molybdenum (wt.%) | 10 | 10 | - |
| Tungsten (wt.%) | - | - | 16 |

As discussed earlier, NiMo, CoMo, and NiW catalysts are usually supported on γ -alumina. The generation of the NiMoS, CoMoS, and NiWS support phases are responsible for the catalytic activity. Its capacity in terms of scope of desulfurization, activity, and selectivity depends on the properties of the catalyst, the reaction conditions such as temperature, partial pressure of H₂, H₂S, and so on, the nature and concentration of sulfur compounds, the design of the process and reactor. Figure 3 a) presents one of the models that propose the formation of the phases during the HDS process for the CoMoS, and Figure 3 b) the interaction procedure for the CoMoS according to the operating conditions for the HDS [24,25].

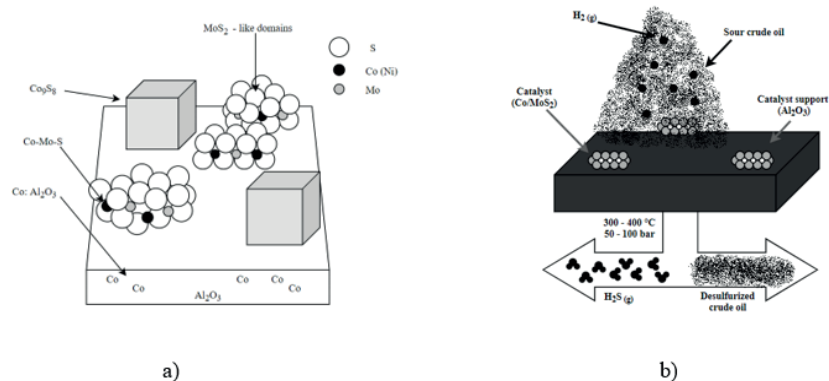


Figure 3

a) Interaction procedures and b) CoMoS formation phases in the HDS process.

As suggested above, the perfect catalyst for HDTs has a high capacity to remove metals, nitrogen, and sulfur in the specific case of HDS. In addition, it must be able to improve other fuel properties, such as the octane/cetane number or the aromatic content, based on local and international environmental legislation. One of the innovations or changes to traditional catalysts is to modify the active phase's nature, change its proportion, introduce additives, or completely change the active component. For instance, some additives tested with good results are fluorine, phosphorus, vanadium, or iron as promoters [26-28].

Another change is replacing the catalysts' sulfides with carbides or nitrides [29]. Catalysts with noble metals (Rh, Pd, Ru, Pt) have been prepared for the HDS of thiophene [30]. In the ultra-deep HDS of diesel, the use of heteropoly acids ($H_3PW_{12}O_{40}$ and $(NH_4)_6H_2W_{12}O_{24}$) supported on Al_2O_3 and SBA-15 have increased the catalytic action [25]. In addition, alternative supports and combinations have emerged as suitable alternatives to improve HDS processes. Also, in DBT treatment through HDS, the titanium, zirconia, carbon, and silica oxides are excellent. Likewise, another promising study for the treatment of DBT is the effect of the support combinations, for instance, silica-alumina, $TiO_2-Al_2O_3$, and ZrO_2-TiO_2 [14,31].

At the beginning of the 1980s, the development of catalytic supports based on activated carbon for HDS began due to its low cost and easy recovery of the active metal through the combustion of carbon [32, 33]. Activated carbon-supported catalysts were shown to be less sensitive to deactivation by poisoning due to coke formed [33]. The HDS processes of thiophene and its derivatives have used FeS_2 catalysts supported on activated carbon, which presented high chemical activity. The metal charge was up to 2 atoms/nm² per surface area of support [34,35]. The studies on the HDS of the DBT using NiMo catalysts supported in the alumina-activated carbon (AAC) system



showed good stability and high activity [36]. These properties are attributed to the mesoporous structure of the support and the high dispersion of Ni and Mo on the support. The most recent technologies in the design of supports are the coating with nanoparticles of aluminosilicates and mesoporous carbon structures. To evaluate the HDS of 4,6-DMDBT, a dispersion of the MoS₂ catalyst was carried out on these new supports, and the results obtained were an activity of about 3.5 times greater than the use of only aluminosilicates as support, with high dispersion and robust stability of the nanoparticles on the support [37]. Nanoporous materials are exciting in this line of new materials due to their various industrial application possibilities. These new materials include clay minerals, inorganic silica gel-type gels, zeolites, alumina, and activated carbons. These materials have a high surface area with nanometric porosities [38]. In 2012 and 2013, researchers conducted studies of cordierite monolith coatings with carbon nanotubes. This type of support obtained a high surface area, good pore distribution after acid pretreatment of the support, and excellent dispersion of carbon nanotubes. They utilized them to evaluate the HDS of naphtha; the sulfur content in this fuel decreased from 2,670 ppm to 13 ppm [39,40].

4. Diesel HDS and its impact on the fuel market in Ecuador

4.1. Diesel production and hydrodesulfurization in Ecuador

Ecuadorian oil is considered a medium to heavy oil with high sulfur content. The premium diesel (higher demand) produced in the country has 500 ppm of sulfur, which complies with national regulations but not international regulations of 10 ppm. Hence the importance of the hydrodesulfurization process in refineries. In recent years the REE has made several technical stops to carry out five temperature adjustments in the reactor from 326 °C to 338 °C; with these adjustments, the hydrodesulfurization unit has reached a level of diesel production with a maximum content of 110 ppm of sulfur [8], and for the following years corrective measures are scheduled to increase the severity of the process (increasing the temperature or pressure in the fractions), with this it is expected to obtain a diesel premium with sulfur concentrations in ranges close to 80 ppm. Nonetheless, even to comply at least with the Ecuadorian Standard NTE INEN-1489 (2012) in the other types of diesel, EP Petroecuador imports diesel and mixes it with that of national production because deep hydrodesulfurization is not yet possible in your diesel HDS units. Therefore, trimetallic catalysts are an excellent alternative since they have been shown to decompose the so-called refractory molecules.



4.2. Comparison of trimetallic catalysts with bimetallic catalysts

CoMo is a bimetallic catalyst and is very effective in HDS because its products come from the direct desulfurization route. This is due to the effect of Co on the structural phase of mass. However, this does not happen with deep HDS since most of the sulfur compounds in fuels cannot be decomposed because they are highly refractory, which induces them to remain after normal HDS. For instance, one of the molecules that represent the deep HDS is the 4,6 - DMDBT, where from the DBT, the sulfur bound in the disubstituted dialkyl molecules must be eliminated, but because the dialkyl radicals that are in the 4,6 positions have a steric effect prevent hydrogenolysis of the bond S-C. For this reason, modifying the promoter and adding Ni to facilitate this reaction to follow the direct desulfurization route is necessary. This procedure allows for higher conversions eliminating the steric effect [14]. Accordingly, adding a third metal with catalytic activity makes it easier to achieve desired conversion levels.

NiMoW and CoMoW trimetallic catalysts compatible with SBA-15 modified with titania or zirconia have been used for deep HDS. The molecules that were tested for sulfur removal were DBT and 4,6-DMDBT. NiMoW/Zr-SBA-15 was the most active catalyst for sulfur removal in less time, Figure 4. Adding titanium and zirconia to the NiMoW and CoMoW catalysts conferred a higher HDS activity, which was more significant for the Ni-promoted samples [41].

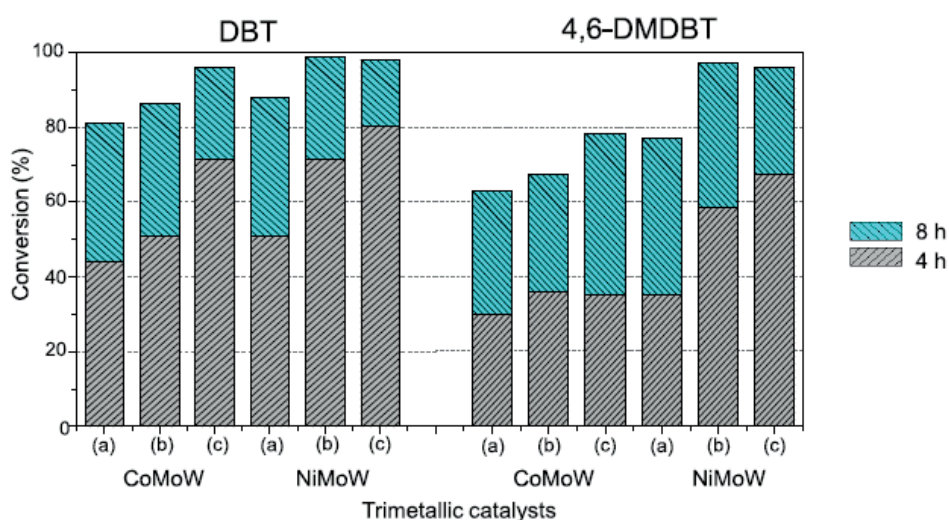


Figure 4

Conversions of DBT and 4,6-DMDBT were obtained at 4 and 8 h reaction times using trimetallic CoMoW and NiMoW catalysts supported on: (a) SBA-15; (b) Ti-SBA, and (c) Zr-SBA.

In addition to conventional supports, clays (modified montmorillonite) supported trimetallic catalysts have also been tested. Using a NiMoW-clay hybrid removed 99.8



% of the sulfur present in DBT compounds and provided an excellent 168-hour stability for industrial kerosene (2,400 ppm sulfur). The clay modified with organic cations allowed the metal ions to be easily dispersed evenly between the sheets, allowing the generation of more excellent active sites and easy access to these due to the laminar characteristics of the clay [42]. Therefore, by the improvements that the add-on of an active third metal brings to the properties of conventional catalysts, trimetallic catalysts are a good option for removing refractory compounds, which is the goal of achieving a complete HDS of diesel.

The hydrodesulfurization process reduces the percentage of sulfur in the oil fractions. The process is efficient in the presence of hydrogen and a catalyst. Environmental regulations in many countries need more “friendly” transportation fuels with lower sulfur contents (10 ppm). As discussed above, the sulfur content in fuels is a concern because, during combustion, it is converted to SO_x, which contributes to acid rain. Alumina-supported Co(Ni) or Mo(W) catalysts are typically used in HDS reactions. The beginning of using alumina support is related to its remarkable mechanical and textural properties and relatively low cost. However, evidence of a robust metal-support interaction has prompted much research to study new supports. Many references can be found using materials as HDS catalyst supports in the literature. For example, studies in the application of silica-based mesoporous meshes as catalytic supports. Mesoporous Hexagonal Silica (MHS), SBA-15, and SBA-16 have attracted significant attention as potential HDS supports. Previous studies have shown that when MHS modified with Ti is used as a support for Co (Ni) Mo phases, catalysts with higher catalytic activity are obtained compared to a commercial CoMo/Al₂O₃ catalyst in the HDS reaction of DBT. This may be related to a better dispersion of the active phases on the surface of the support due to the effect of Ti. In the same way, recent results show that pure and modified mesoporous materials of SBA-15 and SBA-16 are suitable supports for CoMo and CoMoW catalysts evaluated in the HDS reaction of DBT. Regarding the active phase, bimetallic formulations have generally been used. Until 2017, the catalyst that exhibited the highest catalytic activity for HDS reactions was the so-called NEBULA (New Bulk Activity). This is based on transition metals (Ni, Mo, and W), which Soled et al. [43] patented in 2001.

4.3. Technical-economic evaluation of the use of trimetallic catalysts

As time passes, in each country, the regulations on atmospheric emissions become more rigorous because of the combustion of fossil fuels. It is necessary to modify the



combustion systems and improve the refining operations. In the case of diesel, the current standard that many countries are adopting is Euro VI, which establishes a sulfur emission limit of 10 ppm (Figure 5).

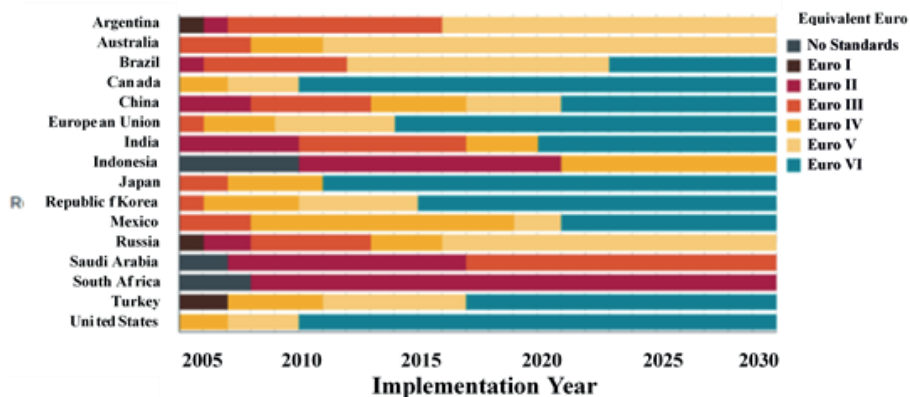


Figure 5

Year of implementation (all sales and patents/registrations) of emissions standards for heavy diesel-powered vehicles in G-20 economies [44].

To reach the new international standards (USA, European Union) of sulfur content of diesel fuel (between 50 and 10 ppm), a substantial increase in the current hydrodesulfurization capacity (HDS) is necessary since most of the existing refineries reduce the sulfur content up to 500 ppm. Depending on the type of refinery, some will be able to reach the new standards through modifications of their HDS units, but other refineries will have to do so from new plants.

In the short time and to reach the new standards, the possibilities of process innovations are restricted to modifying the operating conditions and using more catalysts or new, more active catalysts. Other options include (a) improving the purity of the feed hydrogen through the use of adsorption or membrane processes and further washing of the sulfhydic acid in the recycle gas, modifying the residence time in the reactor; (b) The decrease in polyaromatic compounds; (c) new vapor and liquid distributors within the reactor to improve desulfurization efficiency; and (d) better control of the reactor temperature by injecting gas. A strategy has been used to add a third component as an additive, for example, NiCoMo, NiMoW, and VNiMo catalysts [6,24], to improve the characteristics of the catalysts used in HDS. The Esmeraldas State Refinery mainly uses two types of commercial catalysts [21]; the products' descriptions are as follows (Table VI).

These catalysts can be modified by adding a third metal component. Knowing the availability and cost in the Ecuadorian market is necessary to optimize resources with the least investment expense. The metallic impregnation ratios vary from 1 % to 10 %. After



Table 6

Commercial catalysts used by REE.

| | Catalyst | |
|--------------------------------------|---|---|
| | Type LD 145 Catalysts (HR 648) | TYPE HR 306 C Catalysts (HR 626) |
| Supplier | Procatalyse Catalysts and absorbents (Axens Company) | Procatalyse Catalysts and absorbents (Axens Company) |
| Function | Selective hydrogenation of unsaturated pyrolysis cuts at the top of the first reactor bed | Hydrodesulfurization of distillates |
| Amount | 11 m ³ | 97 m ³ |
| Description and chemical composition | High-purity alumina beads loaded with nickel and molybdenum oxides. Particle size diameter 2-4 mm | Very high-purity extruded cylindrical alumina loaded with cobalt and molybdenum oxides. |
| Typical composition | NiO (8 wt.%) MoO ₃ (8 wt.%) | CoO (3 wt.%) MoO ₃ (14 wt.%) |
| Physical properties | | |
| Superficial area | 140 m ² /g | 210 m ² /g |
| Mass density | 0.8 g/cm ³ | blow loaded: 0.67 g/cm ³ dense loaded: 0.76 g/cm ³ |
| Pore volume | 0.45 cm ³ /g | 0.5 cm ³ /g |
| Estimated cycle duration | 2 years | 2 years |
| Estimated life | 6 years | - |
| Particle size: | - | Diameter 1.2 mm, long 4 mm |
| Losses on ignition at 500 °C: | - | 0.5 wt.% |
| Resistance to mass compression: | - | 159.5 psi |

(-) Data not reported.

this, there is an oversaturation of the catalyst. Ecuador has Molybdenum deposits in the Bolivar province and the Cotacachi canton (Imbabura province). The approximate total reserves in the country are 865 million pounds, according to available documents and reports with the Canadian standard NI 43-101. China is the world's largest molybdenum producer, covering around 45% of the market, followed by Chile with 20 %. In 2015, EP Petroecuador made a purchase of 4,442.00 m³ of catalyst at the cost of US \$ 3,368,133 per m³, and to this cost must add the purchase cost to other countries of diesel with low sulfur content to meet the parameters established in the Ecuadorian standard NTE INEN-1489 (2012). This cost will decrease if it is possible to obtain national catalysts that achieve deep HDS by increasing the activity of the bimetallic catalyst by adding a third component, the costs per metric ton decrease significantly. On the other hand, a cost-benefit analysis of the Euro VI standards on emissions in heavy vehicles in Argentina estimated that for every US\$ 1.00 that is invested to reach the standards of the Euro VI standard in 30 years, US\$ 3.60 would be generated in benefit to human health, this



due to reduced exposure to pollutants generated by diesel combustion. Likewise, the increased cost benefits will be more visible if they are applied in the short term and not in the long time (Table VII).

Table 7

Projection of net benefits for the period 2021 to 2025 (30 years).

| Stage | Private accumulated costs (millions USD) | Accumulated health benefits (millions USD) | Net profit (millions USD) |
|-----------------|--|--|---------------------------|
| Euro VI in 2021 | 620 | 2202 | 1583 |
| Euro VI in 2023 | 559 | 1990 | 1432 |
| Euro VI in 2025 | 502 | 1787 | 1285 |

The significant part of this study is that Argentina belongs to South America, and the impulse to its policies and improvements in the quality of its diesel fuel has repercussions in the region. Thus, proposals such as using trimetallic catalysts to achieve deep hydrodesulfurization levels are viable options for Ecuador. This is the path that Ecuador must follow to reach the international goal of one day reaching 0 ppm of sulfur and other components.

5. Conclusions and recommendations

1. Ecuador produces crude with an average sulfur content of 2.35 %, which is why it is considered bitter crude. This causes distillates, gasoline, fuel oil, and diesel, among others, to contain high concentrations of sulfur after the distillation process. This is one of the causes why one of the largest refineries in the country processes in its HDS diesel unit with an average sulfur content of 7000 ppm.
2. At the REE, various technical shutdowns have been carried out to adjust the thermodynamic conditions of the diesel hydrodesulfurization unit to reach a sulfur content level of 110 ppm in the fuel. However, increasing the severity of the process has not been the only alternative. The performance and capacities of the conventional catalysts used in the process can be improved. This has led to the use of supported catalysts, unsupported catalysts, and trimetallic catalysts.
3. One of the promising catalysts is thus obtained through the impregnation of Ni, Mo, and W in mixtures of Al_2O_3 - Ga_2O_3 oxides, a process carried out through the pore-filling method. This type of catalyst has made it possible to extract



sulfur from the so-called refractory molecules. This procedure is known as deep hydrodesulfurization.

4. Using trimetallic catalysts such as NiMoW could not only assist in breaking down refractory molecules and thus achieve ultra-low sulfur in diesel, but indirectly it would also help improve human health, considerably reducing respiratory diseases caused by particles. Suspended and diminish the acid rains that are more frequent daily, altering the ecological equilibrium. Savings offset changing health, infrastructure maintenance, and environmental remediation technology costs.
5. Investing in the country's refineries is necessary to reach ultra-low sulfur concentrations and, as far as possible, up to 0 ppm of this element. To achieve this, it is required to obtain ultra-deep hydrodesulfurization units (UDHDS) and reactive distillation systems. These are currently widely used in refineries around the world with successful results.
6. Along with this modernization in hydrodesulfurization processes and all fuel refining processes, the quality of automotive systems must begin to alleviate. To not only bring down the emissions generated by these fuels but also reduce the consumption of these.

Acknowledgments

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ABBREVIATIONS

ASTM American Society for Testing and Materials

BNT Benzonaphthothiophene

BT Benzothiophene

C₁ Methane

C₂ Ethane

C₂₀ Icosane

C₅ Pentane

C₆ Hexane

C₉ Nonane

CN Combined Nomenclature



CoMo Copper-Molybdenum
COx Carbon Oxide
DBT Dibenzothiophene
DNT Dinaphthothiophene
FAME Fatty Acid Methyl Esters
H₂S Hydrogen sulfide
HD Hydrogenation
HDS Hydrodesulfurization
HDT Hydrotreatment
INEN Servicio Ecuatoriano de Normalización
MMBls/day Millions of Barrels per Day
MoS₂ Molybdenum Disulfide
N₂ Molecular Nitrogen
NiMo Nickel-Molybdenum
NiW Nickel-Tungsten
NN-PR Neural network for pattern recognition
NOx Nitrogen Oxide
O₂ Molecular Oxygen
OPEC Organization of Petroleum Exporting Countries
REE Refinería Estatal de Esmeraldas
SOx Sulfur Oxide
UDHDS Ultra-Deep Hydrodesulfurization
ULS Ultra-Low Sulfur
US EPA the United States Environmental Protection Agency
VGO Vacuum Gas Oil

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