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Título: Diesel Hydrodesulfurization and its Impact on Fuel Market in Ecuador

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I dedicate this thesis to my parents, my brother, and my sister. Because they were the ones who were always there for me, with their unconditional support and love, and thanks to them I was able to fulfill this goal.

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RESUMEN

En esta tesis se analizó de manera general el proceso de hidrodesulfuración para la obtención de diésel con bajo contenido de azufre, el nivel de procesamiento en el Ecuador, la calidad del diésel nacional en comparación con otros países, las necesidades técnicas y económicas del proceso, además del cambio o mejora de los catalizadores para alcanzar la hidrodesulfuración profunda. En la revisión bibliográfica se encontró que lamentablemente en los yacimientos ecuatorianos el contenido de azufre es muy alto. En 2018, Ecuador produjo 3.53 MMkg de azufre de los procesos. No obstante, a pesar de las mejoras en las refinerías del país solo se ha alcanzado a disminuir hasta 110 ppm el contenido de azufre en el diésel. Actualmente, Ecuador regula las emisiones de azufre a través de la norma ecuatoriana INEN 1489 (2012), esta norma de acuerdo con el uso del diésel y al límite permitido de contenido de azufre clasifica al combustible en tres tipos, Diésel No. 1 (3000 ppm), Diésel No. 2 (7000 ppm) y Diésel Premium (500 ppm). No obstante, Ecuador busca alinearse con los países que tienen regulaciones más estrictas, como es el caso de la Unión Europea, la norma que regula las emisiones de azufre en esta comunidad es la Euro VI, la cual limita la concentración a 10 ppm.

Algunas de las modificaciones para alcanzar los estándares internacionales en las unidades de hidrodesulfuración de las refinerías del Ecuador está la de cambiar los sistemas catalíticos o mejorarlos. Una de estas mejoras es el empleo de catalizadores trimetálicos soportados y no soportados. Estos catalizadores logran descomponer las moléculas llamadas refractarias (ejemplo, Dibenzotiofeno y 4,6 - Dimetildibenzotiofeno) que se encuentran en la hidrodesulfuración profunda y que catalizadores normalmente usados como el CoMo o MoW no logran hacerlo. Un ejemplo de la capacidad de estos catalizadores fue la evaluación realizada a escala laboratorio de un catalizador conformado por NiMoW soportado en Al_2O_3-Ga_2O_3, se empleó al Dibenzotiofeno como molécula modelo para evaluar su capacidad catalítica, mediante la medida de concentración de azufre en la misma. Por lo tanto, propuestas como el uso de catalizadores trimetálicos para lograr alcanzar los niveles de hidrodesulfuración profunda son una opción muy viable para el Ecuador. Dado que en este momento el país está buscando mejorar sus procesos de refinación y además está planificando construir una nueva planta de hidrodesulfuración y una unidad de procesamiento de combustible bajo la modalidad BOT (construir, operar y transferir) en Manabí.

Palabras claves: diésel, azufre, Ecuador, hidrodesulfuración, refinerías, catalizadores trimetálicos, planta de hidrodesulfuración.

ABSTRACT

In this thesis, the hydrodesulfurization process to obtain diesel with low sulfur content was analyzed in a general way, the level of processing in Ecuador, the quality of domestic diesel compared to other countries, the technical and economic needs of the process, in addition to the change or improvement of the catalysts to achieve deep hydrodesulfurization. In the bibliographic review it was found that, unfortunately, the sulfur content is very high in Ecuadorian deposits. In 2018, Ecuador produced 3.53 MMkg of sulfur from the processes. However, despite the improvements in the country's refineries, the sulfur content in diesel has only been reduced to 110 ppm. Currently, Ecuador regulates sulfur emissions through the Ecuadorian standard INEN 1489 (2012), this standard in accordance with the use of diesel and the permitted limit of sulfur content classifies the fuel into three types, Diesel No. 1 (3000 ppm), No. 2 Diesel (7000 ppm) and Premium Diesel (500 ppm). However, Ecuador seeks to adjust with the countries that have 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.

Some of the changes to reach international standards in the hydrodesulfurization units of the Ecuadorian refineries is to modify the catalytic systems or better them. One of these advances is the use of supported and unsupported trimetallic catalysts. These catalysts manage to decompose the so-called refractory molecules (for example, Dibenzothiophene and 4,6-Dimethyldibenzothiophene) that are found in deep hydrodesulfurization, and that normally used catalysts such as CoMo or MoW cannot do so. An instance of the capacity of these catalysts was the laboratory-scale evaluation of a catalyst made up of NiMoW supported in Al2O3-Ga2O3, Dibenzothiophene was used as a model molecule to evaluate its catalytic capacity through the concentration of S on it. Therefore, proposals such as the use of trimetallic catalysts to achieve deep hydrosulfurization levels are a very viable option for Ecuador. Given that at this time the country is trying to improve its refining processes and is likewise planning to build a new hydrodesulfurization plant and a fuel processing unit under the BOT modality (build, operate and transfer) in Manabí.

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

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ABBREVIATIONS

AAC	Alumina Activated Carbon
ASTM	American Society for Testing and Materials
BCH	Bicyclohexyl
BHP	Broken Hill Proprietary
BNT	Benzonaphthothiophene
BOT	Built Operation Transfer
BT	Benzothiophene
C_1	Methane
C_2	Ethane
C_{20}	Icosane
C_5	Pentane
C_6	Hexane
C_9	Nonane
CHF	Cyclohexylphenyl
CN	Combined Nomenclature
CoMo	Copper-Molybdenum
COx	Carbon Oxide
DBT	Dibenzothiophene
DFT	Density functional theory
DNT	Dinaphthothiophene
EIA	Energy Information Administration
FAME	Fatty Acid Methyl Esters
FGD	Flue Gas Desulfurization
H_2S	Hydrogen sulfide
HCl	Hydrochloric Acid
HD	Hydrogenation
HDS	Hydrodesulfurization
HDT	Hydrotreatment
HF	Hydrofluoric Acid
HHDBT	Hexahydrodibenzothiophene

INEN	Servicio Ecuatoriano de Normalización
MMBls/day	Millions of Barrels per Day
MoS_2	Molybdenum Disulfide
N_2	Molecular Nitrogen
NiMo	Nickel-Molybdenum
NiW	Nickel-Tungsten
NN-PR	Neural network for pattern recognition
NOx	Nitrogen Oxide
O_2	Molecular Oxygen
OPEC	Organization of Petroleum Exporting Countries
REE	Refinería Estatal de Esmeraldas
SOx	Sulfur Oxide
THBT	Tetrahydrodibenzothiophene
UDHDS	Ultra-Deep Hydrodesulfurization
UK	United Kingdom
ULS	Ultra-Low Sulfur
US EPA	United States Environmental Protection Agency
VGO	Vacuum Gas Oil
WS_2	Tungsten Disulfide

CHAPTER I

1. INTRODUCTION

Humanity has depended on the use of energy resources since it found a way to control, produce and use fire. Through time, this dependence on energy resources has increased for several reasons, the increase in population, the development of industries and transportation. With respect to the latter, oil and its derivatives are the main source of energy since they are liquids with a high energy content. The derivative of greater demand is diesel, which is mainly used as fuel [1-3]. Consequently, diesel has a significant role in the economic system, not just nationally, but globally.

Although there are new energy options, diesel remains profitable and efficient as a fuel [1]. It is for this reason that we should keep the attention on diesel and thus be able to meet the needs of the market. Nevertheless, the combustion of diesel produces nitrogen oxides (NOx), and carbon oxides (COx), in addition, as the diesel also has sulfur in its chemical composition, they produce sulfur oxides (SOx); the same that in contact with water vapor in the atmosphere, it produces sulfuric acid (H_2SO_4), coming back to the surface and giving rise to "acid rain" [4, 5]. Additionally, they cause operational problems, such as corrosion or the poisoning of catalysts [6, 7]. In consequence, the processes to remove sulfur in a refinery are very necessary.

Among the hydrotreatment (HDT) processes used to reduce the content of sulfur in a refinery the hydrodesulfurization (HDS) is the most important, this is a procedure in which a hydrogen treatment is given to the different fractions of crude oil. Furthermore, to achieve a deep desulfurization when obtaining diesel, modified catalysts are applied, supported or unsupported. The level of desulfurization required depends on the nature of the oil fraction, selectivity and activity of the catalyst, operating conditions, and process design.

In Ecuador the companies that oversee oil extraction and refining of its derivatives are Petroamazonas and EP Petroecuador, respectively. On the other hand, the refinery with the largest crude processing capacity nationwide is the Refinería Estatal de Esmeraldas (REE) (110,000 Bls/d - 2018), designed and constructed between 1975 and 1977 [8]. In 2019, Ecuador experienced a total production of 531,000 Bls/d of crude [9]. Similarly, in this year Ecuadorian crude undergone the refining operation to obtain derivatives, said production was 142,000 Bls/d, showing a decrease of 10.7% compared to 2018. As well, there was a decrease in the national demand of derivatives (2.4 %), and the total annual demand was 91.0 MMBls, in daily volume, the production of derivatives was 207,193 Bls [10]. In this work, of the derivatives produced, we will emphasize diesel, for being the fuel with the highest demand in the nation (36.2 % of the total) and one of the main emitters of sulfur in the environment and other pollutants.

National diesel can be found in three types: Diesel No. 1, Diesel No. 2 and Premium Diesel. These three types of diesel represent a great percentage of the national production of derivatives with 11.77 MMBls/year [8]. The automotive sector uses a great percentage of the diesel produced at the national level, followed by the industrial sector, shipping industry, among others.

In 2018, Ecuador produced 3.53 MMkg of sulfur, a consequence of its refinement processes. The Premium Diesel (higher demand) produced in the country has 500 ppm of sulfur, which complies with national regulations, but not with international regulations. (10 ppm, Euro 5-European emission standards) [11]. Hence the importance of the hydrodesulfurization process in refineries. To comply with the latter, EP Petroecuador imports diesel and mixes it with that of national production, which is not feasible with respect to 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 the sulfur content in it.

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 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 to be completely eliminated. In addition to considering whether the country's refineries with their infrastructure could produce ultra-low-sulfur diesel. So, this study proposes to analyze a potential improvement in the diesel hydrodesulfurization process with the integration of NiMoW trimetallic catalysts supported on alumina and gallium oxides. These catalysts demonstrated to have higher desulfurization conversion in pilot tests [6, 14].

1.1. Problem Statement

As diesel is the derivative with the highest demand in Ecuador, its most important aspect is the quality, in terms of sulfur content. The raw material that leaves the refineries, even with a high sulfur content, 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 twice the national production. In October 2018, the diesel import figures were 2,514.5 MBls, while the national production was 995.9 MBls and the internal consumption was 2980.9 MBls (Figure 1). This is because the production of diesel needs to mix with diesel that delivers a lower amount of sulfur to be able to commercialize it in the domestic marketplace.

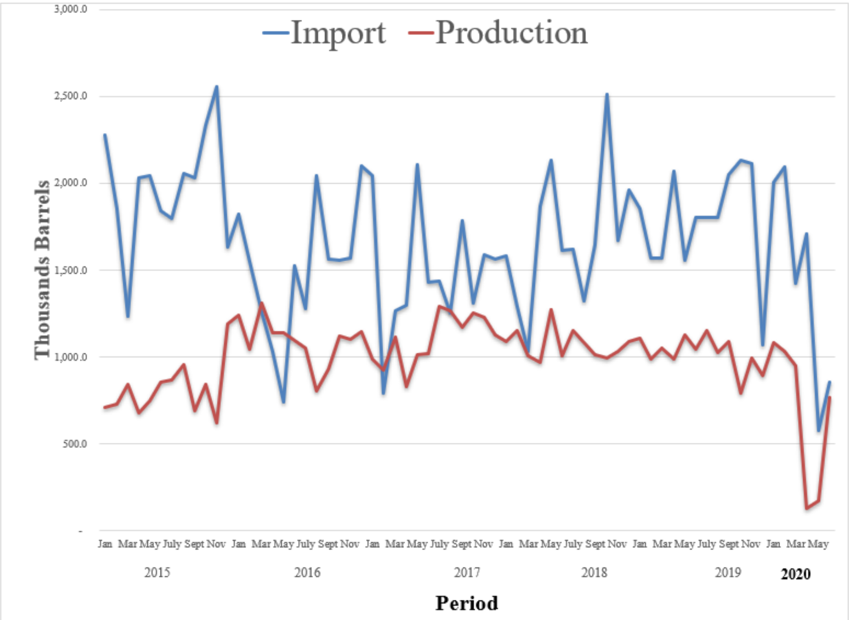


Figure 1. *Diesel Production and import, 2015-2020.*

Sulfur compounds in exhaust emissions from diesel combustion processes are the main air pollutants. Consequently, in Ecuador, emissions of polluting gases increase over the years, because the desired diesel quality is not yet achieved.

As the need for refining heavier crude oil with a higher content of sulfur compounds in Ecuador, more sophistication of the active catalysts is required in the HDS process, because of the poisoning and deactivation of these is more easily. Besides, this causes operating costs to increase and consequently the cost of diesel to the public. Therefore, NiMoW trimetallic catalysts are a good option to achieve deep hydrodesulfurization levels. In this way, a cost benefit analysis is necessary in the utilization of this technology.

1.2. Objectives

1.2.1. General Objective

To carry out a comprehensive analysis of diesel production in Ecuador and the impact of the use of NiMoW trimetallic catalysts supported on alumina-gallium in the hydrodesulfurization process.

1.2.2. Specific Objectives

- To analyze the diesel production system and the sulfur removal process in the refineries of Ecuador.
- To identify alternatives to improve the hydrodesulfurization process of diesel streams for the domestic market.
- To evaluate alumina-gallium supported NiMoW trimetallic catalysts in the hydrodesulfurization process.
- To evaluate the economic feasibility of the use of NiMoW trimetallic catalysts supported on alumina-gallium in the country's refineries.

CHAPTER II

2. BACKGROUND AND LITERATURE REVIEW

2.1. Diesel Fuel Technical Review

The drive for the use of diesel as a fuel dates back to the developments of hydrocarbon-based engines by Rudolf Christian Karl Diesel (1858 - 1913). The word diesel also applies to the fuel called fuel oil, diesel oil or diesel. It is obtained from crude oil (diesel-oil) or from vegetable oils (biodiesel) [2].

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 (Figure 2). Compose of 64 wt.% of aliphatic hydrocarbons, that is to say, a number of carbons predominantly in the C_9 - C_{20} range, 5 wt.% of aromatic hydrocarbons (including benzene and polycyclic aromatic hydrocarbons), and 1-2 wt.% of olefinic hydrocarbons [15].

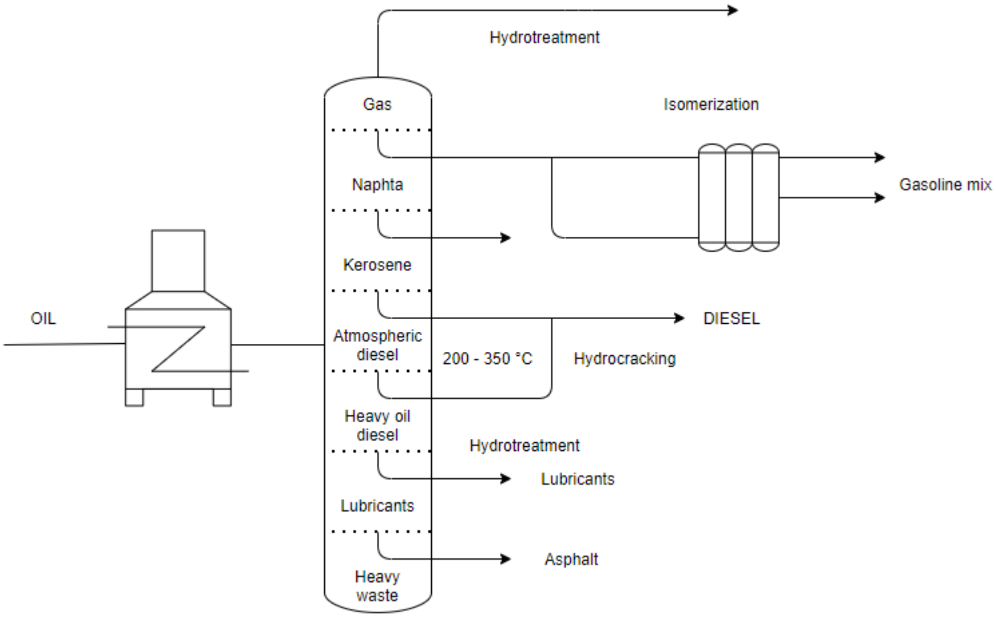


Figure 2. *Typical atmospheric distillation unit of crude oil* [3].

Its production consists, in the first place, of the distillation of crude oil, and its separation into different fractions of boiling ranges. Secondly, this fraction is refined by cracking, branching / isomerization, and aromatization. As a last step, unwanted contents are removed, among the most important is sulfur [16].

The important 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].

2.2. Uses of diesel

Diesel as a fuel is very important for the transport and electricity generation sector. It is mainly used as a fuel in diesel engines. Among the main uses of diesel are road, rail, shipping industry, mining, construction and logging, electric power generation, and military transport.

According to the use of diesel it is categorized as follows [3]:

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

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

- **Diesel No. 1**: Fuel used in industrial or domestic external combustion appliances.
- **Diesel No. 2**: Fuel used in the following sectors: industrial, fishing, electrical, maritime transport, and so forth, except for automotive usage.
- **Premium Diesel**: It is the fuel utilized in auto-ignition engines for the propulsion of 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.

2.3. Quality specifications

In the 1960s, various social demonstrations were held in the United States in order to make environmental consciousness for the solving of 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, which is the office of the United States federal government that is responsible for protecting human health and protecting the environment: air, water and soil. This commenced with the implementation of regulations that limited pollutant emissions from the diverse sources mentioned. As of december 2010, in the United States, all diesel fuel sold for 2007 and later model vehicles required to be Ultra Low Sulfur Diesel (ULSD) graded. That is, a maximum sulfur emission of 15 ppm was allowed.

2.3.1. Quality of US diesel fuel

In the United States, the agency that is 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 7 grades of diesel (Table 1).

Table 1. *Diesel fuel grades defined by the ASTM D975 standard.*

Grade	Description	Max Sulfur
No. 1-D S15	A special-purpose, light middle distillate fuel for use in diesel engine applications with frequent and widely varying speeds and loads or when abnormally low operating temperatures are encountered. 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 fuels 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

Nonetheless, the sulfur content according to the EPA regulations in 2010, determined that for all automobiles in densely populated cities their maximum allowed content is 15 ppm (w/w) which corresponds to grade 1- D S15 for D975. This fuel is called Ultra Low Sulfur Diesel. For other cities, the ASTM D975-94 standard still applies, which admits a maximum emission of 50 ppm of sulfur (Table 2).

Table 2. *Diesel properties according to ASTM D975-94 specification* [18]

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 requires higher cetane number

(-): Data not reported.

2.3.2. Quality of European diesel fuels

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 fuel suppliers in Europe. Starting from the late 1990s, several diesel fuel properties including cetane number, sulfur content, and Fatty Acid Methyl Esters (FAME) biodiesel content are likewise subject to environmental regulations.

Whereas the EN 590 standard is mainly focused on on-road applications, many European Member Countries define the same fuel for use in non-road mobile machinery, simply with the addition of a marker or dye for taxation purposes. Other member countries accept a separate standard for fuel for off-road mobile applications.

Some of the important observation of the EN 590 standard were:

- **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 non-road diesel fuels. Sometimes referred to as Euro 1 diesel fuel.
- **EN 590:1996**—This standard reflected a new sulfur limit of 500 ppm. Cetane number remained at 49. Sometimes referred to as Euro 2 diesel fuel.
- **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).
- **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.%.
- **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.

Regulatory Terms. In the EU regulatory language, “gas oil” is the term used to describe a wide class of fuels, including diesel fuels for on road vehicles, fuels for non-road vehicles, as well as other distillate fuels. Within the gas oil classification, fuels for on road vehicles (typically with sulfur content below 0.05 wt.%) are referred to as “diesel fuels”, whilst fuels for non-road mobile machinery (typically with sulfur content up to 0.2 wt.%) are denoted to as “gas oils intended for utilization by non-road mobile machinery (including inland waterway vessels), agricultural and forestry tractors, and recreational craft” [11]. These terms are used in the nomenclature in the EU Common Customs Tariff. Different goods assigned unique CN (Combined Nomenclature) codes to identify the tariffs that apply. Diesel fuel for on-road applications has a CN code of 2710-19-41. Gas oils for non-road mobile machinery can acquire a CN code of either 2710-19-41 or 2710-19-45 depending on sulfur level [11].

Table 3 summarizes the European standards created from 1993 to 2009 for gasoline and diesel. We also see how, as time goes by, the euro standards become more rigid with respect to the sulfur content, which ranges from 500 ppm in Euro II to 10 ppm in Euro V.

Table 3. *Comparison of the maximum permitted concentrations from the combustion between gasoline and diesel in the European Union* [19].

Gasoline				
	EN 228: **1993** Euro II	FQD- Dir. 98/70/EC **EN 22:1999** **2000** Euro III	FQD - Dir. 2003/17/EC **EN 228:2004** **2005** Euro IV	FQD - Dir. 2009/30/EC **EN 228: 2012(*)** **2009** Euro V
Aromatics, vol%, max	-	42	35	35
Olefins, vol%, max	-	18	18	18
Benzene, vol%, max	5.0	1.0	1.0	1.0
Oxygen, wt%, max	-	2.7	2.7	2.7 3.7
Sulfur, ppm, max	500	150		-
RVP, kPa	35 - 100	60/70	60/70	60/70
Lead, g/L, max	0.013	0.005	0.005	0.005
Use of additives	-	-	-	MMT limited by Mn max 6,0 mg/L from 2011, max 2,0 mg/L from 2014
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 %	7 %

(-) Data not reported.

2.3.3. Quality of Ecuador diesel fuels

Agreeing to the Ecuadorian Technical Standard INEN (NTE INEN 1489, 2012), the minimum permissible requirements for the use of diesel in its different modalities are classified into 3 types: diesel No. 1, diesel No. 2 and premium diesel (Table 4):

Table 4. *Requirements for 3 types of Diesel.*

Requirements	**Diesel No. 1**			**Diesel No. 2**			**Premium Diesel**		
	Unit	**Minimum**	**Maximum**	**Unit**	**Minimum**	**Maximum**	**Unit**	**Minimum**	**Maximum**
Flash point	°C	40		°C	51		°C	40	
Water volume and sediments	%	-	0.005	%	-	0.05	%	-	0.05
Carbonaceous residue over 10% of the distillation residue (W/W)	%	-	0.15	%	-	0.15	%	-	0.15
Ash content (W/W)	%	-	0.01	%	-	0.01	%	-	0.01
90% distillation temperature	°C	-	288	°C	-	360	°C	-	360
Kinematic viscosity	mm^2/s (37.8°C)	1.3	3	mm^2/s (40°C)	2	5	mm^2/s (40°C)	2	5
Sulfur content (W/W)	**%**	**-**	**0.3**	**%**	**-**	**0.7**	**%**	**-**	**0.05**
Copper corrosion grade	-	-	-	Classification	-	No.3	Classification	-	No. 3
Cetane index calculated	-	40	-	-	45	-	-	45	-
Biodiesel content (W/W)	-	-	-	%	NOTE	5	%	NOTE	5

(-) Data not reported

For the different types of diesel used in Ecuador, Table 4 shows the permissible limits of compounds considered as pollutants in the environment, in the case of sulfur, the range goes from 500 ppm to 7000 ppm. The importance of compliance with these standards lies in the fact 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 (see **Appendix A**). An example of this damage is that suffered by the metropolis of Quito, a study carried out by Flores and Bonilla in 2010 identified that 50% of the surface of the city are affected by acid rain, the acid values of rainfall were lower at a pH of 5.6, this is due to the fact that the atmosphere is polluted with sulfur and nitrogen oxides, coming from Thermoelectric power plant and vehicular traffic, which by contact with humidity and rain become sulfuric and nitric acid [20].

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

2.4. Hydrodesulfurization (HDS)

The hydrodesulfurization unit (HDS) is a fundamental process to remove the sulfur combined within the fuel molecules as impurity, in refining HDS is one of the most important operations performed after crude oil fractionation. The heavier the crude, it will cause a higher non-volatile fraction, therefore, there will be a higher sulfur content, in Ecuador the sulfur content in crude varies between 2.1 to 2.35 wt.% [21]. Table 7 indicates the physicochemical properties of the organosulfur compounds that can be found in a diesel stream, the concentration and types of compounds will depend on the source of the oil, the compounds with higher boiling points such as 4,6-Dimethyldibenzothiophene (4,6-DMDBT) are the ones with the greatest resistance. The non-volatile fraction increases as it arrives at its boiling point. In addition, when there is a higher sulfur content in the crude oil there is a catalyst poisoning, this likewise affects the quality of the diesel, reducing the yields of the process and in the end, the diesel consumed without treatment, causes very serious environmental problems.

Table 7. *Physicochemical properties of some sulfur compounds found in crude oil* [22].

	Melting point (°C)	**Dipole moment (Db)**	**Molecular Weight**	**Critical Pressure (psi)**	**Specific Gravity (15.6 °C)**	**True Boiling Point (°C)**	**Critical Temperature (°C)**	**Critical Volume (m^3/kmol)**
Thiophene (C_4H_4S)	-38.06	0.540	84.142	825.221	1.061	84.31	306.35	0.219
Benzothiophene (C_8H_6S)	31.5	0.630	134.202	600.424	1.222	220.05	481	0.349
2-Methylthiophene (C_5H_6S - 01)	-63.21	0.675	98.269	712.097	1.017	112.71	336	0.275
3-Methylthiophene (C_5H_6S - 01)	-68.81	0.956	98.169	712.097	1.019	115.55	340	0.276
Debienzothiophene ($C_{12}H_8S$)	98.82	0.791	184.262	559.816	1.184	333.6	624	0.512
3-Ethyl-2,5-Dimethylthiophene ($C_8H_{12}S$)	-78	0.222	140.249	472.798	1.079	183.15	396	0.424
2-Methyl-benzothiophene (C_9H_8S)	51.65	1.124	148.229	580.120	1.119	246	507	0.438
4,6-Dimethyldibenzothiophene ($C_{14}H_{12}S$)	152.65	0.390	212.315	432.189	1.263	387.3	666.4	0.618
2-Ethylthiophene (C_6H_8S - 01)	-63	0.438	112.196	639.582	0.990	134.15	353.6	0.328
2-n-Propylthiophene ($C_7H_{10}S$)	-63	0.450	126.222	564.167	0.967	158.65	376.2	0.381
2,5-Dimethylthiophene (C_6H_8S - 02)	-63	0.510	112.196	646.834	0.952	136.95	356.9	0.328
2,7-Dimethylbenzothiophene ($C_{10}H_{10}S$)	68.5	0.720	162.255	501.804	1.059	255.7	498.3	0.49
4-Methyl-Dibenzothiophene ($C_{13}H_{10}S$)	66.2	0.812	198.288	488.751	1.201	349.8	631.1	0.565
2-Propylbenzothiophene ($C_{11}H_{12}S$)	114.2	1.010	176.282	456.845	0.949	290.6	534.5	0.582
2-Butylbenzothiophene ($C_{12}H_{14}S$)	152.65	0.947	190.309	411.885	0.971	308.8	545.7	0.635
2-Ethylbenzothiophene ($C_{10}H_{10}S$ - 02)	9.35	0.971	162.255	510.506	1.087	258	502.7	0.464
2,3-Dimethylbenzothiophene ($C_{10}H_{10}S$ - 03)	9.15	1.163	162.255	504.704	1.107	265	513	0.482
2,3,5-Trimethylthiophene ($C_7H_{10}S$ - 02)	-58	0.752	126.222	526.459	0.973	164.65	383.8	0.398

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. 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 and in addition to poisoning the catalyst, Figure 3.

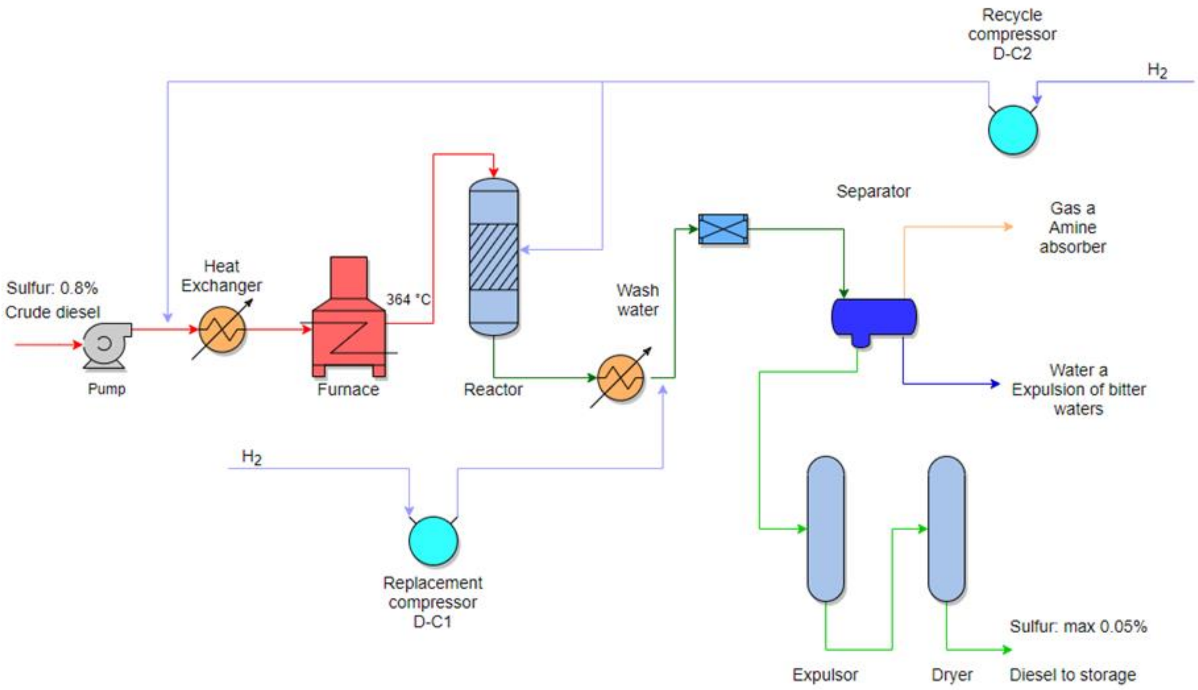


Figure 3. *Diagram of the diesel hydrodesulfurization unit (HDS).*

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

Diesel fraction + H_2 $\longrightarrow$ Diesel + H_2S (1)

(with oleophilic sulfur in its molecules) (with low sulfur content)

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

In Ecuador, the diesel hydrodesulfurization unit is in the area of catalytic units 3 of the REE, this unit possesses a reaction and separation section, its processing capacity in 2011 was 24,500 Bls/d [21].

2.4.1. Important sections in the HDS unit

To obtain diesel with a lower sulfur content of crude oil, the HDS unit must have a Reaction Section and a Separation Section.

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 the obtaining of 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.

Reaction section

The HDS unit receives a raw diesel feed load from a prime distillation plant, as well known as atmospheric distillation. The feed stream initially reaches a load tank, then passes to a pump to increase the pressure and mix it with a flow of hydrogen. The diesel-hydrogen mixture enters a heat exchanger or preheater, and then a second heater where the conditions are adjusted so that it enters the reactor. The optimal reactor for a pilot scale evaluation is one with a catalytic bed, for example that of the Nitto Koatsu Company (Figure 4), where the main catalyst is Nickel-Molybdenum. The reaction system normally 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. These are operated by current, in other words, the liquid and gas phase flow in the same direction and the catalyst mass remains fixed.

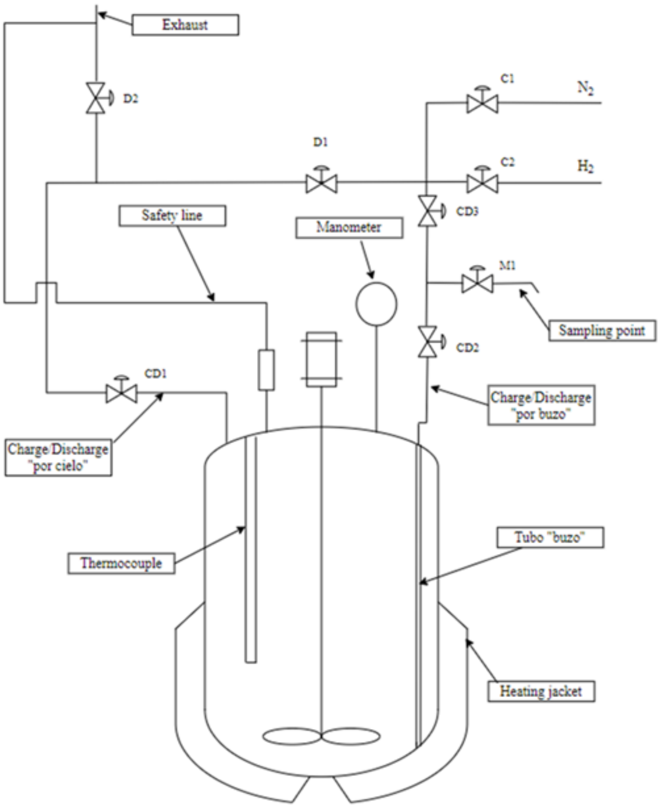


Figure 4. *Stainless steel catalytic bed reactor used for laboratory scale HDS testing* [23].

As it has seen previously, the chemical reaction in the reactor is between the organic sulfur compounds and the hydrogen fed, organic compounds and hydrogen sulfide are the products obtained. The hot effluent that comes from the reactor is used to exchange energy with the feed in the pre-heater, later it goes to a cooler, and then 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.

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 that contains a minor sulfur composition passes to a fractionating tower, where it is separated into desulfurized diesel and bitter gasoline. The diesel obtained in the fractionating tower is the dry end product with a lower sulfur content. At the end, the amine absorber treats the sour gas transforming it into sweet gas, removing the hydrogen sulfide (Figure 5). The diesel obtained in the crude units is subject to the hydrodesulfurization process, this produces diesel with low sulfur content (less than 0.05 wt.%) and free of nitrogen compounds.

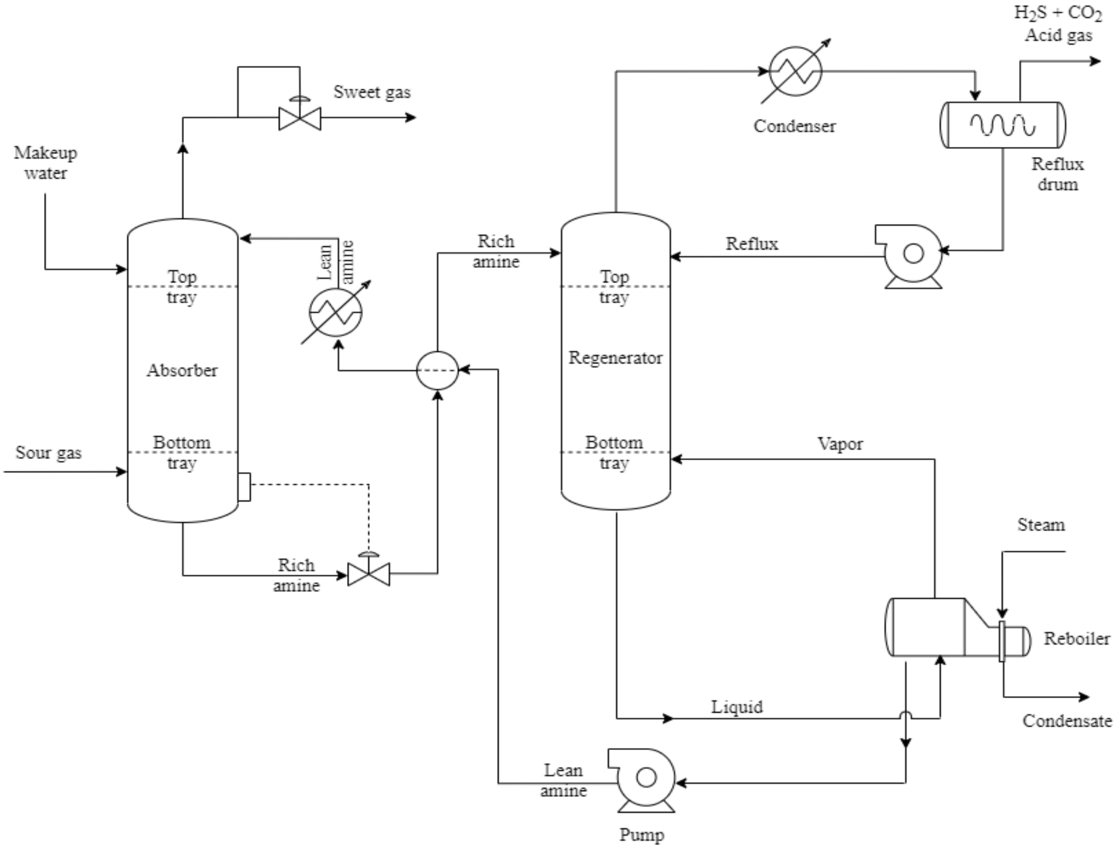


Figure 5. *Process Flow diagram, amine treatment.*

A principal component of the hydrodesulfurization units to operate are solid catalysts, these accelerate reaction times optimizing energy consumption and operating costs. It is necessary to know in depth catalysis and its procedures to be able 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.

2.5. Catalysts

The catalysts have been used for approximately 2000 years, where the first applications that have reference are the elaboration of bread, cheese and wine. However, it was not until 1835 that Berzelius defined as a catalytic force, the force exerted by small amounts of external origin on the course of the reaction [24]. In 1984, Otswald expanded Berzelius's definition, he defined that a catalyst is a substance that accelerates the rate of chemical reaction without being consumed, it only works as a transitory system that decreases the activation energy and is recovered at the end of the process (Figure 6).

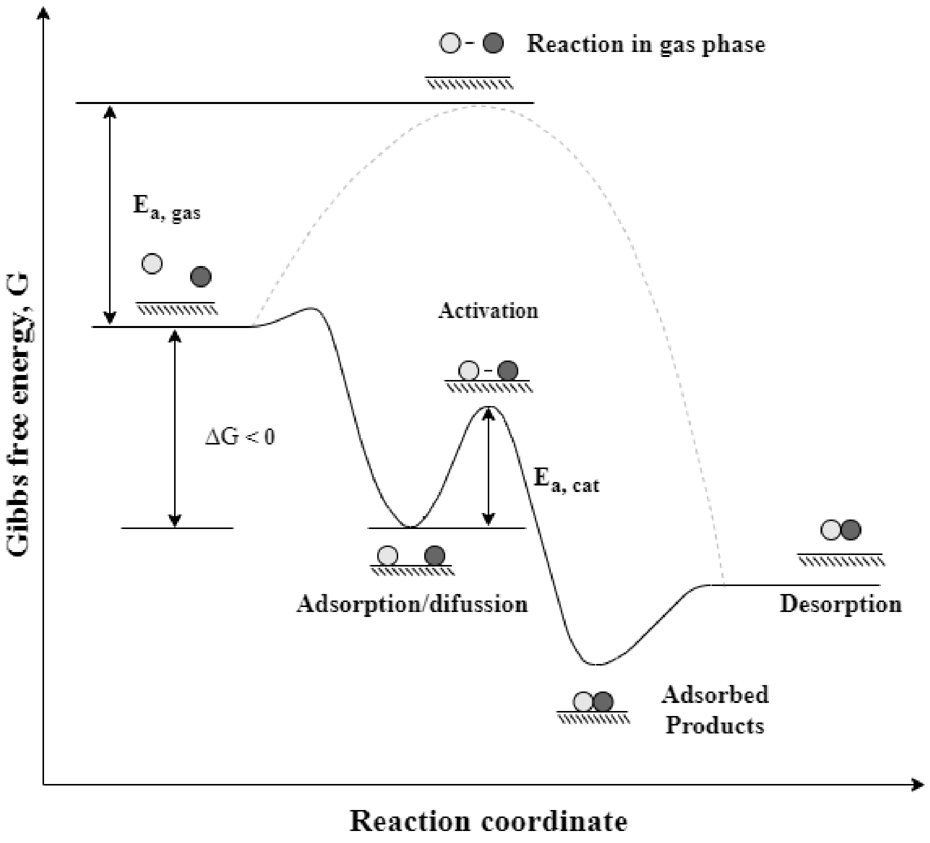


Figure 6. *Scheme of a spontaneous reaction without catalyst (dotted line) and without catalyst (smooth line).*

The science that studies this process is catalysis, in which three general types of catalysis are defined [25].

- **Homogeneous catalysis:** is when the reactants and the catalyst form a homogeneous system and on that point is only one single phase, this type of catalysis is common in dissolution reactions and in the gas phase, among which the most outstanding are acid-base catalysis.

- **Heterogeneous catalysis:** is when the components of the reaction and the catalyst are in distinct phases, more commonly when the catalyst used is in the solid phase, this increases the reaction rate of systems in the gas phase and in solutions.
- **Enzymatic catalysis:** is when the catalyst is an enzyme that comes from a biological system, this type of catalysis is very specific because it acts on certain molecules leaving the rest of the system unaltered. Enzyme catalysis can be seen as homogeneous because the enzyme and the substrate are in aqueous solution.

A catalyst can be composed of three parts that increase its rendering and effectiveness. The first is the site or active agent, which is 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 a support generating active sites. The second is the support, this is 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 (Table 8). The third component is the promoter, this is a chemical substance that improves catalytic properties, increases resistance to deactivation, improves selectivity and performance [6].

Table 8. *Solid supports for catalysts.*

Catalyst support	**Specific surface area, m^2/g**	**Uses**
γ-alumina	150-300	Multiple uses
α-alumina	5-10	Hydrocracking
Silica	200-800	NOx reduction/Polymerization
Titania	50-100	Selective oxidation
Active carbon	~1200	Oxichlorination, hydrogenation (fine chemicals)
ZSM-5 Zeolite (MFI)	400	Cracking/Isomerization/Dehydration
MOR Zeolite	500	Light paraffin hydroisomerization, oligomerization, aromatic alkylation and transalkylation
SBA-15	800	HDS, catalytic reforming, oxidative desulfurization process

The methods of preparing these supports are diverse, by precipitation, gelatin (sol-gel), impregnation, melting, anchoring and by hydrothermal transformation. Commonly in these methods, templates are used to guide the shape of the supports giving different structural models (Figure 7).

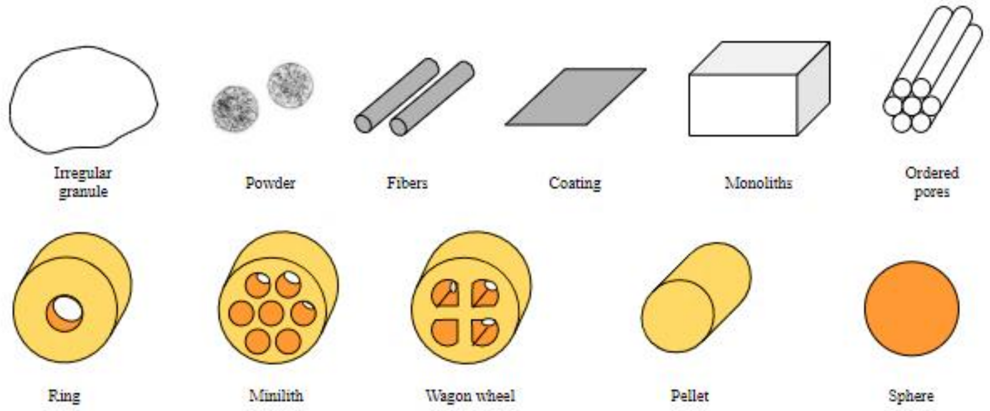


Figure 7. *Structural forms according to the application of catalytic supports.*

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.

2.5.1. Characteristics that catalysts must have for the HDS process

The first catalysts applied in the HDS process were those used in the hydrogenation of liquids derived from coal that had high sulfur content [26]. 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 that are 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. As one can observe in Table 7, the properties of some of the sulfur compounds found in crude oil. In conformity with these properties, the processes and catalytic systems are designed for their elimination.

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) [27]. This suggests that the concentration of the alkyl-DBTs are found in the crude fractions with boiling points above 300 °C. Furthermore, the fractions in the range of 300-340 °C contain a high concentration of C_1/C_2-DBT together with C_5/C_6-BT, while at temperatures below 300 °C alkyl-BT are present. However, it must be emphasized that the distribution of these compounds will also depend on the origin of the oil [7].

In the same way, as has been observed, benzothiophenes and dibenziotophenes are found in intermediate sections (Figure 8), these molecules are known as refractory, because in a conventional hydrotreating process they persist in much lower concentrations when being less reagents. Therefore, for the modeling of a catalyst these molecules are employed as the groundwork for designing catalysts for HDS processes [14].

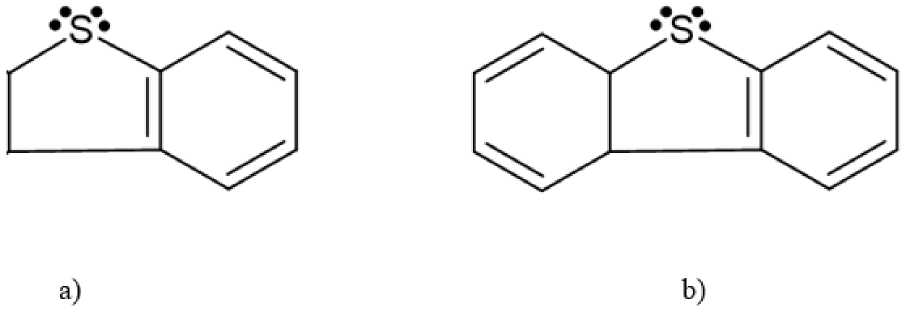


Figure 8. *Sulfurized model compounds for study in the HDS: a) benzothiophene (BT) and b) dibenzothiophene (DBT).*

Figure 9 presents the reaction mechanism used as the basis for the HDS of DBT. The conversion of DBT can be carried out through two parallel routes, first by direct hydrogenolysis, producing biphenyl, the second by direct hydrogenation (HD) producing hexahydrodibenzothiophene (HHDBT) or tetrahydrodibenzothiophene (THDBT) followed by desulfurization to obtain cyclohexylphenyl (CHF) to finally transform into bicyclohexyl (BCH).

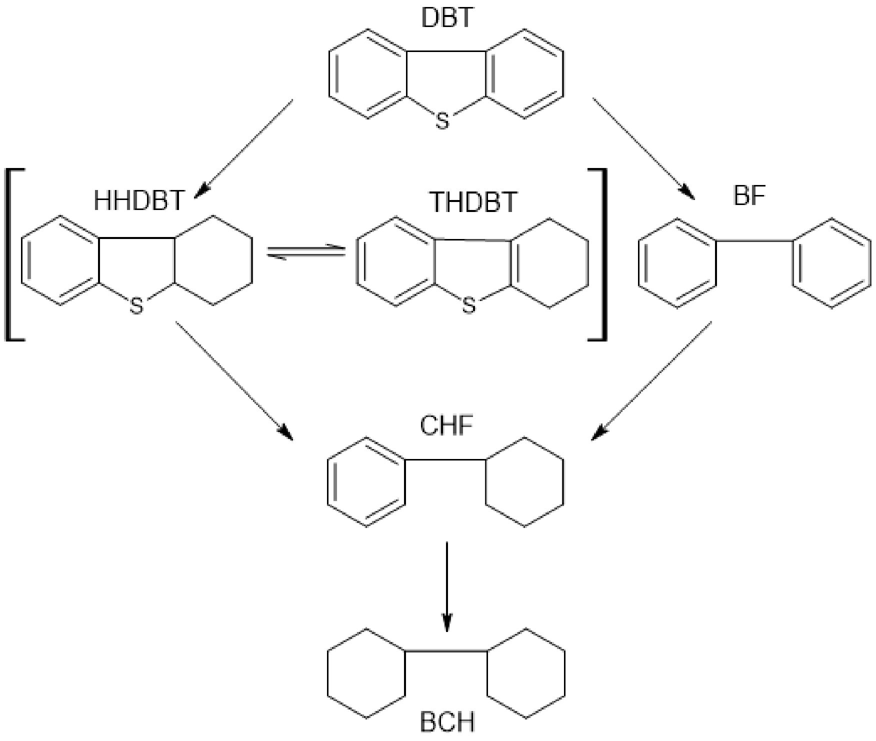


Figure 9. *Reaction mechanism for the hydrodesulfurization of DBT.*

Transition metals are the most preferred in HDS reactions [28]. The primary effect in the hydrodesulfurization of DBT is related to the position of the metal in the periodic table and where the sulfides that form these metals have a higher activity than that of Mo sulfide (Figure 10). The active form obtained from these sulfurized metals constitutes the reduction-sulfurization of the oxidized forms [29].

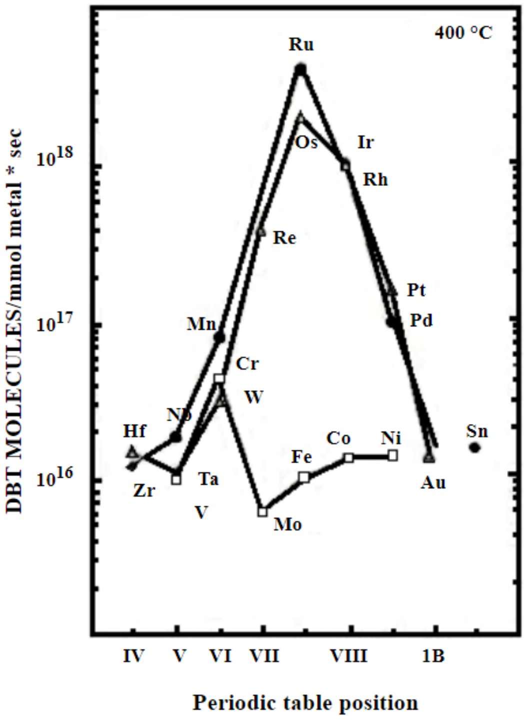


Figure 10. Fluctuation of the hydrodesulfurization activity of DBT for different transition metal sulfides [28].

The most active are the transition metal sulfides that are in the second and third rows of the periodic table, these have a strong *4d* and *5d* character respectively. Those in the first row of the transition elements, despite having a *3d* character, present less activity and a not very clear behavior. In summary, the order of activity can be described as follows [6]:

$RuS_2 > Rh_2S_3 > PdS > MoS_2 > NbS_2 > ZrS_2$: second row

$OsS_x > IrS_x > ReS_2 > PtS > WS_2 > TaS_2$: third row

In two ways, some authors have explained the interaction of bound sulfur (S-C) with the structure formed by transition metal compounds [30]. In the first way, the vacancies or active sites adsorb the sulfur compounds, the S-C bond initially becomes unstable due to the increase in electron density, and so the bond breaks, now the sulfur remains bound on the catalyst structure. At the same time, the release of H_2S creates a new vacancy due to the serial instability of the molecules. The second route happens between the exchange of sulfur with H_2S, when a vacancy is occupied by a sulfur that comes from the H_2S formed during the HDS reaction, the next thing is that another sulfur that is unstable in another position of the catalyst structure is released as H_2S thus forming a vacancy again (Figure 11).

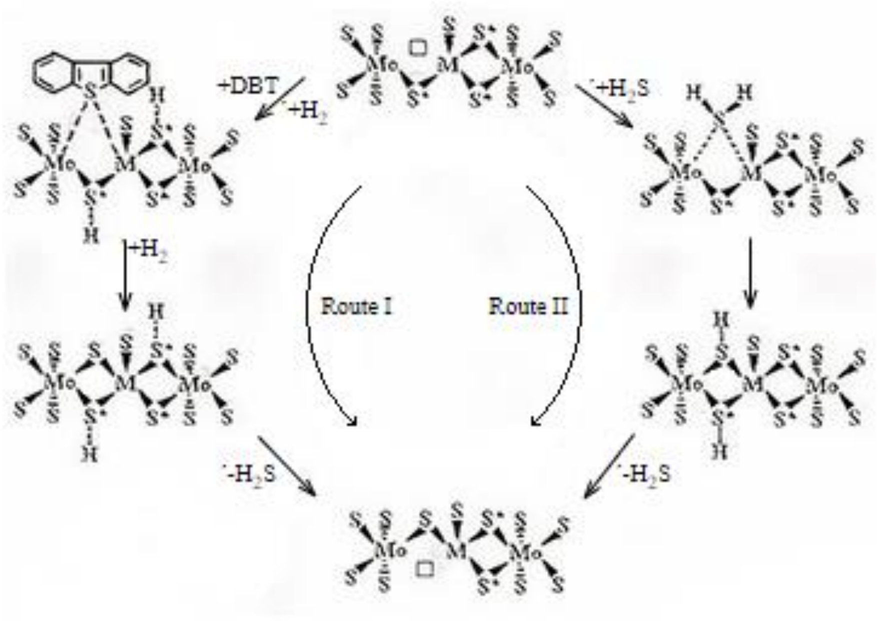


Figure 11. *Reaction mechanism of DBT on Sulfurized Co(Ni)-Mo/Al_2O_3 catalysts* [26].

In both types of mechanisms, on the surface of the catalyst the occupation and generation of vacancies in the catalyst always occur due to the unstable interaction of sulfur with the vacancy. Therefore, the structure will obtain mobile vacancies due to a rapid adsorption-desorption of H_2S that generate interconversions of active sites and bonds with sulfur.

According to the order of the atoms in their crystalline system, they generate vacancies in the transition metal sulfide structures. For example, WS_2 and MoS_2 crystal formation through the stacking of sheets, each sheet is made up of two sheets of sulfur atoms and one sheet of molybdenum, the atoms in the sheets form bonds in a covalent manner, while between the sheets the bond is mainly by Van der Waals type forces (Figure 12). The pile-up of the sulfur sheets is hexagonal and according to their formation procedure have a number of morphological defects [30].

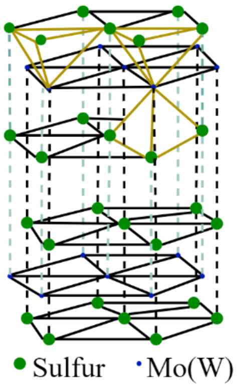


Figure 12. Illustration of the unit cell of Mo and W sulfides.

Figure 13 illustrates the stacking model of the MoS_2 structure, which explains the generation of vacancies or mobile active sites during the HDS reaction, this representation is known as the "Rim-Edge" model [31]. This model describes how for *n* layers of metal sulfide there are two types of sites:

- Rim sites, located on the outer sheets, nearby to the basal plane and susceptible to the reacting environment, both hydrogenation and direct desulfurization can take place on these sites.
- Edge sites, located on the inner laminae, where there is no exposed basal plane surface. Only direct desulfurization can be performed out at these sites.

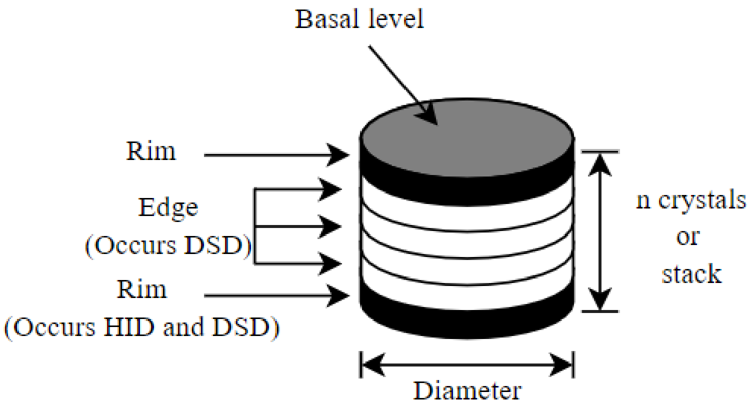


Figure 13. *"Rim-Edge" model of an MoS_2 catalytic particle [6, 31].*

The amount or percentage of active sites in the structure does not depend on the diameter of the crystalline system, but on the stacking of the sheets when they form the crystals, therefore, the model relates the selectivity and the activity of the reaction. An important parameter to consider is the mode of stacking in the direction of the plane [001]. Furthermore, it is significant to emphasize that the more the crystallinity of the transition metal sulfide structures decreases, the greater their catalytic activity will be due to the vacancies generated by the loss of structural sulfur [32].

2.5.2. Conventional catalysts

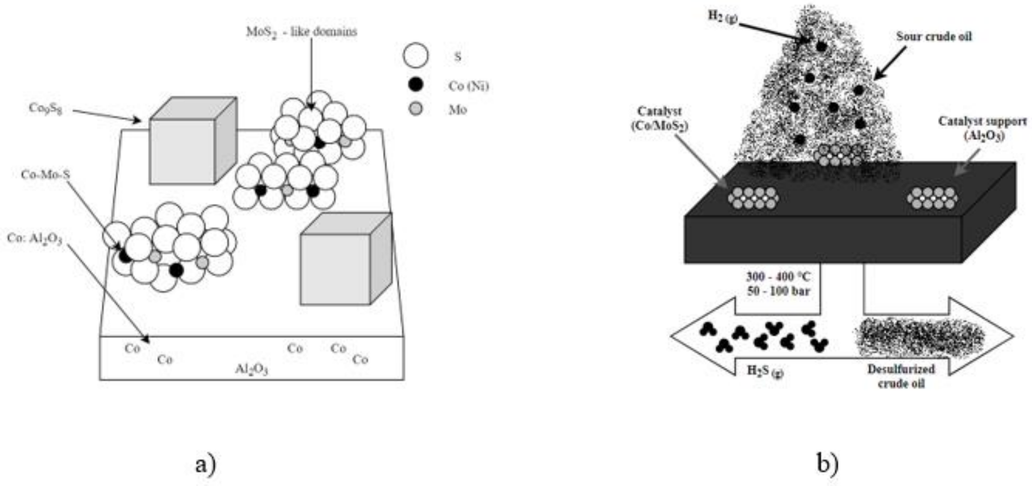
The most common catalysts used in HDS are based on binary systems of molybdenum-cobalt oxides and nickel-molybdenum oxides dispersed on alumina support surfaces. Cobalt and nickel act as promoters to increase catalytic activity. The catalyst acquires the active form through its sulfidation process, mainly during the feeding stage and also when it is treated before use.

According to the type the fuel load is the preference of the catalyst, the most popular alternative is CoMo because it reacts with most sulfurized organic molecules in the presence of hydrogen gas. Even so, this type of catalyst does not allow reaching all the desired level 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 right option. The composition of the catalyst will depend on the desired activity. Table 5 presents the most typical compositions of the most common catalysts used in the hydrodesulfurization of diesel.

Table 5. *Commercial catalysts and their typical compositions [12].*

	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 phases on the NiMoS, CoMoS and NiWS support 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 H_2, H_2S, and so on, the nature and concentration of sulfur compounds, the design of the process and reactor. Figure 14 a) presents one of the models that proposes the formation of the phases during the HDS process for the CoMoS, and Figure 14 b) the interaction procedure for the CoMoS according to the operating conditions for the HDS [33, 34].



a) b)

Figure 14. *a) Interaction procedures and b) CoMoS formation phases in the HDS process.*

2.6.3. Unconventional catalysts

As suggested above, the perfect catalyst for HDTs is one that has a high capacity to remove metals, nitrogen and in the specific case of HDS, sulfur. In addition, it must have the ability to improve other properties of the fuel, such as the octane/cetane number or the aromatic content, all this based on local and international environmental legislation. One of the innovations or changes to traditional catalysts is to modify the nature of the active phase, changing its proportion, introducing additives or completely changing the active component. For instance, some of the additives that have been tested with good results are fluorine, phosphorus, vanadium or iron as promoters [22, 35-37].

Other changes made is to replace the sulfides present in the catalysts with carbides or nitrides [38]. Catalysts with noble metals (Rh, Pd, Ru, Pt) have been prepared for the HDS of thiophene [39]. 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 [34]. In addition, alternative supports and combinations have emerged as a good alternative to improve HDS processes.

Also, in the treatment of DBT through HDS the oxides of titanium, zirconia, carbon and silica are excellent, likewise for the treatment of DBT another of the promising studies is the effect of the combinations of supports, for instance, silica- alumina, TiO_2-Al_2O_3 y ZrO_2-TiO_2 [14, 40].

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 [41, 42]. Activated carbon supported catalysts were shown to be less sensitive to deactivation by poisoning due to coke formed [42]. 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/nm^2 per surface area of support [43, 44]. The studies carried out on the HDS of the DBT using NiMo catalysts supported in the alumina-activated carbon (AAC) system showed good stability and high activity [45]. 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 the mesoporous carbon structures. To evaluate the HDS of 4,6-DMDBT, a dispersion of the MoS_2 catalyst was carried out on these new supports, the results obtained were an activity of about 3.5 times greater than the use of only aluminosilicates as support, with a high dispersion and strong stability of the nanoparticles on the support [46].

In this line of new materials, nano porous materials are of high interest, due to their various possibilities of industrial application. Examples of these new materials are clay minerals, inorganic silica gel type gels, zeolites, alumina and activated carbons. These materials have a high surface area with nanometric porosities [47]. In 2012 and 2013 researchers carried out studies of coatings of cordierite monoliths with carbon nanotubes, this type of support obtained a high surface area, good pore distribution after acid pretreatment of the support and an excellent dispersion of carbon nanotubes, This type of support where they dispersed the Co-Mo catalyst, they utilized it to evaluate the HDS of naphtha, the sulfur content in this fuel decreased from 2,670 ppm to 13 ppm [48, 49].

2.6.4. The role of polymers in hydrodesulfurization processes

Thus far, the diesel desulfurization process known as HDS has been discussed, or on conventional or non-conventional catalysts, but within the processes for the elimination of organosulfur compounds is the process of Non-Hydrodesulfurization (Non-HDS). This procedure consists of the use of functionalized polymeric membranes (polyvinyl alcohol, polyvinyl chloride, polymethyl acrylate, among others), these membranes are coated with particles with adsorption capacities, such as activated carbon, clays, zeolites or metallic ions [50]. This functionalized polymeric membrane creates a neural network type system, which is selective for organosulfur compounds. Desulfurization by adsorption through these materials is inexpensive, very sophisticated equipment is not used, and it is environmentally friendly. Furthermore, it does not decrease the cetane number of diesel fuel or alter any other properties of diesel.

Nevertheless, many research are still missing to improve the adsorption capacities of functionalized polymeric membranes, so the testing are carried out with simulation processes, such as the use of molecular dynamics simulations (MD Method), Neural network for pattern recognition (NN-PR) and Density functional theory (DFT). With these simulation systems the development time and the effort of the measure for the detection of desulfurizing agents are considerably diminished [51].

Nonetheless, all investigations come at a cost, either experimentally or theoretically. In the case of Ecuador, it is necessary for the country to invest and assistance this type of technological development in universities, it is also necessary for private and public companies to visualize that investing in new technologies in the country would reduce dependence on imports and variations in the supply market

2.6.5.- Production and key projects of the oil industry in the world and Latin America

US Energy Information Administration (EIA) projects a sustained growth in the demand for oil and gas in the world in the coming years, as well as the consumption of nuclear energy, coal and renewable energies (Figure 15). This contributes to the development of greater infrastructures for the processing or obtaining of these resources. But due to the concern of the contamination that these processes will generate, in all the countries of the planet increasingly rigorous legislation is being developed and employed. Such is the case with diesel fuel, where stricter impurity emission limits are being imposed. In particular, the United States Environmental Protection Agency (US EPA) recently proposed rules that would limit the sulfur content to 0.05 % by weight and the aromatic content to 20 % volumetric in diesel for road traffic. Since 2005, the European Economic Community also has been working with regulations for sulfur content in gasoline between 30-50 ppm, in fact, HDS processes with zero sulfur content are the clearest trend for the next 10 or 15 years. In this context, producing ultra-low sulfur gasoline (ULSG) presents a challenge in technological development for refineries, which leads to higher investment costs.

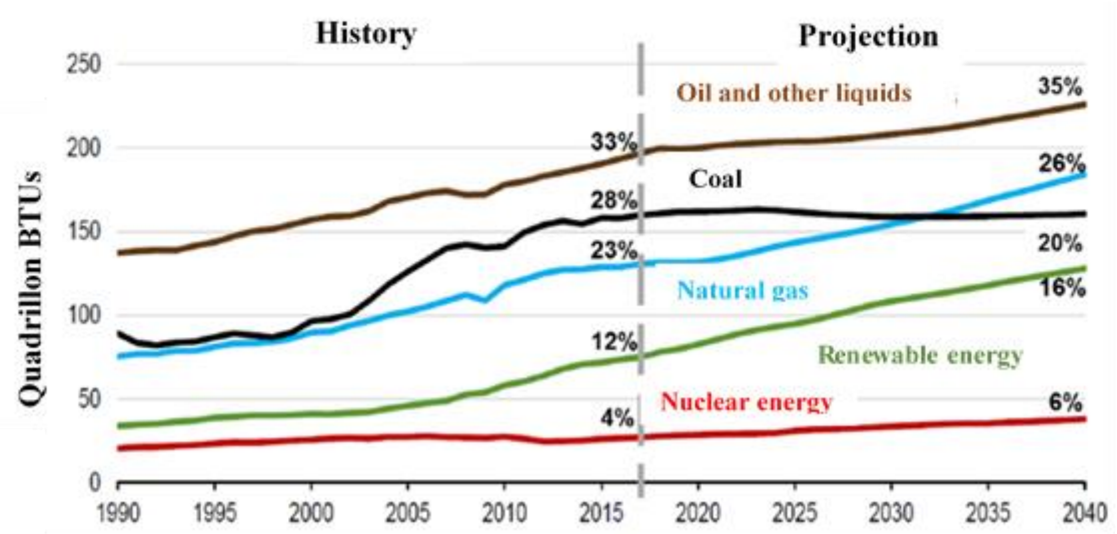
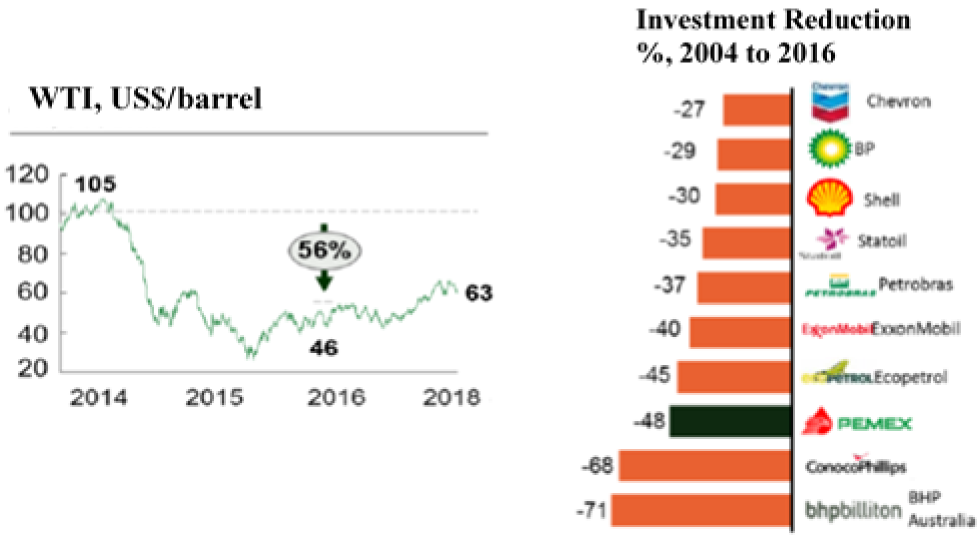


***Figure 15**. Projections of fuel consumption in the world* [52].

During the 2014-2016 period, the main oil companies along the planet suffered from the fall in oil prices, which caused a reduction in their investments due to the loss of profitability in their projects. The giant international oil companies experienced declines in their investments in exploration and production, refining and marketing. Chevron, British Petroleum, Shell, Statoil, Petrobras, Exxon / Mobil, Ecopetrol, Conoco/Phillips and Broken Hill Proprietary (BHP), suffered a fall between 27 and 71 % on their investments due to the drop in the price of a barrel of crude within this period [53] (Figure 16).



a) b)

Figure 16. *a) Price per annual barrel for the 2014-2018 period and b) Percentage of reduction in investment by the largest oil companies in the world.*

Even so, according to the Organization of the Petroleum Exporting Countries (OPEC), the increases in world distillation capacity for the period 2017-2022 will be around 7,6 million barrels per day (MB/d). This is mainly due to increases in demand in developing countries. The majority of such increases are in the Asia-Pacific region with 49 %, and the Middle East with 27 %, while the remaining regions combined add only 24 % of the total. Regionally, five regions are expected to have a glut of refined products: The United States and Canada, the Middle East, Europe, Russia, the Caspian Sea countries and China, for a total of 2,4 MB/d by the year 2022. On the opposite, the Asia Pacific region excluding China, Latin America and Africa, will have a deficit of 0.8 MB/d by the year 2022 [54].

Figure 18 presents a graph that allows knowing the percentage increases in the 2017-2018 periods of the refining capacity of different nations. As can be seen, Iran, India, Taiwan and Oman, had increases of more than 6 % in this area in 2017, with this being the last country. In this same year, other nations, such as China and Pakistan, experienced an increase in their refining capacity greater than that observed for Ecuador [9, 54]. Nonetheless, for the period of

2018 Ecuador had a rebound in the refining of up to 2.1 % due to the improvements made for the refining of crude oil [13, 55].

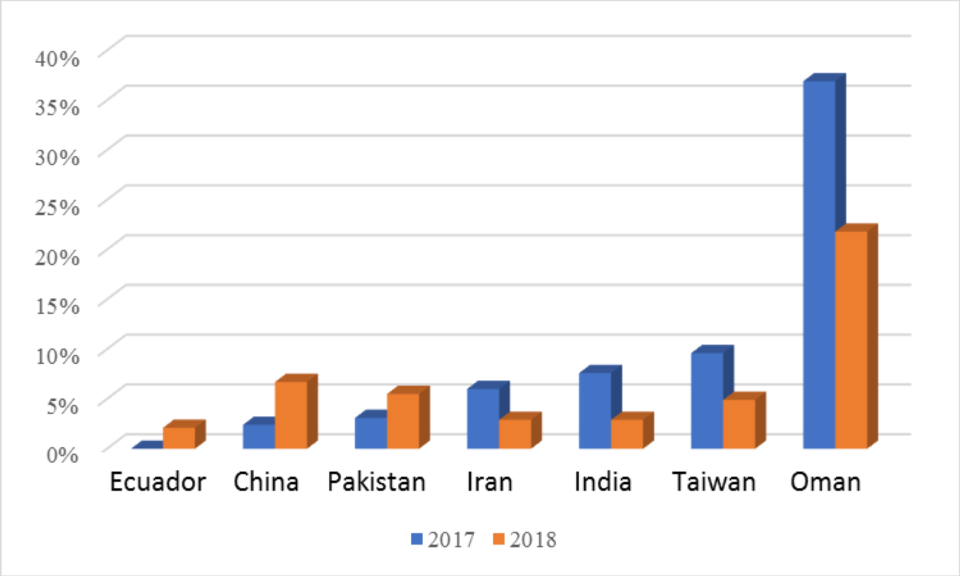


Figure 17. *Percentage increase in refining capacity in the 2017 and 2018 periods.*

Ecuador, like China, managed to advance in the crude refining process by improving their processing plants and investing in new technologies to meet international standards, such as achieving a diesel HDS of up to 80 ppm [13]. Although the goal is to achieve an HDS of up to 10 ppm that would be in the quality range of ultra-low sulfur diesel and that corresponds to reaching the Euro V standard [11].

On the other hand, despite the troubles generated by the COVID-19 pandemic, Latin America continues with the development of projects to produce derivatives and gas. Investments range from US$ 22 billion for subsequent years. Some of the countries that propose to develop these investments are the following [56].

Mexico

The Dos Bocas Refinery will increase its processing capacity of up to 340 MB/d of heavy crude oil to produce fuels and petrochemical inputs. The contemplated investment is up to US$ 8 billion. For the HDS, coking and gas generation processes, Mexico awarded contracts to companies such as Samsung Engineering, KBR, ICA, Fluor, Hosto Group and Associated Constructors DBNR.

Mexico is also seeking to increase the capacity of six other state refineries, such as Salamanca, Minatitlán, Madero, Tula, Santa Cruz and Cadereyta and the investment contemplated according to the Mexican engineering firm Rengen is approximately US $ 3 billion [56].

Colombia

This year, Colombia contemplated the construction of the Sebastopol refinery, but due to the problems generated by the COVID-19 pandemic, the construction was proposed for the end of 2023 or early 2024. Despite the problems, this project still has the support of the financier of VIP Group International, which is a private investment fund based in the United States. The refinery is part of a US $ 6 billion power pole proposal that would also include two 135MW combined cycle power plants and a hydrogen production plant for fuel cell vehicles.

The Australian engineering firm WorleyParsons is the one that designs and develops the construction schedule for the project. The Sebastopol refinery will have a production capacity of between 100 MB/d and 150 MB/d of diesel, gasoline, jet fuel and other crude derivatives. About US $ 5 billion is the investment considered for the construction of the refinery, while for the hydrogen production plant, it will have an estimated cost of US $ 600 million and for the power plants of US $ 400 million.

Perú

By 2021, the state oil company Petroperú intends to begin modernization work for its Talara Refinery. To achieve this goal, State-owned enterprise will carry out several calls for bids, one will consist of a 432-day contract for consulting services to prepare the technical conditions and the estimated investment for the implementation of logistics warehouses, another for a 365-day contract to catalog and optimize spare parts inventory. Furthermore, it intends to expand its water supply capacity to cover the cooling requirements of the processing and auxiliary units of the plant to be modernized. It is estimated that the project requires an investment of close to US $ 4.7 billion.

Ecuador

The Ecuadorian government plans to set up a bidding process this year for a 20-25-year contract to operate the Esmeraldas refinery, one of the country's largest. Among the improvements they intend to carry out are the installation of a line to convert waste into clean products at the site and the construction of a new high-conversion plant on the Pacific coast in the BOT model (built, operation, transfer). The companies that have shown the greatest interest are the Chinese CNPC and Sinopec, Grupo Cobra, Repsol and 38 others.

The government of Ecuador expects to make an investment of around US $ 1 billion, with this the Esmeraldas refinery could produce fuel of Euro-5 quality. Currently the plant has a processing capacity of 110 MB/d and produces around 62 % of derivatives in Ecuador.

CHAPTER III

3. METHODOLOGY

The construction of a thesis work has different parameters, once the problem to be investigated has been identified, the next steps consist of building up the objectives, to achieve these objectives various evaluation criteria or support mechanisms are established (Figure 18).

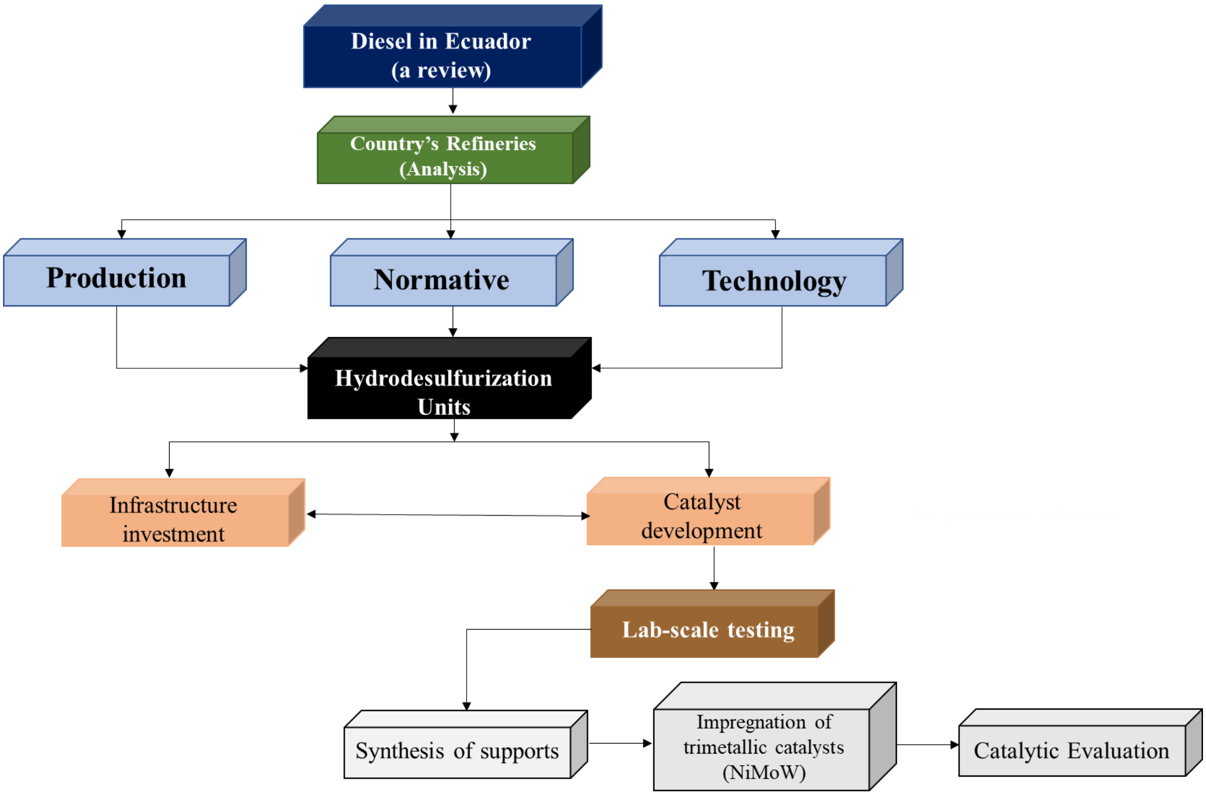


Figure 18. *Methodology diagram.*

According to the previous Figure 18, the first step consisted of identifying the status of diesel production in Ecuador, later it was identified where it was processed and which companies are in charge of all operations from extraction to production. Sale in the national market. In this review, its production level and the units that process diesel was classified. It is very important to note that national and international regulations or standards are of the utmost importance, because of the fact that they establish the quality of diesel in its different presentations. Therefore, refineries are obliged to produce diesel, according to specifications. In this way, the technology needs in the refineries and the main changes to be made in the hydrodesulfurization units were identified. The necessary public and private investments. Furthermore, the adaptation or change of the catalysts already used normally was emphasized.

The search base was essentially on the internet network on the following pages.

a) EP Petroecuador
b) BP Statistical Review of World Energy
c) Dieselnet
d) World Outlook
e) Servicio Ecuatoriano de Normalización (INEN)
f) Elsevier
g) Scopus
h) among others

3.1. Hydrodesulfurization in Ecuador

The production of derivatives and especially diesel in Ecuador is mainly in charge of the REE, which has a refining capacity of 110,000 Bls/d. This data is found in degree works in Ecuadorian Universities and in the quarterly or annual reports of the oil sector, these reports are constructed by the Central Bank of Ecuador, where it 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.

3.2. Alternatives to improve the hydrodesulfurization process of diesel

During the reference reviews it was found that the technology exists to reach levels of ultra-deep hydrodesulfurization units (UDHDS) with the modification of catalysts, for this a deep review was made in browsers such as Elsevier and Researchgate, where the procedures were found. As well as the synthesis of trimetallic catalysts, supported and unsupported. 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 browsers.

On the other hand, it was searched for information related to the use of functionalized polymeric membranes coated with adsorbent particles such as clays, zeolites and metallic ionic molecules. This is to understand the non-HDS processes.

3.3. Evaluation of a trimetallic catalyst

In this section, to reconfirm the ability of trimetallic catalysts to remove the so-called refractory molecules, the NiMoW catalyst and the Al_2O_3/Ga_2O_3 support were synthesized through the pore filling method [14, 33]. A series of AlGa-X materials with the different weight percent of Ga_2O_3 (X = 20, 25, 30 wt.%) were planned to be synthesized by the co-precipitation method [14]. The characterization techniques proposed to study their textural properties of the synthesized supports and NiMoW catalysts were N_2 adsorption-desorption isotherms (S_{BET}), high-resolution transmission electron microscopy (HRTEM), these characterizations results can be seen in **Appendix C**.

3.3.1. Synthesis of supports

For the synthesis of mixed oxides Al_2O_3 and Ga_2O_3, the co-precipitation method was used, aluminum nitrate and gallium nitrate were used as precursors. For each preparation, 1 g of the alumina carrier was mixed with an aqueous solution of $Ga(NO_3)_3{*}H_2O$ containing the amount of gallium salt in order to obtain support with a nominal composition of 20, 25, and 30 wt.% of metal. This solution was in agitation (200 rpm) for two hours, after that, NH_4OH was mixed in, and the new solution was in agitation (380 rpm) for five minutes. Then, this solution was calcined at 500 °C with a heating rate of 1 °C min^{-1}.

3.3.2. Catalysts Preparation

The obtained supports were used to prepare NiMoW trimetallic catalysts, which were incorporated into the support through a pore filling impregnation. The precursors of the metals used for Ni, Mo, and W were nickel nitrate, ammonium heptamolybdate, and ammonium metatungstate, respectively. The materials obtained were sulfided at 400 °C for 2 hours at a heating rate of 5 °C/min. The trimetallic catalysts obtained NiMoW/AlGa-X where X is equal to 20, 25 or 30 wt.% by weight of Ga_2O_3 were evaluated in the hydrodesulfurization reaction of dibenzothiophene.

3.3.3 Catalytic Activity

The HDS of DBT was performed in a 500 mL batch Parr reactor, magnetically stirred (1,200 rpm) equipped with four baffles on the wall to prevent vortex formation. The operations conditions were 320 °C under a hydrogen atmosphere of 725.2 psi for 8 h, using 400 mg of sulfided catalyst and $1.22*10^{-3}$ mole of DBT dissolved in 100 mL hexadecane (to simulate an industrial process). Nitrogen was used to flush the reactor, also the reactor was heated under stirring to reach the reaction temperature. The reaction time was counted when the hydrogen was introduced. To control the total pressure, hydrogen was added constantly during the reaction. Aliquots of sample were periodically taken (every 15 minutes) and then analyzed quantitatively by gas chromatography. The catalytic activity was expressed by the initial reaction rate.

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

In various references and informative sources, it has been mentioned that Ecuador is in search of updating, improving and building new hydrodesulfurization units. To validate this information, a meticulous search was carried out on the official pages of EP Petroecuador and the Central Bank of Ecuador, in addition to search publications that made regarding to this information. Moreover, information was sought on the types of catalysts used by the REE and traced back to the supplier in order to analyze them and consider the possibility of modifying them to increase their performance and average lifetime.

CHAPTER IV

4. RESULTS

4.1. Diesel production and hydrodesulfurization in Ecuador

Petroamazonas and EP Petroecuador in Ecuador are the companies that oversee oil extraction and refining of its derivatives. The refinery with the largest crude processing capacity nationwide is the REE with 110,000 Bls/d [8]. In 2019 Ecuador experienced a production of 531,000 Bls/d of crude, most of the crude oil produced was destined for export [9]. Similarly, in this year its derivatives production was 142,000 Bls/d, showing a decrease of 10.7 % compared to 2018. As well, there was besides a decrease in the national demand of derivatives (2.4 %), and the total annual demand was 91.0 MMBls, in daily volume, the production of derivatives was 207,193 Bls. In this work, of the derivatives produced, we emphasized diesel, for being the derivative with the highest demand in Ecuador (36.2 % of the total) and one of the main emitters of sulfur in the environment and other pollutants.

Ecuador produces three types of diesel representing a great percentage of the national production of derivatives with 11.77 MMBls/year from the various refineries. The automotive sector uses a great percentage of the diesel produced at the national level, followed by the industrial sector, shipping industry, among others.

In 2018, Ecuador produced 3.53 MMkg of sulfur, a consequence of the production of derivatives. The premium diesel (higher demand) produced in the country has 500 ppm of sulfur, which complies with national regulations, but not with 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 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 excellence 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 their 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 present 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 represents the deep HDS is the 4,6 - DMDBT, where from the DBT the sulfur bound in the disubstituted diakyl 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, it is necessary to modify the promoter; adding Ni to facilitate this reaction to follow the direct desulfurization route. This procedure allows for higher conversions eliminating the steric effect [14]. Accordingly, the addition of a third metal with catalytic activity makes it easier to achieve desired levels of conversion.

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. Where NiMoW/Zr-SBA-15 was the most active catalyst for sulfur removal in less time, Figure 19. The addition of titanium and zirconia to the NiMoW and CoMoW catalysts conferred a higher HDS activity, this effect being greater for the Ni-promoted samples [57].

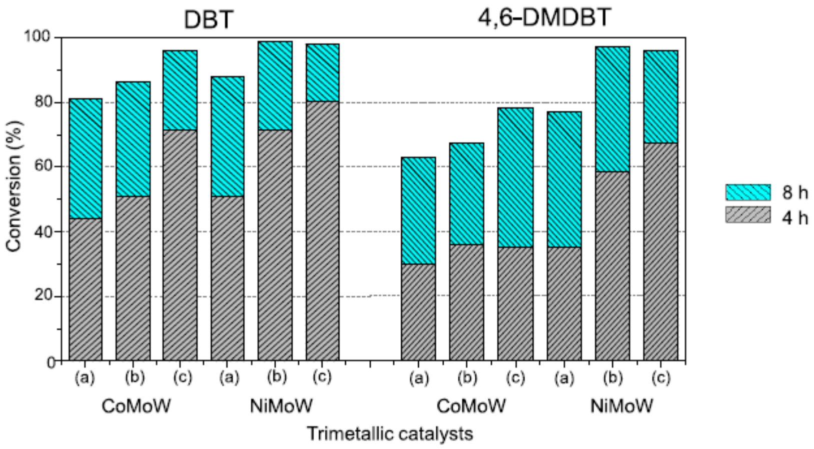


Figure 19. *Conversions of DBT and 4,6-DMDBT obtained at 4 and 8 h reaction time using trimetallic CoMoW and NiMoW catalysts supported on: (a) SBA-15; (b) Ti-SBA and (c) Zr-SBA* [57].

In addition to conventional supports, the use of clays (modified montmorillonite) supported trimetallic catalysts has also been tested. The use of a NiMoW-clay hybrid removed 99.8 % of the sulfur present in DBT compounds, as well as providing a very good 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 greater active sites and due to the laminar characteristics of the clay, easy access to these [58].

Therefore, in accordance with the improvements that the add-on of an active third metal brings to the properties of conventional catalysts, trimetallic catalysts are a really good option for the removal of refractory compounds, which is the goal to achieve a complete HDS of diesel.

The hydrodesulfurization process reduces the percentage of sulfur that is in the oil fractions, the process is efficient when it is 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 SOx, which contributes to acid rain. Alumina-supported Co(Ni) or Mo(W) catalysts are typically used in HDS reactions. The beginning of the use of alumina support is related to its remarkable mechanical and textural properties and its relative low cost. However, evidence of a strong metal-support interaction has prompted a large amount of research aimed at the study of new supports. In the literature, a vast number of references can be found in the use of materials as HDS catalyst supports. 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 great 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/Al_2O_3 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 the mesoporous materials of SBA-15 and SBA-16, pure and modified, 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 has exhibited the highest catalytic activity for HDS reactions is the so-called NEBULA (New Bulk Activity), this is based on transition metals (Ni, Mo and W), which has been patented by Soled y col. 2001 [59].

4.3. Trimetallic catalyst evaluation

In this segment, the reconfirmation of the ability of trimetallic catalysts to break down the so-called refractory molecules was carried out, the NiMoW catalyst and the Al_2O_3/Ga_2O_3 support were synthesized and characterized at the Center of Nanoscience and Nanotechnology in Mexico (CNyN-UNAM), a series of AlGa-X materials with the different weight percent of Ga_2O_3 (X = 20, 25, 30 wt.%) were successfully synthesized by the co-precipitation method. The synthesized supports and NiMoW catalysts were characterized by N_2 adsorption-desorption isotherms (S_{BET}), and high-resolution transmission electron microscopy (HRTEM), some details of those characterizations can be seen **Appendix B.**

For the catalytic evaluation, the concentration of DBT and the initial reaction rate were calculated. In the Figure 20 can observe the concentration in ppm of S in HDS reaction through time to each catalyst. The concentration of sulfur clearly decreases time passes, it means that catalysts fulfill their function, which is remove S from the molecule.

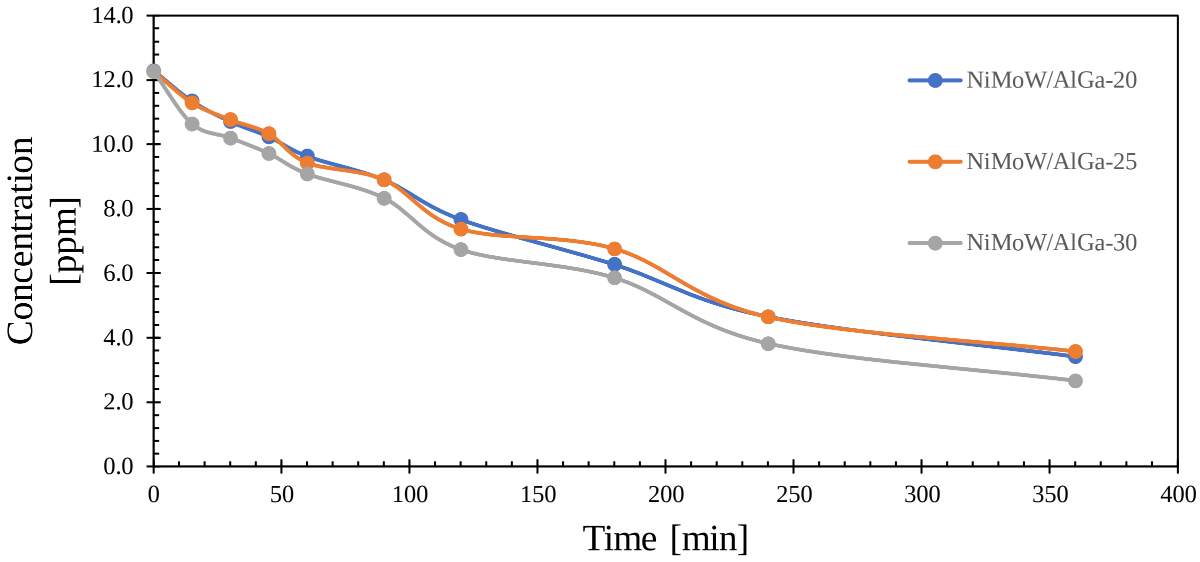


Figure 20. *Concentration in ppm of S in HDS as a function of time using NiMoW with X = 20, 25, 30 wt.% of* Ga_2O_3.

It is necessary to calculate the concentration of DBT to obtain the initial reaction rate of each reaction, the calculation of initial reaction rate can be seen in **Appendix C**. The Figure 21 presents the three catalysts were active in the HDS of DBT with similar activities.

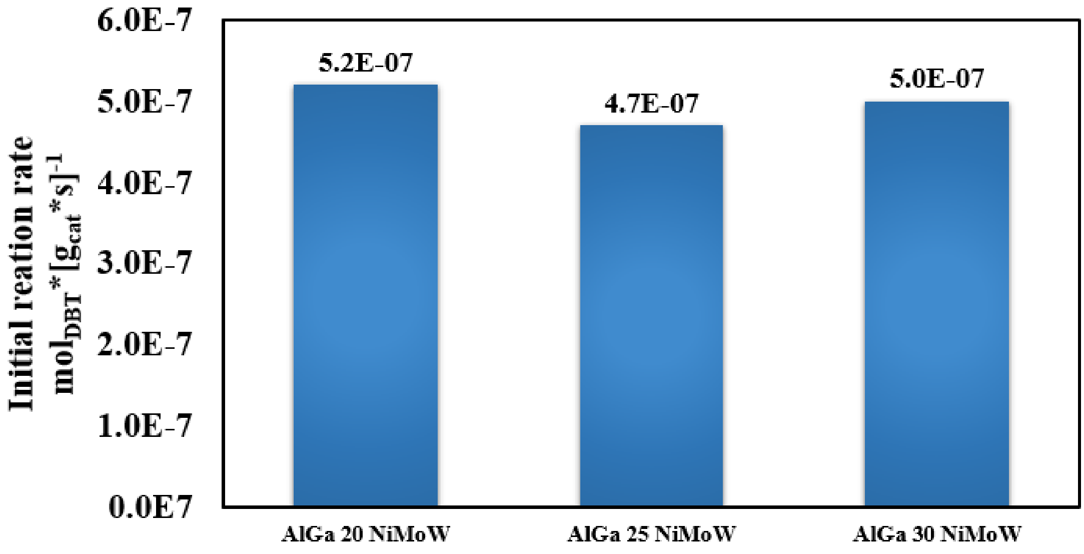


Figure 21. *Initial reaction rate for AlGaX NiMoW with X = 20, 25, 30 wt.%* Ga_2O_3.

Increasing the amount of support with gallium does not increase the initial reaction rate and does not reduce the time to reach the maximum DBT conversion. Therefore, to achieve a good dispersion of the catalyst in the support mixture, it is recommended to use the smallest value of X.

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

As time passes and 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 as well as 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 22).

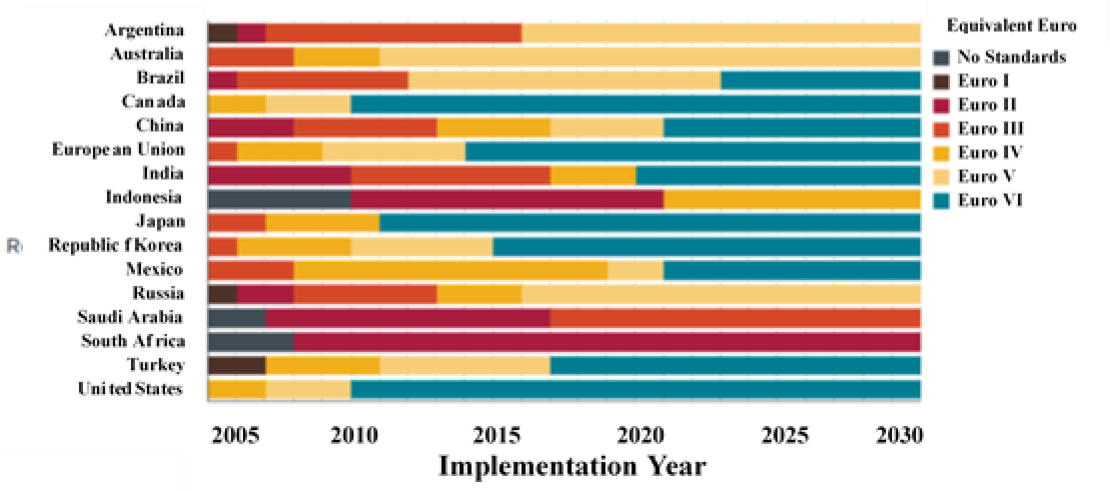


Figure 22. *Year of implementation (all sales and patents / registrations) of emissions standards for diesel-powered heavy vehicles in G-20 economies* [60].

To reach the new international standards (USA, European Community) 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 current 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 (Figure 23).

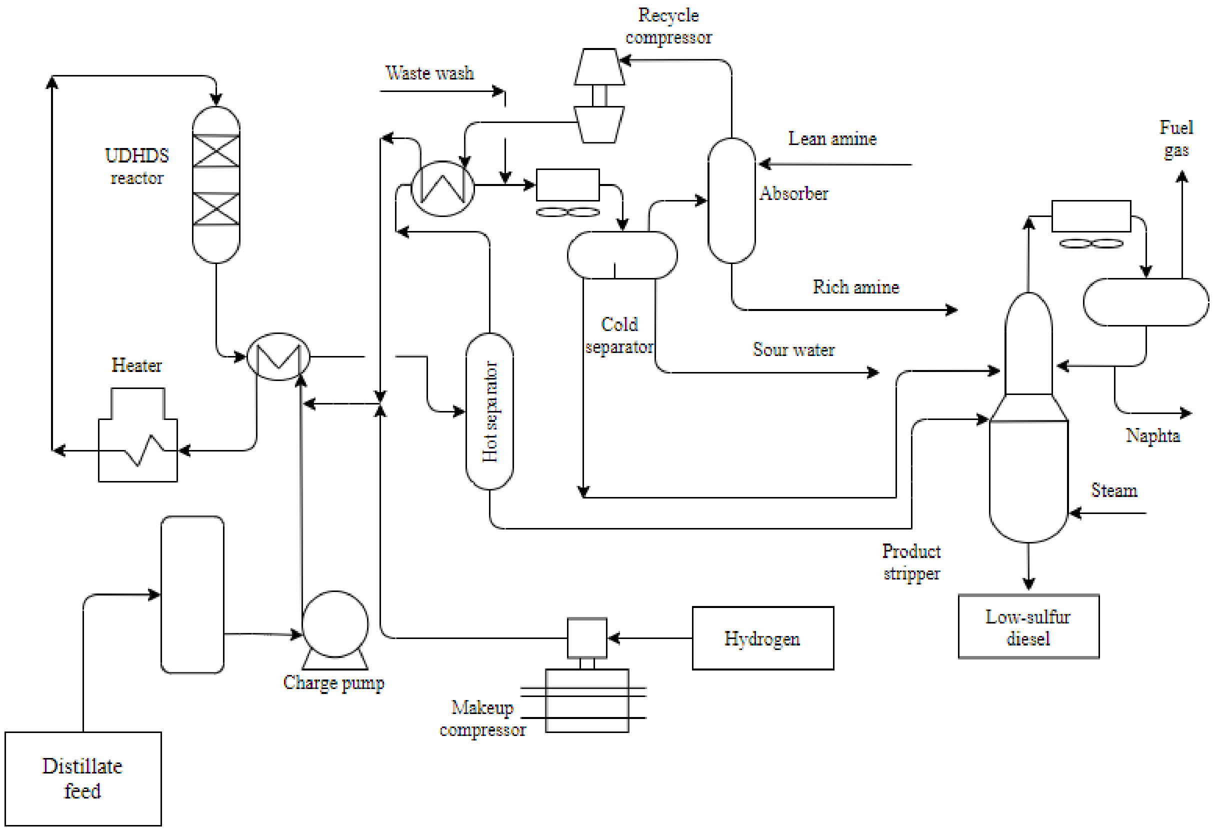


Figure 23. *Diagram of the Deep Hydrodesulfurization Unit.*

In the short time and to reach the new standards, the possibilities of process innovations are restricted to modifying the operating conditions and the use of more catalyst 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 through further washing of the sulfhydric 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.

To improve the characteristics of the catalysts used in HDS, a strategy has been used to add a third component as an additive, for example, NiCoMo, NiMoW and VNiMo catalysts [6, 33]. The Esmeraldas State Refinery mainly uses 2 types of commercial catalysts; the description of the products is as follows (Table 6) [21].

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 ºC:	-	0.5 wt.%
Resistance to mass compression:	-	159.5 psi

(-) Data not reported

These catalysts can be modified by adding a third metal component, to carry out this it is necessary to know the availability and cost in the Ecuadorian market, so that the resources can be optimized with the least investment expense. The metallic impregnation ratios vary from 1 % to 10 %, after this there is an oversaturation of the catalyst. Ecuador has deposits of Molybdenum in the Bolivar province, and in the Cotacachi canton (Imbabura province), see **Appendix D**. 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 % (Table 7).

Table 7. *Main producers of molybdenum in the world.*

MOLYBDENUM	Mine production (tons)		Reserves (thousand tons)
	2016	2017	
United States	35800	44600	2700
Argentina	800	800	100
Armenia	6300	6300	150
Canada	2710	3000	150
Chile	55600	58000	1800
China	130000	130000	8300
Iran	3500	3500	43
Mexico	11900	12000	130
Mongolia	2440	2400	160
Peru	25800	26000	2200
Russia	3000	3000	1000
Turkey	900	900	100
Uzbekistan	450	450	60
World total	279200	290950	16893

In 2015, the Public Hydrocarbons Company of Ecuador EP Petroecuador made a purchase of 4,442.00 m^3 of catalyst at a cost of US $ 3,368,133 per m^3, 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 INEN 1489 (2012). This cost would 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 VI standard in 30 years US$ 3.60 will be generated in benefit to human health, this due to reduced exposure to pollutants generated by diesel combustion. Likewise, the cost benefits that would increase will be more visible if they are applied in the short term and not in the long term (Table 8).

Table 8. *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 consists of the fact that Argentina is a nation belonging to South America, which the impulse to its policies and improvements in the quality of its diesel fuel has repercussions in the region, this is the path that Ecuador must follow to reach the goal international to one-day reach 0 ppm of sulfur and other components.

Thus, proposals such as the use of trimetallic catalysts to achieve deep hydrosulfurization levels are a very viable option for Ecuador. Given that at this time the country is trying to improve its refining processes and is also planning to build a new hydrodesulfurization plant and a fuel processing unit under the BOT modality (build, operate and transfer) in Manabí.

CONCLUSIONS AND RECOMMENDATIONS

- 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, 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.
- 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, there is the possibility of increasing the performance and capacities of the conventional catalysts used in the process, this has led to the use of supported catalysts, unsupported catalysts and trimetallic catalysts, among other.
- 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.
- The use of trimetallic catalysts such as NiMoW could not only assist to break 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 also diminish the acid rains that every day are more frequent and that alter the ecological equilibrium. The cost of changing technology is offset by savings in health, infrastructure maintenance and environmental remediation.
- It is necessary to make investments in the country's refineries in order to reach ultra-low sulfur concentrations and, as far as possible, up to 0 ppm of this element. To achieve this it is necessary to obtain ultra-deep hydrodesulfurization units (UDHDS) and reactive distillation systems, these are currently widely used in refineries around the world with successful results.
- Along with this modernization in hydrodesulfurization processes and in all fuel refining processes, the quality of automotive systems must begin to ameliorate. To not only bring down the emissions generated by these fuels but also reduce the consumption of these.

- During the development of this thesis, figured out the need for pilot plants that allow the simulation of chemical reaction processes, this in order test new prototypes of solid catalysts that can be used in hydrodesulfurization processes. Therefore, a viable proposal is to start building pilot plants or combustion prototypes in universities, so that researchers have the possibility of carrying out tests that are closer to reality.

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APPENDIX

APPENDIX A:

Acid Rain

Environmental impact: Acid rain

Later on the industrial acceleration, the climatic behaviors began to stop being cyclical and to generate major disasters, the scientific community began to analysis more in depth the phenomena registered comparing them with those of past years. This contributed to the generation of climate models and the realization of predictions, the results gave bad expectations for the times to come. As well, these alterations in the climate and specifically in the rain cycles, were accompanied by another phenomenon known as acid rains, which started to harm human health, crops, woods, jungles, and so forth.

The acid rain phenomenon includes from precipitation, deposit, deposition, wet deposition of acidic substances dissolved in water, rain, snow and hail. In addition to dry deposition or precipitation, where aerosols or acid gaseous substances deposited as ash, soot or as gases on surfaces.

In 1983, the most industrialized nations recognized the tremendous risk that being generate and agree to reduce the pollution generated by sulfur oxides (SOx), although today this emission is already exceeded by nitrogen oxides (NOx) coming from the exhaust of motor vehicles, domestic and industrial sources [4, 61].

The origin

At this moment the term “Acid Rain” is very familiar, but it was a term coined 120 years ago by the British Chemist Angus Smith who conducted studies on air quality in Manchester, England. In the 1950s a monitoring network of the quality of rain in northern Europe and it was at this time that the widespread incidence of acid rain was recognized. Although it was at the Stockholm Conference in 1972 that the subject was first talked about it. In more recent times, acid rain is a cause for interest, because it is spreading massively around the planet, breaking ecological balances and wreaking havoc on health and infrastructure in urban centers. The origin of acid rain can be both natural and artificial.

The acid rain generated naturally is due to various meteorological phenomena, for example, volcanic eruptions that emit COx and SOx gases into the atmosphere in large quantities and that become acids liquid in contact with humidity, as well as emissions in smaller amounts of hydrofluoric acid (HF) and hydrochloric acid (HCl). On the other hand, the ash dust can be acidic depending on the substance it has adsorbed. Other natural factors that can generate acid rain are lightning strikes, such as generated in the southern region of Lake Maracaibo, in Venezuela (Figure A. 1), lightning breaks the nitrogen and oxygen molecules producing different types of molecules, including nitrogen oxides and ozone. The northern lights are another of the natural phenomena that produce the components of acid rain, due to when the particles that are part of the solar storms collide with the N_2 and O_2 found in the stratosphere, generating nitrogen oxides. It is estimated that 1% of acid rain originates through this stratospheric phenomenon [5].

Figure A. 1. *Lightning strikes at the confluence of the Catatumbo River with Lake Maracaibo, in Venezuela.*

As natural biological sources of acid components we have all living organisms, they emit CO_2 caused by respiration, gases of the type SOx and NOx are of bacterial origin. Finally, acid rain generated artificially or better said from an anthropogenic source, is due to the emission of large quantities of substances into the atmosphere due to human activity. Power plants and automobiles emit large amounts of COx, SOx, NOx, water vapor and other toxic substances. One time these gases reach the troposphere, they come into contact with microdroplets that form clouds, these dissolve the gases forming acid substances that, when there are optimal weather conditions, precipitate returning to the Earth's crust causing various damage (Figure A.2).

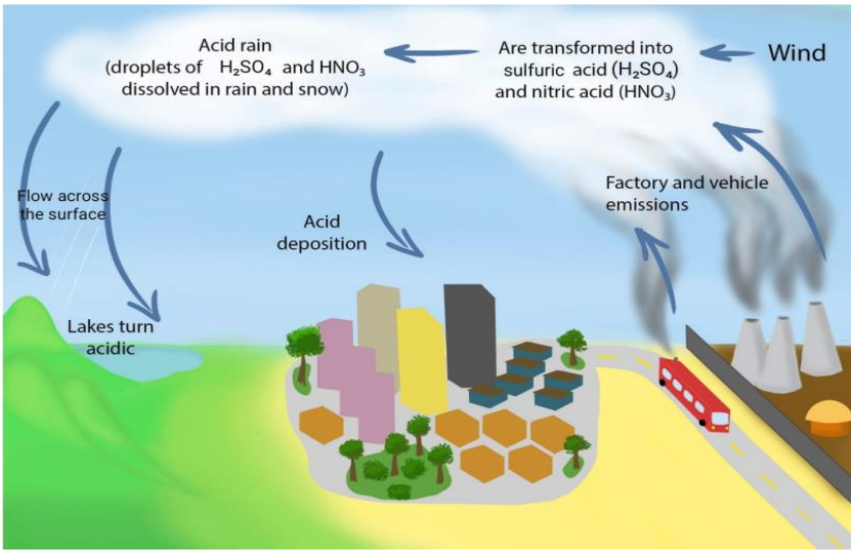

Figure A. 2. *Production of acid rain, due to human activity*.

International implications

At present, the diffusion of the gaseous pollutants that originate acid rain is a problem of international character, because the circulation of the air masses has no edges. Instances of these are polluting waste generated by the explosion of the nuclear reactor in Chernobyl, Ukraine in 1986 or the nuclear accident of Fukushima I in 2011, which caused large amounts of radioactive material to escape into the atmosphere. For that reason, acid rain is a transnational problem, and requires coordinated action to remedy the problem. In this sense, the problem is aggravated because the underdeveloped countries are just beginning to implement policies that lead to the reduction of gaseous pollutant emissions into the ambience. Due to internal policies, these have not been applied efficiently. Therefore, the need to develop low-cost and effective technologies are visualized to try to control the problem from its origin.

Strategies for reducing gaseous pollutants

To reduce acidic rainfall or better known as acid rain, it is necessary to mainly reduce the emission of the most abundant gas, SO_2. This can be done in two ways [5]:

- **Capture of the exhaust gas**: in the combustion chimney the gas pass through basic supports, for example, calcareous dust or calcium oxide. This operation is known as Flue Gas Desulfurization (FGD) and is used mainly in thermal power plants where coal is burned. In 1973 Japan and the USA already had 43 facilities, and by the year 2000 in 27 countries they had 678 FGD facilities.

- **Capture of the sulfur from the fuel before being burnt up**: this treatment is known as Hydrodesulfurization, this process was developed by the French chemist Paul Sabatier at the end of the XIX century, this consists of reacting the fuel with hydrogen gas, at high pressures and temperatures, using metallic catalysts. In this way, sulfur is removed from oil or natural gas, producing hydrogen sulfide as a by-product that is removed within the process stages.

Other sulfur removal mechanisms are currently being developed as well as improving combustion technologies in gasoline or diesel-based engines. Nevertheless, in the energy sector, there is a boom in the development of new energy sources that do not generate pollutants.

APPENDIX B:

Preparation of nano trimetallic NiMoW slabs over Al_2O_3 and Ga_2O_3 mixed oxides for deep sulfur removal of diesel fuel

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PREPARATION OF NANO TRIMETALLIC NiMoWS SLABS OVER Al_2O_3 AND Ga_2O_3 MIXED OXIDES FOR DEEP SULFUR REMOVAL OF DIESEL FUEL

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Abstract: Synthesis of binary mixed supports of Al_2O_3/Ga_2O_3 were obtained with a different weight percent of Ga_2O_3 by co-precipitation method and after calcination used for the preparation of trimetallic catalysts. The supports were impregnated by the pore filling method. Prepared catalysts were tested in the hydrodesulfurization reaction of dibenzothiophene diesel model compound in a batch reactor. The supports and catalysts were widely characterized by several techniques to know their properties.

Keywords**:** *Mixed oxides, Mesoporous Materials, Hydrodesulfurization, Dibenzothiophene.*

Introduction

The sulfur compounds of the exhaust emissions from gasoline and diesel fuels combustion processes are the major components of air pollutants, which are very harmful to human health and the environment. Increasing demands on the quality of diesel fuels force producers to decrease the sulfur content to 10 ppm. In order to meet these specifications, there is a need for more efficient processes and more active catalysts. Traditional hydrodesulfurization (HDS) catalysts are Mo or W based supported on alumina and promoted by Ni or Co in a sulfided state [1].

In this research, a series of AlGa-X materials with the different weight percent of Ga_2O_3 (X = 20, 25, 30%) were successfully synthesized by the co-precipitation method. The synthesized supports and NiMoW catalysts were characterized by N_2 adsorption-desorption isotherms (S_{BET}), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), scattering electron microscopy (SEM).

Materials and methods

Synthesis of mixed oxides of Al_2O_3 and Ga_2O_3 by the co-precipitation method. For the synthesis were used as precursors of Al and Ga aluminum nitrate and gallium nitrate, respectively. In this one, the amount of gallium oxide was varied to obtain 20, 25 and 30% of Ga_2O_3 in the support. The obtained supports were used to prepare NiMoW trimetallic catalysts, which were incorporated into the support through of a pore filling impregnation. The precursors of the metals used for Ni, Mo, and W were nickel nitrate, ammonium heptamolybdate, and ammonium metatungstate, respectively.

The materials obtained were sulfided at 400° C for 2 hours at a heating rate of 5 ° C / min. The trimetallic catalysts obtained NiMoW / AlGa-X where X is equal to 20, 25 or 30% by weight of Ga_2O_3 were evaluated in the hydrodesulfurization reaction of dibenzothiophene (DBT) in a batch reactor with a concentration of 500 ppm of S, 55 bar of hydrogen, at 320 ° C

Results and discussion

The N2 adsorption-desorption isotherms and the pore size distribution curves of the AlGa-X support are shown in Fig. 1. The materials showed similar type IV isotherms with H1-type hysteresis loop and narrow mesoporous distributions, which are the typical behaviors of the mesoporous materials. The supports showed a narrow pore size distribution (PSD) and an average surface area of 320 m^2 g^{-1} with an average pore size of 3 nm and a pore volume of 0.3 cm^3 g^{-1}.

The TEM analysis allow us to observe the sulfide phases over the supports. As seen the trimetallic sulfided phases NiMoWS were successfully formed as several black lines arising from the central Mo or W of the MoS_2 of WS_2 slabs were detected. The Fig. 2 shows images of these analysis for AlGa-X 20, 25, and 30 % respectively. For the catalytic evaluation, the results are shown in the Fig. 3, we can observe the initial reaction rates for the 3 samples tested.

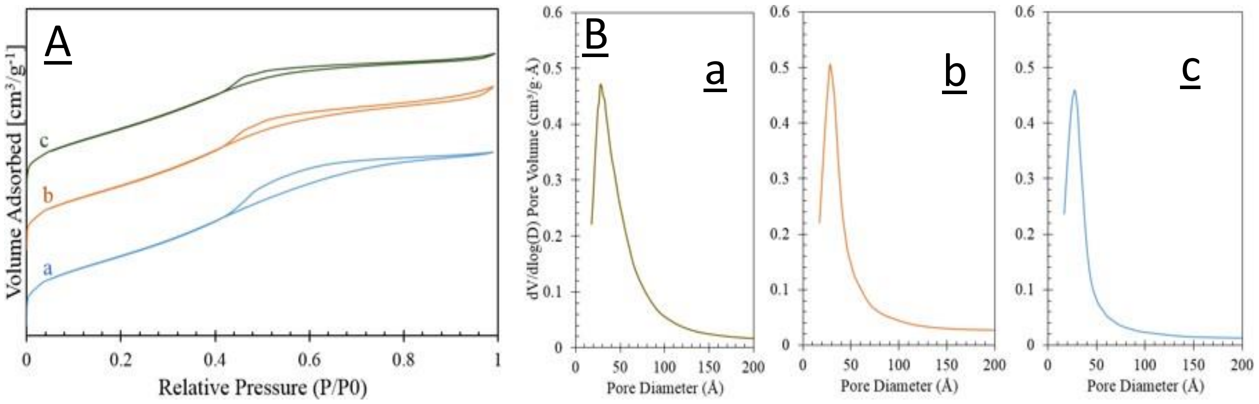

Figure 1. A) Nitrogen adsorption/desorption isotherms, B) Pore size distribution for a) AlGa-20, b) AlGa-25, c) AlGa-30.

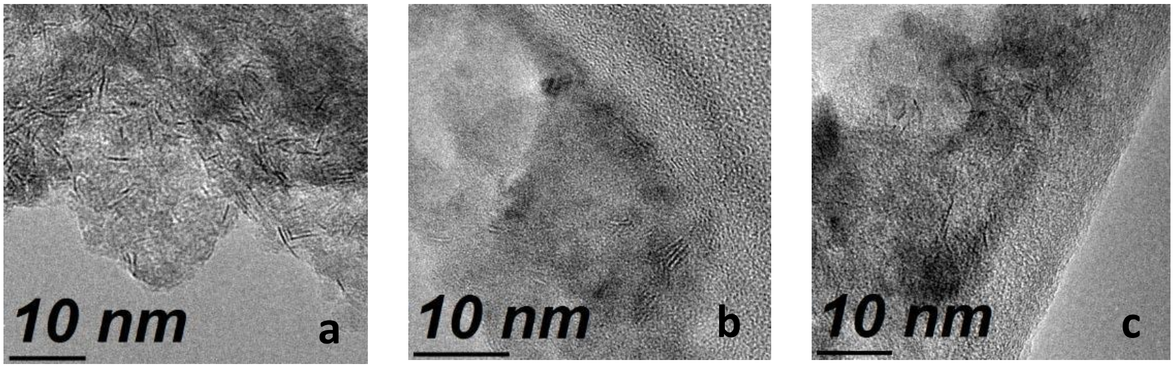

Figure 2. Transmission electron microscopy (TEM) analysis for a) AlGa-20, b) AlGa-25, c) AlGa-30.

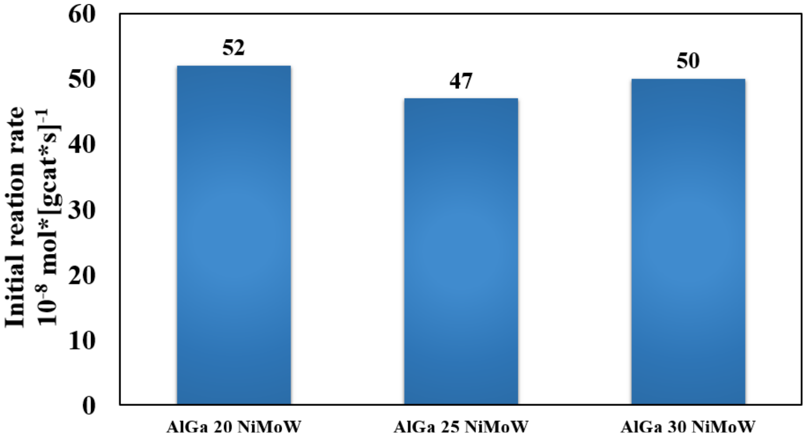

Figure 3. Initial reaction rate for AlGaX NiMoW with X = 20, 25, 30 % Ga2O3.

As we can observe the three catalysts were active in the HDS of DBT with more or less the same activity. Only small differences were observed also in the selectivity.

Conclusions

It was possible to synthesize mixed oxides of AlGaX by the co-precipitation method. Supports were obtained with suitable textural properties. The catalysts were synthesized by a pore fill method filling method obtaining trimetallic catalysts NiMoW. Observing the images of the catalysts by TEM analysis is important to conclude that the materials have a good dispersion of the active phases. The preparation of NiMoW/AlGa-X 20, 25, and 30 induced good catalytic activity. The catalysts showed almost the same initial reaction rate, this suggests that the variation of Ga_2O_3 does not affect the reaction rate of the catalysts. Further characterizations is in progress to fully understand this behavior.

Acknowledgments

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APPENDIX C:
Initial Reaction Rate Calculation

1. Postulate a rate law

$$-r_A = kC_A^{\propto}$$

where α and k are to be determined.

2. **Process data in terms of the measured variable.** Rewrite the mole balance in terms of the measured variable, in this case concentration.

$$-\frac{dC_A}{dt} = -r_A = kC_A^{\propto}$$

$$-\frac{dC_A}{dt} = kC_A^{\propto}$$

3. **Look for simplifications.**
4. **Calculate $-r_A$** as a function of reactant concentration to determine the reaction order. In this case, as the reactor is a batch reactor, then it must be to determined $-\frac{dC_A}{dt}$. The equal – area differentiation method was used.

   1. Tabulate the $(y_i\ , x_i)$ observations.
   2. For each interval, calculate $\Delta x_n = x_n - x_{n-1}$ and $\Delta y_n = y_n - y_{n-1}$.
   3. Calculate $\frac{\Delta y_n}{\Delta x_n}$ as an estimate of the average slope in an interval x_{n-1} to x_n.
   4. Plot these values as a histogram versus x_i. The value between x_2 and x_3, for example, is $\frac{(y_3 - y_2)}{x_3 - x_2}$. Refer to Figure C.1.

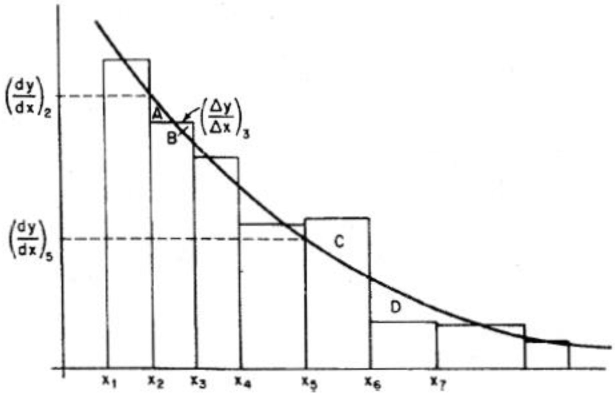


Figure C. 1. *Graphical method to calculate the area under the histogram.*

   5. Draw in the smooth curve that best approximates de area under the histogram. From the definitions of A_x and A_y we know that:

$$y_n - y_1 = \sum_{i=2}^{n} \frac{\Delta y}{\Delta x} \Delta x_i$$

The equal – area method attempts to estimate $\frac{dy}{dx}$ so that

$$y_n - y_1 = \int_{x_1}^{x_n} \frac{dy}{dx} dx$$

that is, so that the area under $\frac{\Delta y}{\Delta x}$ is the same as that under $\frac{dy}{dx}$, everywhere possible.

6. Read estimates of $\frac{dy}{dx}$ from this curve at the data points $x_1, x_2, \ldots$.

5. **Determine α and k.** Using the graphical method, the following table can be set up:

Time	t_0	t_1	t_2	t_3
Concentration	C_{A0}	C_{A1}	C_{A2}	C_{A3}
Derivative	$\left(-\frac{dC_A}{dt}\right)_0$	$\left(-\frac{dC_A}{dt}\right)_1$	$\left(-\frac{dC_A}{dt}\right)_2$	$\left(-\frac{dC_A}{dt}\right)_3$

Now:

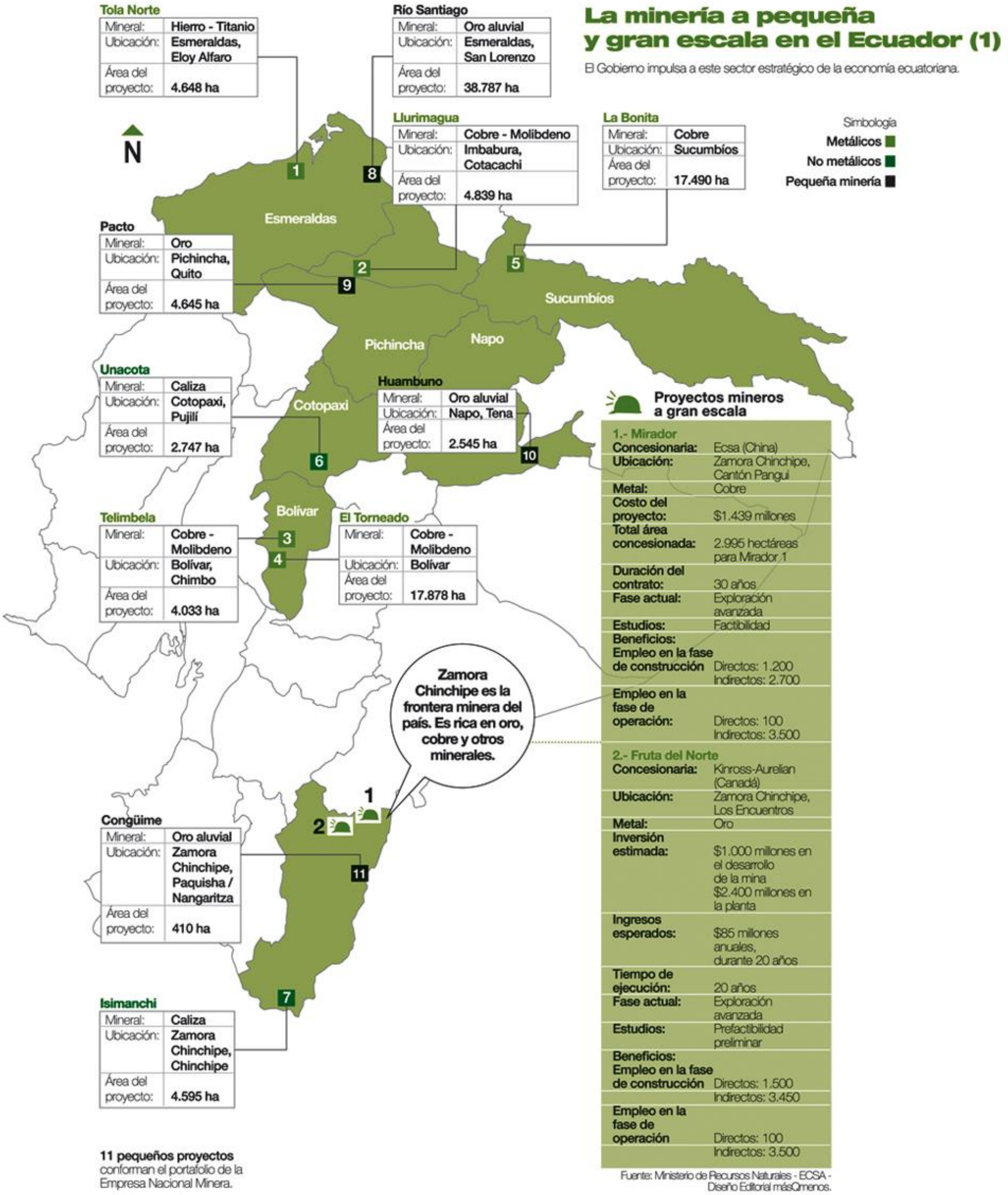
$$\ln\left(-\frac{dC_A}{dt}\right) = \ln \mathrm{k_A} + \propto \ln \mathrm{C_A}$$

For ***initial*** reaction rate, $\propto = 1$,

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln \mathrm{k_A} + \ln \mathrm{C_A}$$

k can be calculated.

APPENDIX D:
Ecuador mining map



La minería a pequeña y gran escala en el Ecuador (1)

El Gobierno impulsa a este sector estratégico de la economía ecuatoriana.

Tola Norte

Mineral:	**Hierro - Titanio**
Ubicación:	**Esmeraldas, Eloy Alfaro**
Área del proyecto:	**4.648 ha**

Río Santiago

Mineral:	**Oro aluvial**
Ubicación:	**Esmeraldas, San Lorenzo**
Área del proyecto:	**38.787 ha**

Llurimagua

Mineral:	**Cobre - Molibdeno**
Ubicación:	**Imbabura, Cotacachi**
Área del proyecto:	**4.839 ha**

La Bonita

Mineral:	**Cobre**
Ubicación:	**Sucumbíos**
Área del proyecto:	**17.490 ha**

Simbología
Metálicos 🟩
No metálicos 🟩
Pequeña minería ■

Pacto

Mineral:	**Oro**
Ubicación:	**Pichincha, Quito**
Área del proyecto:	**4.645 ha**

Unacota

Mineral:	**Caliza**
Ubicación:	**Cotopaxi, Pujilí**
Área del proyecto:	**2.747 ha**

Huambuno

Mineral:	**Oro aluvial**
Ubicación:	**Napo, Tena**
Área del proyecto:	**2.545 ha**

Telimbela

Mineral:	**Cobre - Molibdeno**
Ubicación:	**Bolívar, Chimbo**
Área del proyecto:	**4.033 ha**

El Torneado

Mineral:	**Cobre - Molibdeno**
Ubicación:	**Bolívar**
Área del proyecto:	**17.878 ha**

Zamora Chinchipe es la frontera minera del país. Es rica en oro, cobre y otros minerales.

Congüime

Mineral:	**Oro aluvial**
Ubicación:	**Zamora Chinchipe, Paquisha / Nangaritza**
Área del proyecto:	**410 ha**

Isimanchi

Mineral:	**Caliza**
Ubicación:	**Zamora Chinchipe, Chinchipe**
Área del proyecto:	**4.595 ha**

11 pequeños proyectos conforman el portafolio de la Empresa Nacional Minera.

Proyectos mineros a gran escala

1.- Mirador

Concesionaria:	Ecsa (China)
Ubicación:	Zamora Chinchipe, Cantón Pangui
Metal:	Cobre
Costo del proyecto:	$1.439 millones
Total área concesionada:	2.995 hectáreas para Mirador 1
Duración del contrato:	30 años
Fase actual:	Exploración avanzada
Estudios:	Factibilidad
Beneficios: Empleo en la fase de construcción	Directos: 1.200 Indirectos: 2.700
Empleo en la fase de operación:	Directos: 100 Indirectos: 3.500

2.- Fruta del Norte

Concesionaria:	Kinross-Aurelian (Canadá)
Ubicación:	Zamora Chinchipe, Los Encuentros
Metal:	Oro
Inversión estimada:	$1.000 millones en el desarrollo de la mina $2.400 millones en la planta
Ingresos esperados:	$85 millones anuales, durante 20 años
Tiempo de ejecución:	20 años
Fase actual:	Exploración avanzada
Estudios:	Prefactibilidad preliminar
Beneficios: Empleo en la fase de construcción	Directos: 1.500 Indirectos: 3.450
Empleo en la fase de operación	Directos: 100 Indirectos: 3.500

Fuente: Ministerio de Recursos Naturales - ECSA - Diseño Editorial másQmenos.

Figure D. 1. *Ecuador mining map* [63].