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Activated carbon from avocado seeds as catalysts support: use in HDS catalysts and other processes

Trabajo de integración curricular presentado como requisito para la obtención del título de Petroquímica

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DEDICATION

To my parents, Marlene and Kleber; and sisters, Evelyn and Marianela, for their love, patience, and effort that has allowed me to achieve another goal today.

Gloria Ginela Imaicela Ordóñez

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To God and Virgin Mary, because along the way, he filled me with many blessings and gave me strength in difficult moments.

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Gloria Ginela Imaicela Ordóñez

RESUMEN

Las estrictas regulaciones ambientales que existen para alcanzar niveles bajos de contenido de azufre producidos por combustibles fósiles han impulsado la mejora de los procesos de refinación catalíticos, en específico el proceso de hidrodesulfuración (HDS). Por esta razón, se requiere del estudio y desarrollo de nuevos catalizadores que sean más activos a moléculas refractarias y resistentes a la desactivación catalítica. El carbón activado, generalmente utilizado como adsorbente para la remoción de contaminantes, posee una elevada área superficial, volumen y tamaño de poro controlado. Además, el carbón activado puede ser producido usando un amplio rango de precursores orgánicos e inorgánicos. Estas características hacen que el carbón activado sea un material atractivo para soporte de catalizadores HDS. El presente trabajo consistió en una revisión bibliográfica que recopila información de diferentes investigaciones enfocadas en las propiedades estructurales y factores que hacían que con el carbón activado se preparen catalizadores con una mejor actividad frente a los preparados con soportes convencionales. Sin embargo, también presenta desventajas, como la baja densidad de empaquetamiento y propensión a la sinterización que hacen que no sea posible su uso a escala industrial. Por consiguiente, es importante continuar desarrollando estudios en esta área. Por otra parte, la industria del aguacate en el Ecuador se encuentra en vías de desarrollo, y se espera el procesamiento de grandes cantidades de aguacate, que generan una cantidad considerable de residuos sólidos, como la semilla y corteza. En la literatura se encuentran trabajos sobre el uso de las semillas de aguacate como adsorbente, por lo tanto se sugiere su investigación como fuente para la obtención de carbón activado usado como soporte catalítico.

Key words: Hidrodesulfuración, catalizadores, carbón activado, soporte, aguacate

ABSTRACT

The strict environmental regulations that exist to achieve low levels of sulfur content produced by fossil fuels have driven the improvement of catalytic refining processes, specifically the hydrodesulfurization process (HDS). For this reason, the study and development of new catalysts that are more active to refractory molecules and resistant to catalytic deactivation is required. Activated carbon, generally used as an adsorbent to remove contaminants, has a high surface area, volume and controlled pore size. Furthermore, activated carbon can be produced using a wide range of organic and inorganic precursors. These characteristics make activated carbon an attractive material for HDS catalyst support. The present work consisted of a bibliographic review that compiled information from different investigations focused on the structural properties and factors that made activated carbon produce catalysts with better activity compared to conventional supports. However, it also has disadvantages, such as low packing density and sintering propensity that make it not possible to use it on an industrial scale. Therefore, it is important to continue developing studies in this area. On the other hand, the avocado industry in Ecuador is under development, and the processing of large quantities of avocado is expected, which generate a considerable amount of solid waste, such as the seed and rind. In the literature there are works on the use of avocado seeds as an adsorbent, therefore its investigation as a source for obtaining activated carbon used as a catalytic support is suggested.

Key words: Hydrodesulfurization, catalysts, activated carbon, support, avocado.

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LIST OF ABBREVIATIONS

4,6-DMDBT	4,6-dimethyl dibenzothiophene
4-MDBT	4-methyl dibenzothiophene
BET	Brunauer-Emmett-Teller
CO	Carbon oxide
DBT	Dimethylbezonthiophene
DDS	Direct desulfurization
FCC	Fluid catalytic fracking
FTIR	Fourier transform infrared
HDM	Hydrodemetallization
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HDS	Hydrodesulfurization
HDT	Hydrotreating
HYD	Hydrogenation
LPG	Liquid petroleum gas
MMBls	Million Barrels
NO_x	Nitrogen oxides
SEM	Scanning electron microscopy
SO_x	Sulfur oxide
TDP	Temperature Programmed Desorption
TEM	Transmission electron microscopy
TOF	Turnover frequency
TPR	Temperature Programmed Reduction
XDR	X-ray diffraction analysis

CHAPTER 1

INTRODUCTION

1.1. Problem Statement

Population growth and economic development have increased demand and consumption of fuels and crude oil-derived products [1]. Worldwide demand for crude oil has caused a reduction in light crude oil reserves and increased the utilization of heavy crude oil [2]. In Ecuador, it is estimated that between proven, probable, and possible reserves, there are 2,239 MMBls of crude oil, of which 99.8% has an average API gravity of 24.9, and the remaining 0.2% corresponds to crude oil with API gravity of 38.7. Therefore, heavy crude oil production will gain ground over time [3].

The issue with heavy oil is that the refining process becomes more complex and costly due to its higher viscosity and heavier molecular composition, with higher concentrations of undesirable elements such as sulfur, nitrogen, and heavy metals that affect the processing of the crude oil fractions and final products such as fuels [4,5]. The quality of fuels has become an essential topic of environmental discussion due to combustion of crude oil fuels generates compounds (SO_x, CO, NO_x) that are harmful to the environment and human health [4]. In response, legislation worldwide has established the reduction of S in fossil fuels [6]. In the case of Ecuador, the National Air Quality Plan of the Ministry of the Environment establishes the need for fuels marketed in the country to comply with international standards; in response, emissions must not exceed 50 ppm of sulfur with respect to diesel [7]. According to the official page of EP Petroecuador, the fuel dispatched in Ecuador has a sulfur content of 150 ppm.

In this context, catalytic refining processes need improvement, mainly hydrodesulfurization (HDS), which removes the sulfur heteroatoms from the molecules of interest [8]. Research in this area focuses on developing HDS catalysts with ideal activity and selectivity for refractory compounds such as 4,6-DMDBT [9]. Although NiMo and CoMo catalysts supported on alumina are conventionally used, other alternative materials such as clay, silica, and carbonaceous materials present great potential as catalyst support. Due to its high adsorption capacity, activated carbon has been widely studied for pharmaceutical and water treatment applications [10,11]. In the area of catalysis, research has highlighted advantages such as resistance to acidic and basic media, stability at high temperatures, ability to create large surface areas and adapt to large pore sizes, and most importantly, that the active phase of the catalyst can be recovered more easily [9,12].

In order to meet the environmental standards for the quality of petroleum fuels, new catalysts for hydrotreatment have been investigated. Furthermore, one of the alternative materials to be used as catalyst support is activated carbon due to its mechanical and structural properties. For years, the possibility of preparing activated carbon from organic solid wastes has been studied. For this reason, this work proposes the use of avocado seed as a source for the preparation of activated carbon as a catalytic support for hydrodesulfurization, thus obtain a high value-added product from wastes that are little used in Ecuador.

1.2. Aim and Objectives

1.2.1. General Objectives

To develop a review about the catalytic activity of activated carbon as catalyst support in refining processes such as hydrodesulfurization and explorer their preparation from avocado seeds.

1.2.2. Specific Objectives

- To review the available literature about activated carbon in the area of the hydrodesulfurization and other catalytic processes.
- To investigate the current situation of avocado in Ecuador and recognize the valorization of its waste (seeds).
- To review the preparation of activated carbon from avocado seeds and its structural properties.

CHAPTER 2
THEORETICAL FRAMEWORK

2.1. Crude Oil

Crude oil is one of the most important natural resources. It is the raw material to the production of fuels for transportation, power generation, and heating purposes; production of specialties such as solvents and lube oils; and production of intermediates, used in the chemical industry [13]. Depending on its characteristics, crude oil is called by different names. In reserves, it can find from light to extra-heavy crude oil; this depends on the API grades [14]; light crude oil has an API > 31.1°, medium 22.3-31.1°, heavy 10-22.3°, and extra heavy < 10°. It can also be called sour or sweet crude; this depends on the sulfur content in the crude. If the crude has < 0.5% sulfur content, it is sweet crude, and if > 0.5%, it is sour crude. Thus, light crude is the most desirable as it is easier to process due to its low viscosity and lower amount of contaminants [15]

The crude oil composition is based on a mixture of hydrocarbons that contains hydrogen (11-14%) and carbon (84-87%) and a small percentage of other elements such as sulfur (0-3%), nitrogen (0-0.2%), oxygen (0-0.5%), chromium-vanadium and nickel [16]. Two groups of hydrocarbons, saturated and unsaturated, can be distinguished in the mixture. Saturated hydrocarbons correspond to alkanes (paraffin) and cycloalkanes (naphthenes). On the other hand, there are non-saturated hydrocarbons; they refer to the alkenes (olefins) and aromatics [17].

Alkanes (paraffin): They are straight (normal) or branched (iso) chains. They generally have from 5 to 40 carbon atoms per molecule. The alkanes from pentane (C_5H_{12}) to octane (C_8H1_8) are refined into gasoline, the ones from nonane (C_9H_{20}) to hexadecane ($C_{16}H_{34}$) into diesel fuel, kerosene and jet fuel, alkanes with more than 16 carbon atoms can be refined into fuel oil and lubricating oil [18].

Cycloalkanes (naphthenes): They have one or more carbon rings. Their presence, depends on the crude type. The lower members of naphthenes are cyclopentane, cyclohexane, and their mono-substituted compounds.They are normally present in the light and the heavy naphtha fractions [18].

Alkenes (olefins): They are hydrocarbons that containing at least one double bond, e.g. ethylene, propylene, butadiene, etc., used for the production of plastics, solvents and, together with aromatics, fibers and synthetic rubbers [18].

Aromatic: They have a ring structure and contain double bonds. They are derived from benzene and have a characteristic smell. Lower members of aromatic compounds are present in small amounts in crude oils and light petroleum fractions [18].

2.2. Refining Process

The crude oil to reach transformed into final commercial products such as LPG, gasoline, kerosene, and diesel oil [19], it needs to undergo refining processes [18]. The refining process is one of the most important industrial activities and consists of physical separations such as atmospheric and vacuum distillations, solvent extractions, adsorptions, and chemical transformations where the catalytic process plays a key role [13]. The following diagram (Figure 1) shows the primary refining processes [17].

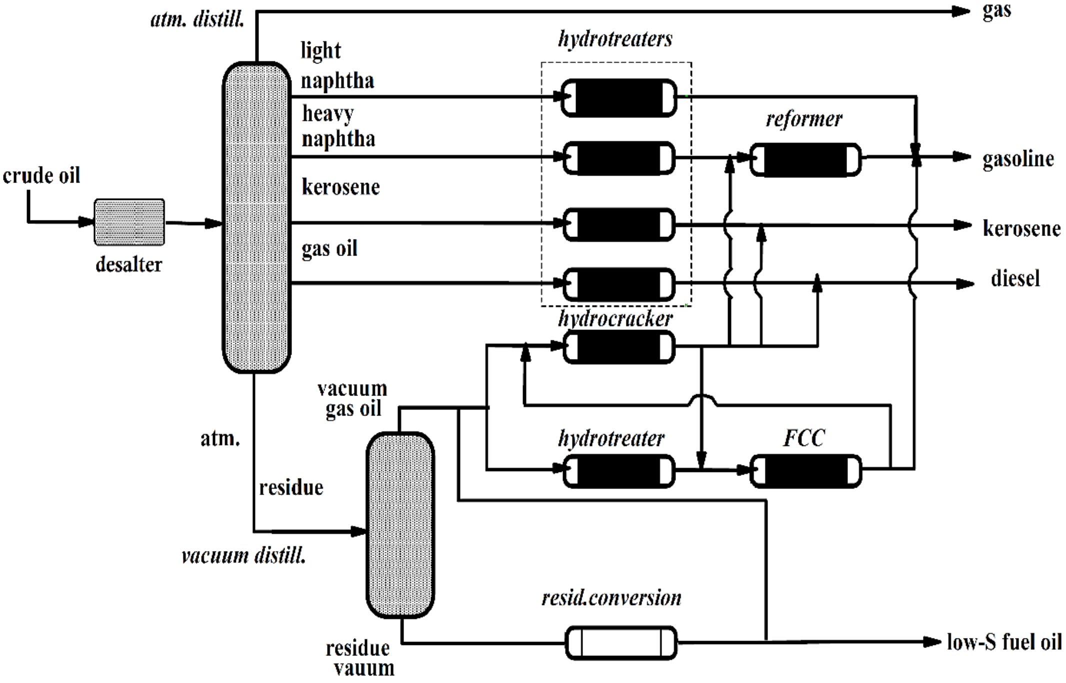


Figure 1. Schematic representation of an oil refinery [19].

First, the crude oil is desalting to prevent the presence of salts causing damage to the refining equipment through plugging and corrosion. It is then passed to distillation columns to separate it into fractions, ranging from Liquefied petroleum gas (LPG) gas, liquids (naphtha, kerosene, and gas oil), to the residue from vacuum distillation [17]; listed in Table 1 with their boiling point, volume (%), density and sulfur content. These fractions must undergo a series of catalytic processes to improve their performance and properties to meet fuel market quality standards [14]. One of the most important processes in refining crude oil and heterogeneous catalysis is hydrotreating (HDT) [17]. This process is described in detail in the following section.

Table 1. *Crude oil fractions and their characteristics* [17].

Fraction	**Boiling point (°C)**	**Volume (%)**	**Density (kg/L)**	**Sulfur (wt.%)**
Gas, LGP		1.5	0.5-0.6	0
Light naphtha ($\leq C_5$)	< 80	6	0.66	0
Heavy naphtha (C_5-C_{10})	80-170	15	0.74	0.02
Kerosene	170-220	9	0.79	0.1
Gas oil	220-360	25	0.83-0.87	0.8
Vacuum gas oil (C_{20}-C_{40})	360-530	23	0.92	1.4
Residue ($\geq C_{40}$)	> 530	20	1.02	2.2

2.3. Catalysis

The term catalysis was introduced more than 150 years ago and is a process that occurs in the presence of a catalyst. A catalyst is a substance that accelerates the rate of a chemical reaction without being consumed in the process [20]. Catalyst can be found in different forms, so catalysis is divided into different fields: homogeneous and heterogeneous catalysis. The main difference is that in the first one, the catalyst and the reactants are in the same phase, and in the second one, the catalyst is in a different phase of the reactants [21]. About 80% of industrial chemical processes involve catalytic steps in which heterogeneous catalysis is used in preference to homogeneous and it is due to the easy recovery and recycling of the catalyst and lower cost. Therefore, heterogeneous catalysis represents the most important catalytic system [17,22]. The main characteristics are that it is carried out with a solid catalyst with reactants in gaseous or liquid phase [21].

The reactions take place at the surface, a solid-fluid interface, so adsorption of at least one of the reactants on the catalyst is required to form an unstable intermediate compound for the reaction to proceed [20]. The catalytic reaction is carried out in the following steps.

1. **Diffusion**: It is the approach of the reactants to the surface of the solid and the exit of the products from the surface of the solid. It is a determining factor for the reaction rate [23].
2. **Adsorption**: It is a process that involves the formation of bonds; therefore, it is called chemisorption. The adsorbate gives up its electrons to the vacancy of the adsorbent and forms a bond. In a multi-reactant system, at least one must chemisorb [12].
3. **Surface Reaction**: Chemical reactions that take place on the surface. There is breakage and formation of bonds between the reactant molecules or the active surface of the catalyst to form the product [17].
4. **Desorption**: This is the counterpart of adsorption, where the active sites are released and become available for the next reaction [17].

2.4. Hydrotreating

Hydrotreating is one of the essential processes in crude oil refining [17]. The function of hydrotreating is the saturation of olefins and the removal of 90% of polluting heteroatoms such as sulfur, nitrogen, oxygen, and heavy metals from the crude oil fractions [24]. To avoids equipment damage, catalyst poisoning in downstream stages and produces better quality fuels [25]. For the process to take place, a high purity hydrogen stream and a selective catalyst are necessary [14].

According to the type of heteroatom removed, it is called hydrodesulfurization (HDS) for sulfur, hydrodenitrogenation (HDN) for nitrogen, hydrodeoxygenation (HDO) for oxygen, and hydrodemetallization (HDM) for metal [18]. However, hydrotreating generally focuses on HDS for being sulfur, the pollutant that exists in the highest proportion and causes the most significant inconvenience [17].

2.4.1. Sulfur Compounds

Sulfur is present in the crude oil in its different fractions. Atmospheric distillation fractions contain approximately 1000 ppm S while heavy fractions contain, on average more than 3000 ppm S; after the HDS process, the content is reducing to 150-300 ppm for light fractions and 500 ppm for heavy fractions [6].

The existing sulfur compounds are mercaptans, sulfides, disulfides, thiophene, benzothiophene, and their derivatives. As the crude fractions become heavy, the compounds become more complex and more difficult to desulfurizer [24]. Figure 2 shows the variation of sulfur compounds reactivity and the difficulty to desulfurize them [4]. The desulfurization of mercaptans, sulfides, disulfides, and thiophene is more accessible than aromatic compounds such as benzothiophene, dibenzothiophene, and others especially substituted compounds such as 4,6-dimethyl dibenzothiophene (4,6-DMDBT). This is because they have a steric hindrance close to the sulfur atom, then less reactive. They also have difficulty adsorbing on the catalyst surface. Therefore, more severe HDS pressure and temperature conditions are required [26].

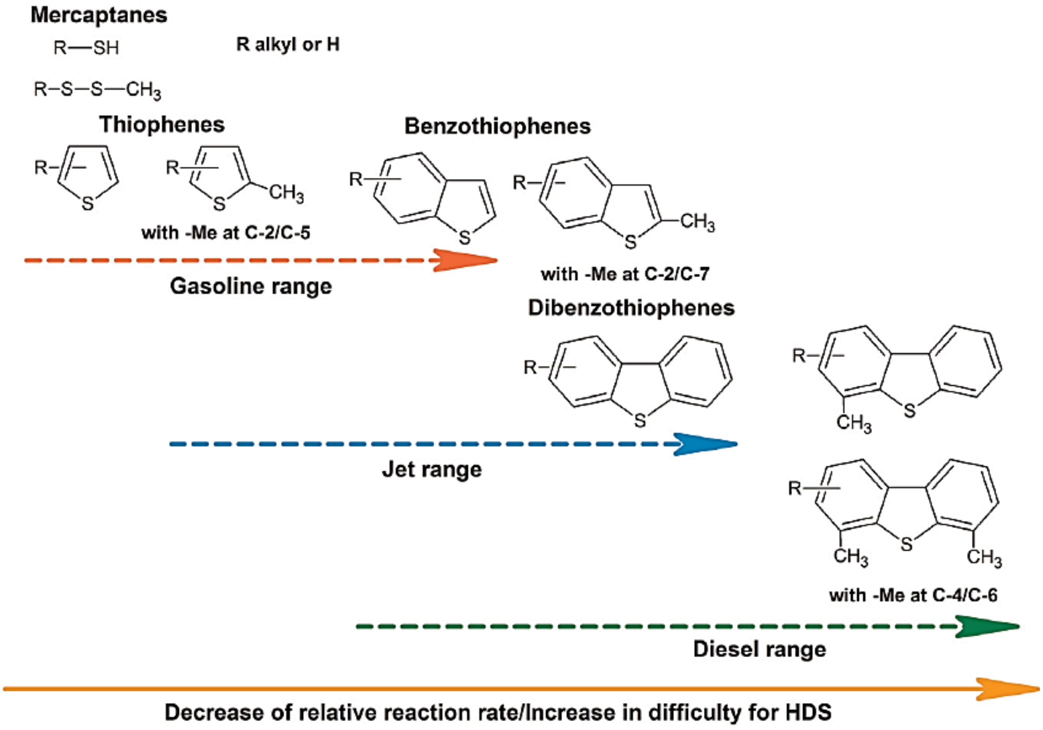


Figure 2. *Sulfur compound in different fractions of the distillate and their relative reactivity for HDS* [4].

2.4.2. HDS Process

The feedstock is mixed with a high purity hydrogen stream, preheated in a furnace, then charged at high pressures into a catalytic reactor where it comes into contact with Co- Mo catalyst, and reactions occur. The average conditions for the HDS process are: temperature, 260-440.5 °C, hydrogen pressure: 10-204 atm, hydrogen flows: 250-10000 SCF/bbl, feed space velocity: 0.5-5.0 volumes of liquid per volume of catalyst per hour [17]. The operating conditions depend on the density of the feed, desulfurization level required, and the catalyst activity [24]. The process is carried out in the HDS catalytic unit shown in Figure 3.

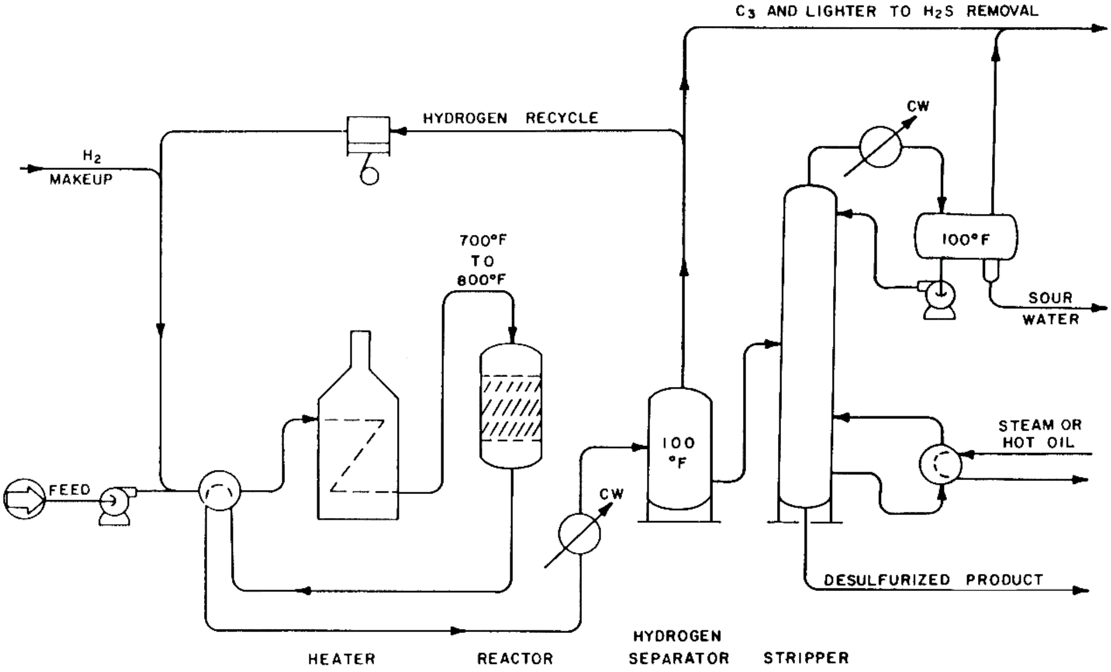


Figure 3. *Hydrodesulfuration unit* [27].

2.4.3. Operational variables in HDS

Temperature: The variable has the most significant influence on the reaction rate. Increasing this variable favors HDS reactions. However, it also increases the formation of coke on the catalyst, reducing the catalyst lifetime [26].

Space velocity: This is the ratio between the volumetric flow rate of the feed (m^3/h) and the amount of catalyst in the reactor (m^3). Like temperature, it helps to control the reaction. If the space velocity decreases, the reaction rate increases because of the decrease in feed flow rate [25].

Hydrogen partial pressure: It is favorable to operate at high-pressure conditions as they favor HDS reactions and reduce coke deposition on the catalyst and polymerization reactions, which affect its performance [28].

2.4.4. HDS Reaction

HDS process is based on hydrogenation and hydrogenolysis reactions that consist respectively in the saturation of the feedstock, ranging from light naphtha to heavy residues (olefins and some aromatic rings), and the breaking of the C-S bonds, respectively [18]. In order to convert sulfur into H_2S and remove it from the hydrotreated material [24]. Route taken by the reaction mechanism depends on the complexity of the compounds present in the feed and the catalyst [8].

According to studies, molecules with higher steric hindrance such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) or 4-methyldibenzothiophene (4-MDBT) must first be hydrotreating. The sulfur acquires flexibility and can be readily available adsorbed on the catalyst's active sites, and the reaction occurs; this route is called hydrogenation (HYD). Whereas, for simple compounds such as thiophene or dibenzothiophene (DBT), the preferred route is direct desulfurization (DDS) direct desulfurization, where the C-S bond is directly broken and then hydrogenated [4,8]. Figure 4 shows the two proposed mechanisms for the model compound, thiophene.

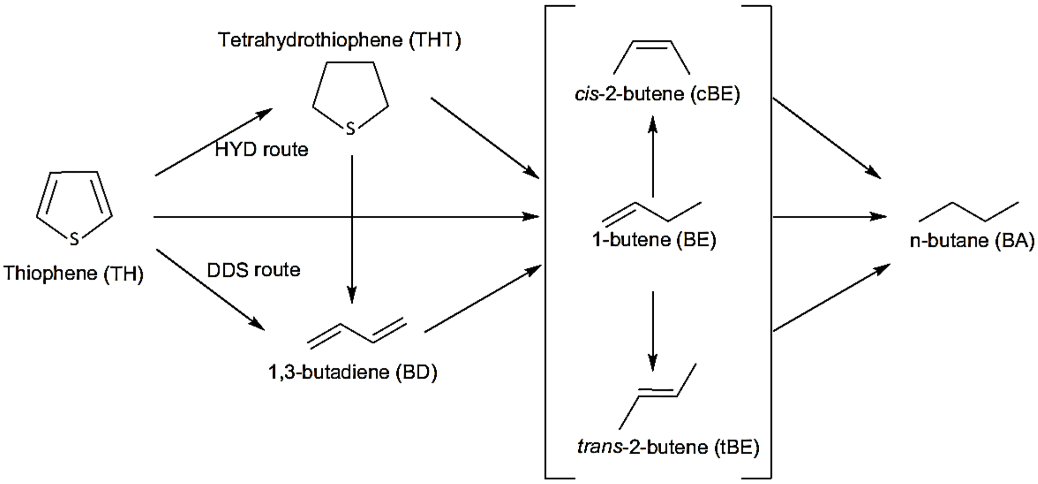


Figure 4. *Proposed thiophene HDS mechanisms* [2].

Regardless of the HDS route, this phenomenon is explaining by the vacancy model, which encompasses the following transformations: 1) adsorption of the sulfur compound to the active sites of the catalyst, 2) hydrogenation of the unsaturated C=C bonds, 3) hydrogenolysis or breaking of the C-S bonds, 4) addition of hydrogen to the broken sulfur-carbon bonds, 5) desorption of the hydrocarbon from the active site and 6) desorption of H_2S S from the active site [29].

2.4.5. Other Catalytic Process

The other catalytic processes involved in the refining process are catalytic cracking (FCC), hydrocracking, catalytic reforming, isomerization, and alkylation.

Isomerization and catalytic reforming are used to improve the octane number of light naphtha and heavy naphtha, respectively, by restructuring them into branched or aromatic compounds; in the presence of platinum and alumina catalysts. Another process to increase the octane number is the alkylation of isobutane with a mixture of olefins and acid - type catalysts. Catalytic cracking (FCC), at high temperatures with acidified clay catalysts, converts the heavy fractions of vacuum gas oil into light fuels and catalytic hydrocracking, in the presence of hydrogen and bifunctional catalysts, breaks down the heavy molecules of atmospheric residues and vacuum gas oil into light products useful in gasolina [21,30]. Almost all fractions before entering these conversion units must undergo a hydrotreating process [18].

2.5. Catalyst

Heterogeneous catalysts are fundamental in large-scale industrial processes such as crude oil refining, transport, energy fuels, polymers, pharmaceuticals, and environmental issues. The catalysts used can be solid materials found as single particles or particles on a support [31,32]. A supported heterogeneous catalyst consists of three components identified as (1) active phase, (2) promoter, which increases catalytic activity, and (3) support with a high surface area that aids dispersion and stability of the active phase [33]. The main reason supported catalysts are used in industry is that they possess properties that allow the catalyst to be more efficient under certain industrial conditions [33]. For example, for high activity, small catalyst particles are required. However, when subjected to catalytic treatment and reaction temperatures, the particles are non-thermostable catalysts with a low active surface area [33]. The support helps to improve and provides properties that help solve the types mentioned above problems.

2.5.1. Catalyst Components

Active Phase: It is the first component chosen in the design of a catalyst. It is responsible for generating active sites (where electrons are accepted) for the catalytic reaction. They are usually dispersed on pores of support in the form of nanoparticles, with a diameter of 1 to 150 nm. These active phases can be metals, metal oxides, and metal sulfides, depending on the catalytic reactions in which they are used [29], as shown in Table 2.

Table 2. *Materials used as active phases and reactions usually catalyzed* [29].

Active Phase	Elements/ Components	Reactions Catalyzed
Metals	Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir, Pl, Au	Hydrogenation, stream reforming, hydro-carbon reforming, dehydrogenation, synthesis (ammonia, Fischer-Tropsch), oxidations
Oxides	oxides of V, Mn, Fe, Cu, Mo, W, rare earth, Al, Si, Sn, Pb, Bi	Complete and partial oxidation of hydrocarbon and CO, acid-catalyzed reactions (e.g., cracking, isomerization, alkylation), methanol synthesis
Sulfides	sulfides of Co, Mo, W, Ni	Hydrotreating (hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation),
Carbides	carbides of Fe, Mo, W	Hydrogenation

Promoter: It is a substance that is added in small quantities (1-5%) to assist the active phase by enhancing or inhibiting catalytic functions. Its functions include increasing selectivity and activity by interfering between the adsorbate-adsorbent bonds. It also prevents or reduces possible catalyst poisoning [25,29]. Some of these and more common promoters are listed in Table 3

Table 3. *Examples of promoters and their functions* [25].

Catalyst	Promoter	Function
Al_2O_3	SiO_2, ZrO_2, P	Improves thermal stability
Support and catalyst	K_2O	Poisons coking sites
	HCL	Increases acidity
	MgO	Retards sintering of active component
Zeolites	Rare earth ions	Increases acidity and thermal stability
Cracking catalyst	Pd	Increases hydrogenation
Pt/Al_2O_3	Re	Decreases hydrogenolysis and sintering
Catalytic reforming		
MoO_3/Al_2O_3	Ni, Co	Increases hydrogenolysis of C-S and C-N
Hydrotreating		

Support: It is the surface on which the active phase is deposited. This component provides the catalyst with properties such as mechanical strength, thermal and chemical stability which are determined by the catalyst preparation conditions and catalytic reactions (temperature, pressure, and mass transfer). They are generally porous materials with a high surface area that is responsible for keeping the active phase stable and well dispersed, this is important when using expensive metals such as platinum, and small amounts of active phase are required [29]. The most commonly used supports are alumina, silica, zeolite, and activated carbon. They are listed with their individual characteristics and applications in Table 4.

Table 4. *Common catalyst supports and their characteristics and applications* [17].

Support	Characteristics	Applications
γ, α-alumina	Surface Area: 150-300 m^2/g Pore Volume: 0.4-0.5 cm^3/g Average pore size: 6 a 40 nm High thermal stability 900 °C	Methanol synthesis, benzene hydrogenation, catalytic reforming Hydrocraking
Silica	Surface Area: 200-800 m^2/g Pore Volume: 0.4 cm^3/g Average pore size: 3 a 20 nm Low thermal stability < 300 °C	Reduction, NO_x/polymerization
Activated Carbon	Surface Area: 1500 m^2/g Pore Volume: 0.5-0.8 cm^3/g Pore size: 0.6-0.2 nm	Removal of heteroatoms such as sulfur and nitrogen
Zeolite	Surface Area: 500 - 100 m^2/g Pore Volume: 0.5-0.8 cm^3/g Pore size: 0.4-1.8 nm Acide sites	Craking/ Isomerisation/ Dehydration

2.5.2. Catalyst Properties

The properties of catalysts are classified into catalytic, chemical and physico-mechanical properties [25]. Catalytic properties (activity, selectivity, and stability) are considered essential for a catalyst and usually change over time. They are determined by chemical properties (composition, concentration of active centers, acidity, oxidation state, and chemical structure) and physic-mechanical properties (mechanical strength, attrition, particle size, density, pore size, specific surface area, and pore volume) [29]. Having established this, a successful catalyst must meet the following requirements [17,34]:

- High activity per unit volume in the reactor, which would result in high productivity from relatively small reactor and catalyst volumes.
- High selectivity produces high yields of a desired product while suppressing undesirable competitive and consecutive reactions. This means that the texture of the catalyst (in particular pore volume and pore distribution) should be improved toward reducing limitations by internal diffusion, which in the case of consecutive reactions rapidly reduces selectivity.
- A catalyst with good stability will change only very slowly over the course of time under conditions of use and regeneration.
- Sufficiently long lifetime with respect to deactivation.
- Possibility to regenerate, particularly if deactivation is fast.
- Reproducible preparation.
- Sufficient thermal stability against sintering, structural change, or volatilization inside the reaction environment (e.g., when steam is a byproduct of the reaction).
- High mechanical strength with respect to crushing (e.g., under the weight of the catalyst bed or during the shaping process).
- High attrition resistance (resistance to mechanical wear).

2.5.3. Catalyst Preparation

The preparation of supported catalysts involves a series of unit operations, starting with the preparation of the catalytic support, then the incorporation of the active phase, and finally the catalytic activation [29]. There are two main methods of catalyst preparation: precipitation-deposition and impregnation [17].

Precipitation-Deposition: This method consists of small crystallites of metal hydroxide or carbonate precipitating from a solution on the support. Thus the powdered support is suspended in a solution of the metal salt, and hydroxide is added, which raises the H and generates a metal hydroxide. Urea is added and heated to 70-90 °C; it is slowly hydrolyzed, causing the pH to rise throughout the solution. When the concentration of the metal hydroxide exceeds the solubility limit, nucleation of the metal hydroxide on the support begins. Once precipitated, the solid is filtered, washed, dried, shaped, and calcined to pass to the activation process by reduction or sulfidation. Supported catalysts of vanadium, molybdenum, nickel, manganese, iron, and copper are obtained by this method [17].

Impregnation: The objective of this method is to fill the pores with a metal salt solution to load the support with active material. The support is heated to remove moisture from the pores, a sufficient amount of metal salt solution is applied to fill the pores of the support and stirred. It is then dried by heating slowly to obtain crystals in the pore. Calcination must be applied as a final step to prevent the crystallized salt from dissolving if the catalyst is exposed to humid environments and to convert the salt to an oxide or metal [25].

2.6. Catalyst in HDS process

Catalysis in the area of hydrorefining was initially developed in the 1920s for the purpose of cracking and obtaining fuels from coal and oil. However, the activity of the catalysts decreased in the presence of heteroatoms, so the elimination of heteroatoms was considered, and catalysts were developed for hydrodesulfurization purposes [10]. In the following decades, studies focused on the improvement of existing catalysts, optimising the support and its properties (composition, texture, acidity and porosity) and many other parameters [19].

These catalysts must have high activity and selectivity for hydrogenation and desulfurization [4]. They are usually composed of metal oxides, with metal loadings of 10-20%, supported on porous materials and subsequently sulfurized in situ [35]. The best known is cobalt molybdate supported on $CoMo/Al_2O_3$ alumina. Hydrodesulfurization catalysts most often contain alumina as a support, typically having a surface area of the order of 2 to 3 x 10^5 m^2/kg, a pore volume of about 5 x 10^{-4} m^3/kg and an average pore diameter of about 10 nm [36]. CoMo based catalysts have been reported to have high desulphurisation activity at relatively low operating pressures (< 4 MPa). Also NiMo base catalysts have been tested in hydrogenation reactions, exhibiting good results in olefin saturation due to their high hydrogenation activity, and NiMo base catalysts show good performance at high pressures [18].

2.6.1. Preparation and activation HDS catalyst

CoMo/Al_2O_3 catalyst is prepared by the impregnation method on Al_2O_3 support, support is immersed in aqueous solutions of cobalt and molybdenum salts, washed, dried, and calcined. The resulting oxide precursors are reduced and sulfided in situ in the reactor with a mixture of H_2S and H_2 (Equation 1 and Equation 2). Conversion temperatures to MoS_2 take place at 300 °C and cobalt conversion at around 150 °C. Activation is necessary to create vacancies or active sites that allow the adsorption of the compounds to be treated [17,29].

$$9CoO + 8H_2S + H_2 \rightarrow Co_9S_8 + 9H_2O \qquad \text{Equation 1}$$

$$MoO_3 + 2H_2S + H_2 \rightarrow MoS_2 + 3H_2O \qquad \text{Equation 2}$$

A scheme of the sulfide catalyst is shown in Figure 3; the active phase Co-Mo-S consists of layers of MoS_2, like a sandwich with Mo^{4+} between two layers of S^{2-} with Co in the edges, another part of cobalt is present in the inactive phase Co_9S_8 and as Co^{2+} ions on the support Al_2O_3. The edges have more catalytic activity than the basal planes and are where adsorption sites are formed [17,37]. There is a model called “rim edge” that explains the activity of the active phase, and it is represented in Figure 5 [4].

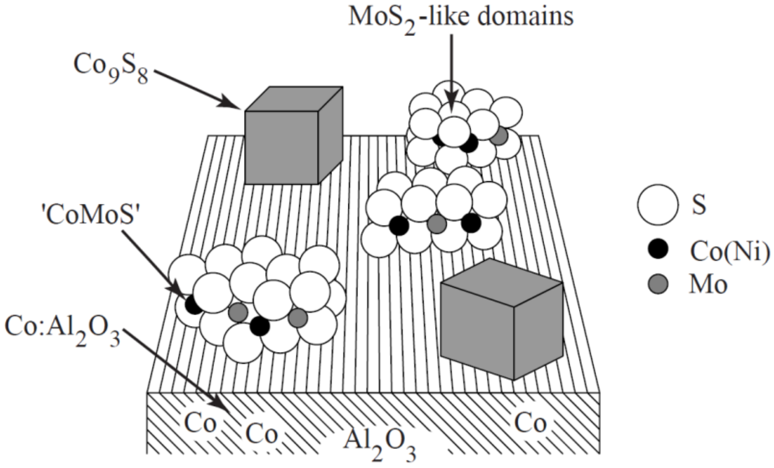


Figure 5. *Structural picture of different phases present in a commercial CoMo/Al_2O_3 catalyst.* [38].

In the conventional catalyst CoMo/Al_2O_3 there are two different Co-Mo-S phases: (1) a type I Co-Mo-S phase with a strong interaction with the support, and (2) a type II Co-Mo-S phase with a weak interaction with the support [19]. The type I phase would be favored in the alumina support because of the Mo-O-Al bonds that hinder Mo sulfidation. The type II phase would be easier to sulfurize because of the weak interaction and would be observed on supports such as carbon or silica [38].

2.6.2. Deactivation and regeneration

The catalyst deactivation produces a notable decrease in the reaction rate; therefore, the regeneration process is fundamental in catalytic processes within the industry. The different types of deactivations can be [39] :

Poisoning: when the reactants' own molecules or impurities are strongly chemisorbed on the active sites.

Fouling: when coke is chemisorbed over the active sites or pores that obstruct the entry of reagents to the active sites [39].

Sintering: is the growth or agglomeration of metallic crystals, reducing the specific area and therefore the catalytic activity.

Chemical degradation: when the active phase redisperses and forms new species, forming a new phase called inactive bulk.

Mechanical failures: when the catalysts suffer fractures own to thermal stress or erosion because of continuous reactor flow.

The catalyst must have at least 80% of its original activity for the regeneration to be valid [40]. Also, care must be taken with high temperatures in in-situ regeneration as temperatures > 600 °C can affect the mechanical strength of the catalyst, above 650 °C molybdenum sintering occurs, and between 500-600 °C, the formation of cobalt aluminates is favored [29].

2.6.3. Active phase HDS catalyst

The functioning of the active phase of the catalyst is related to its structure. Daage and Chianelli proposed the “rim-edge” model for MoS_2 crystals, shown in Figure 6. The model describes a stacking of different discs with two types of sites called rim and edge. The rim sites correspond to the corners of the basal planes and are active for hydrogenation. The edge sites are the inner discs of the stack and are active for C-S bond-breaking [4,41].

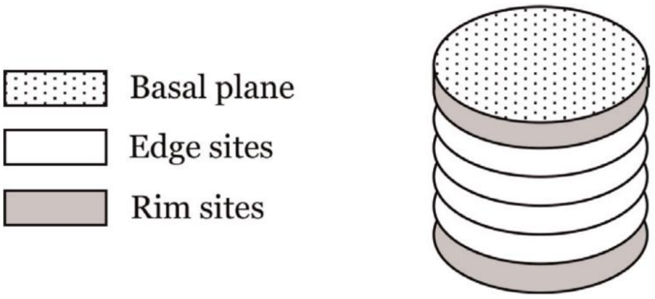


Figure 6. *Rim-Edge Model* [41].

Support is known as an important aspect of hydrodesulfurization (HDS) studies. In this venue, mixed oxide supports received a great deal of attention. A successful support provide mechanical strength as well as high surface area to a catalyst, optimizing the active phase dispersion. The recent information indicated a growing interest in TiO_2 as the support either alone or in combination with Al_2O_3 and SiO_2 materials. However, there exist some stability problems including rapid coking, strong interaction between the support and active compounds as well as difficulties with sulfurization of active phases [42].On the other hand, carbon supported catalyst, one of which is activated carbon. Attract more attention due to their advantageous physiochemical properties while demonstrating higher activities, lower coking and proven ease of recovery of waste [43].

2.7. Activated carbon

Activated carbon (AC) is defined as a carbonaceous amorphous characterized by a large number of micropores and a large surface area. The latter can exceed 1000 m^2/g and even up to 3000 m^2/g. The properties of AC depend on the volume and size distribution of the pores, as well as on the surface functional groups. In addition to porosity, other important physical parameters are particle size distribution, wear resistance, hardness and density. Chemical properties of AC include final analysis, ignition temperature, ash and moisture content [44]. Its characteristics give it a high capacity for adsorption of substances, together with the ease and speed of elimination of the substance from the treated medium. Moreover, once exhausted, it can be regenerated for reusing [45]. Therefore, it is used in processes of adsorption of gases and solutes from solutions, acting as adsorbent, catalyst, and catalyst support [46].

2.7.1. Porous Structure

The high specific surface area values are largely due to the porosity of the carbonaceous materials, with micropores making the greatest contribution to the specific surface area. In principle, it could be assumed that the higher the specific surface area, the best will be the characteristics as adsorbent, since one should also have more spaces to adsorb the adsorbate [47]. However, this is not always true, because the possible "molecular sieve effect" must be taken into account. Thus, depending on the size of the adsorbate molecules, it may happen that these are larger than some of the pores, and therefore, not all of the surface area is accessible to these molecules [48].

Typically, pore size varies between 10 to 100 Å. According to IUPAC International Union of Pure and Applied Chemistry), the pore structure can be distinguished into three types of pores: micropores, mesopores, and macropores [49]. Micropores with a size not exceeding 2 nm gives the structure a high surface area and better retention capacity. While macropores have a size larger than 50 nm and mesopores, between 2-50 nm, are necessary for the transport of the adsorbate. They act as diffusion paths through which the adsorbate circulates until it reaches the micropores [45].

2.7.1. Chemical and Physical Structure of AC

All activated carbons, regardless of their physical form, which are composed of carbon (87%-97%), small amounts of hydrogen heteroatoms, oxygen, nitrogen, and ash content. During the preparation process, functional groups may be generated, such as ($C^{-}OH_2^{+}$), (COH) and (CO^{-}) [49] that possess van der Waals forces, which are responsible for the adsorption process [44].

The physical structure is defined as graphite network amorphous, non-graphitizable-meaning when the AC feedstock undergoes a pyrolysis process. The macromolecular structure is maintained while the heteroatoms volatilize. The residual elements form cross-linked sheets that prevent ordering and pile up irregularly, leaving free interstices that undergo an activation process to form the porous structure [50]. To describe the structure of activated carbon, in 1989, Oberlin compared it to sheets of paper that can be crumpled into a ball with distortions and where the structure is not packed, leaving empty spaces of different dimensions (Figure 7) [50–52].

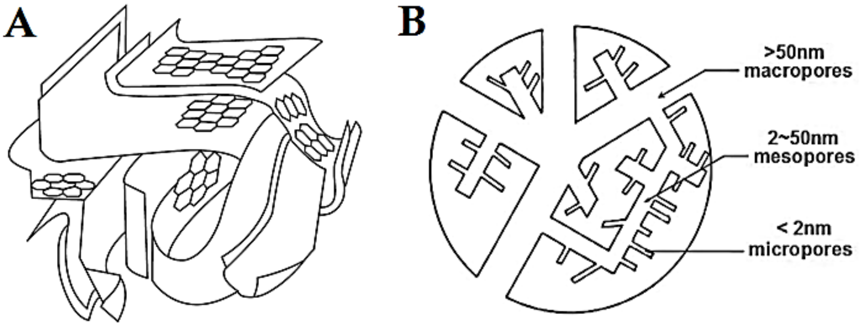


Figure 7. *Schematics of active carbons, A: intertwined structure of the carbonaceous material and B: types of pores formed in AC* [42].

2.7.2. Manufacture of AC

In the market, activated carbon (AC) can be found in different forms, powder, granules, pellets and extrudates (Figure 8), with different pore sizes and functionalities, this depending on the preparation method and precursor [46]. Extrudates are produced by pulverizing AC, mixing with a binder and ex-truding. Low-cost feedstocks such as wood, nut shells, coal, petroleum coke, wastematerials [48], and so on can be used for the preparation of AC. Depending on the feedstock and preparation conditions, a great degree of variance in porosity can be established [44]. Typically, the wood-derived AC is known for its extensive macroporous structure, whereas the coal-based AC can adsorb high molecular substances because of the suitable mesoporosity. Microporous AC can be prepared from the nut-shells [48].

Figure 8. *Different forms of activated carbon; a) powder, b) pellet, c) extruded and d) granular (Adapted from* [46]*).*

2.7.3. Methods of activation of carbons

There are many ways of producing activated carbon, and thousands of patents have been registered worldwide. Nevertheless, all these production methods can be classified into two clearly defined groups in Figure 9. The preparation of AC is carried out by thermal/physical or chemical activation processes [47].

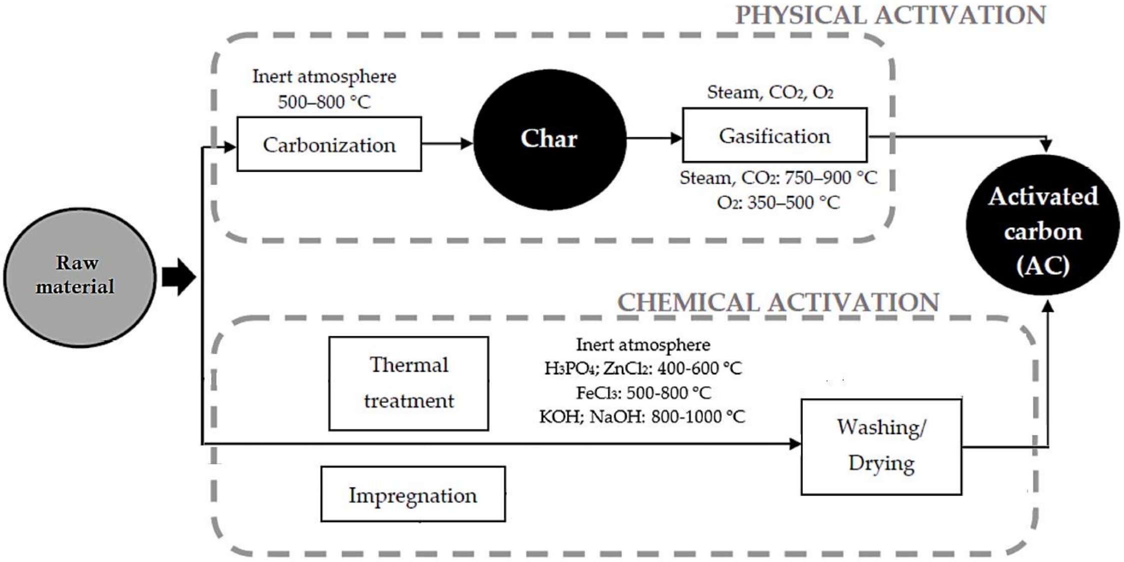


Figure 9. *Scheme of the process of activated carbon manufacturing* [53].

Physical Method

It starts with a carbonization stage with the aim of controlled dehydration and devolatilization, resulting in fixed carbon organized in microcrystalline structures. The microcrystalline structures have irregular free spaces that are blocked by amorphous carbon, tars, and other residues of pyrolytic decomposition (chemical decomposition of organic matter). In order to improve the absorption capacity of the primary coals resulting from carbonization, the activation stage is carried out. Activation is carried out at temperatures between 800 and 1100 ºC in the presence of an oxidizing agent as an activating agent, which can be CO_2 and water vapor. In this stage, a "selective burning" takes place, which is transferred to the carbonized material, increasing its porosity until it is transformed into activated carbon. The oxidation of the carbon and gasification produces a "selective burning" that is transferred to the carbonized material, producing the formation of new pores and developing a microporous structure, which increases the adsorption capacity [44,47].

Chemical Method

First, the raw material is mixed with the activating agent to form a paste, which is then dried and carbonized in a furnace at a temperature of between 200 and 650 °C. The activating agent used depends on the type of carbonizer used. The activating agent used depends on the raw material and the pore volume required; the most commonly used industrially used are zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4), and potassium hydroxide (KOH) [44]. In the process, dehydration takes place, resulting in a porous structure and a high surface area. In the process, some parameters must be taken into account to control the activation, such as the impregnation ratio, the activation temperature, and the residence time [47].

2.7.4. Applications of Activated Carbon

The use of activated carbon was first developed in medical practices, later it was used as a water purifier in reservoir tanks, and the first industrial use it had was in the sugar industry as a decolorizing agent [54]. Then it was used to manufacture the first masks for workers in the chemical industries [55], and also for the Second World War, it was necessary to manufacture activated carbon filters for gas masks [45]. With respect to industrial applications, ACs are grouped into gas-phase and liquid-phase types. The former produced in a larger particle size (granular), are used for removal of pollutants and condensible species from various gaseous streams and effluent [56]. Mostly in a powdered form, AC is used in liquid-phase applications to remove contaminants, e.g., water purification. Recently, attempts have been made to use AC for removing the most refractory multi-ring thiophenic compounds from middle distillates [47,48].

CHAPTER 3
LITERATURE REVIEW

3.1. AC as catalyst support

The problems associated with sulfur in petroleum processing was the main reason behind the development of HDT catalysts. On the other hand, the use of activated carbon as a catalyst dates back many years to the 1920s [38]. However, the development of new materials as catalyst supports displaced the use of activated carbon. Nevertheless, activated carbon has been developed for other applications such as the adsorption of pollutants in wastewater. Figure 10 shows the number of publications related to activated carbon for general applications from 1967 to 2004. However, not all of these publications relate to carbon as a catalyst. In the last 40 years, there have been very few papers related to the use of activated carbon as a support for HDS, however, the results obtained in the existing papers show a potential that should be explored [33].

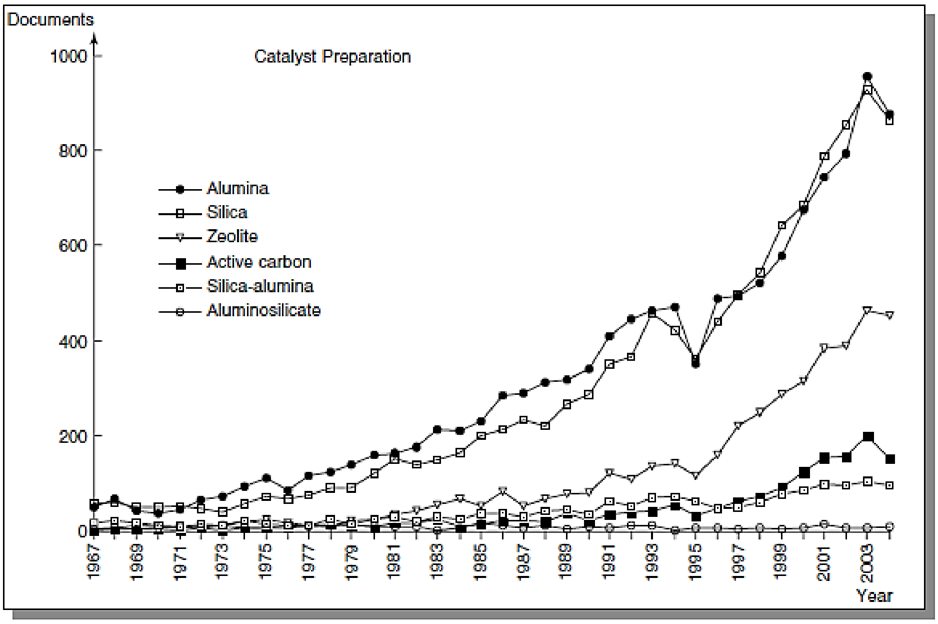


Figure 10. *Number of reports between 1967 and 2004, related to the investigation of different catalytic supports* [33].

de Beer et al. [57] presented a study on the coking propensity of non-sulfided CoMo, Fe, and Mo catalysts during propylene cracking and anthracene carbonization and their catalytic activity for thiophene hydrodesulfurization. A series of catalysts supported on activated carbon, C-black composite, and commercial alumina, were prepared. C-black composites were prepared by blending carbon black particles with polyfufuryl alcohol follwed by carbonization. Metals (Co, Fe) were loaded at different concentrations by incipient wetting technique using the corresponding metal salt solutions and sequential impregnation. The catalysts were presulfided in situ with a H_2S/H_2 mixture, at temperatures since 295 to 673 K over 1 h followed by 2 h at 673 K. Afterwards, catalysts were used to HDS of thiophene. The HDS activity was measure by gas chromatography and the results are shown in Table 5. In general, Cobalt catalysts shown higher than Fe catalysts. The activity had the following order: Al_2O_3 < C-black composite < active carbon. This results could be explained by the high dispersion of the active phase on the support. For this reason, there are differences in activity between carbons and alumina, even two types of carbons. The author suggest, the dispersion carbon types is by oxygen surface groups which are induced by oxidative activation. Another reason is the strenght of metal-support interaction. Carbon supported catalysts tend to a relatively weak Mo-C interaction whoch allows formation of the active MoS_2 phase. To sum up, the essential differences consist on the surface area, metal dispersion, and metal support interaction strength. The rate of carbon deposition on carbon supported catalysts appears to be insensitive to the nature of the metal, whereas the hydrodesulfurization activity is not. Consequently, it seems possible to improve the hydrodesulfurization activity without increasing the coking propensity. Increasing the molybdenum concentration enhances carbon deposition on alumina and carbon supports. The magnitude of this effect is much greater with alumina than with carbon and appears to be related to the inherent acidity of the support and its modification upon addition of the metal.

Table 5. *Hydrodesulfurization activities of catalysts* [58].

Support	**Metal (wt.%)**	**Surface area (m^2g^{-1})**	**Thiophene hydrodesulfurization activity (m^3kg^{-1} (catalyst) s^{-1} x 10^{-3})**
Active carbon (Norit)	Co (3.1) Mo (8.0)	295	17.7
Active carbon (Norit)	Fe (4.0)	290	2.4
C-Black composite (Ketjen)	Co (2.6) Mo (7.9)	408	6.9
C-Black composite (Ketjen)	Fe (4.0)	403	0.6
Al_2O_3 (Ketjen)	Co (3.1) Mo (8.0)	105	3.8
Al_2O_3 (Ketjen)	Fe (5.9)	105	0.1
Al_2O_3 (Ketjen)	Co (3.0) Mo (10.0)	140	3.2

Abotsi and Scaroni [59] developed an review that explores the potential of catalysts supported on carbonaceous materials. The carbonaceous materials considered in this work are carbon black composites, polymer-derived carbons and activated carbon.

Carbon black composites offer better control of pore size distribution as well as mechanical strength. This is obtained by mixing carbon blacks of different particle sizes over a therosetting binder and then carbonizing. It tends to be mesoporous and macroporous. Polymer-derived carbons are obtained from carbonization of synthetic organic substances, which gives them the characteristic of being free of polluting inorganic matter. This material tends to have a pore size of approximately 300 Å which makes it suitable for hydrotreating large refractory molecules. On the other hand, activated carbons can also be produced from a wide range of precursors. Activated carbon often tends to have a high degree of microporosity, however gasification compensates for this deficit. Gasification enlarges existing pores, creates new pores and develops surface area. It mentions details of the functional groups that form on their surface and the importance of controlling the conditions and preparation methods. Primarily, nitrogen and oxygen functional groups tend to have a greater influence on catalytic activity. Oxygenated carbons can be classified as positively and negatively charged carbons. Positive charge on carbons are due to low formation temperatures and are associated with surface oxides. In contrast, negatively charged carbons are obtained from oxygen-containing functional groups and can be released as CO.

HDT catalysts are prepared with solutions of corresponding metal salts.The most important preparation techniques are co-impregnation, sequential impregnation, gas phase adsorption of the metal precursor and incipient wetting. Calcination temperatures for carbon supported catalysts it is important that they are considerably low to avoid sintering. Finally they make a comparison with alumina on thiophene HDS and it is shown that AC develops better activities. This difference is related to preparation methods, degree of dispersion of the active phase, structural properties, metal-support interaction, metal loading, among others.

Rankel [60] analyzed the behavior of CoMo catalysts supported on AC hydroprocessing Arab Heavy 345 $°C^+$ and the effects of the type of the used support, preparation method and sequence of application of Co and Mo. Operational conditions were T = 400-412 °C, with P_{H2}= 10 MPa during 17 days . The used support were lignite-derived (AC); Darco and Alfa and a catalyst $CoMo/Al_2O_3$. The preparation methods were: (a) conventional co-impregnation and (b) by sequential impregnation, first Mo and then Co.

First, method (b) shows better HDM, HDS and conversion, due to method (a) is prone to form Coal phase decreasing the active sites. On the other hand between CoMo/Alfa (b) and CoMo/Darco (b), Darco indicate better HDM catalytic activity due to its larger pore size (100-400 Å) which allows it to react with large metal-containing molecules. When comparing CoMo/Darco (b) with CoMo/Al_2O_3 there is a higher HDS activity by alumina. However, for HDM registers a lower percentage than AC Darco, which becomes noticeable as the days go by (Figure 11).

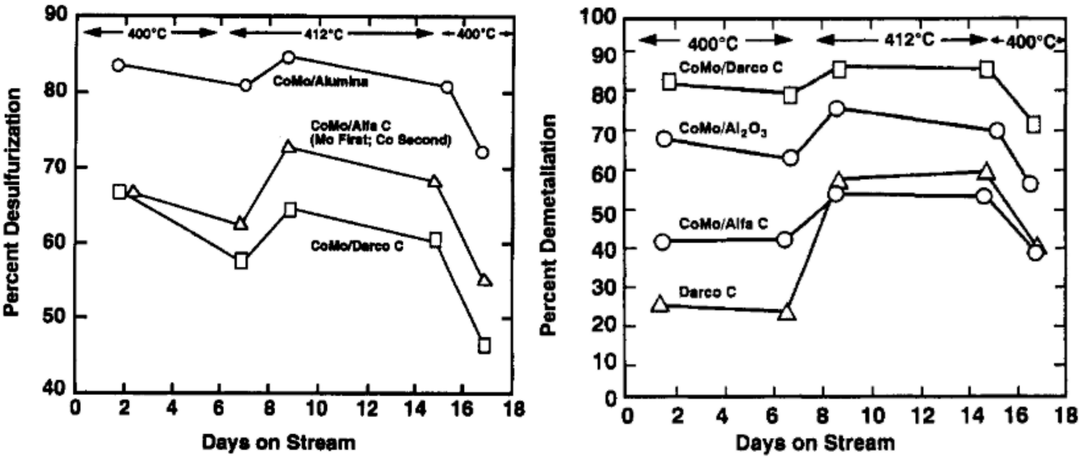


Figure 11. *Percent desulfurization and demetallation of Arab Heavy 345°C*$^+$ [60].

In 1999, Farag et al.[61] examined activity of catalysts CoMo supported on activated carbon (AC) for hydrodesulfuration of model compounds DBT and commercial diesel fuel. Also, analyzes the effect of temperature on selectivity. AC supported catalysts, A and B (Table 6) were prepared by conventional successive impregnation method (I) and the sequential impregnation method with sulfidation between impregnation (II). The catalytic process was carried out at P_{H2} = 2.9 MPa with T = 300-380 °C and time of 30 min.

Table 6. *Characteristics of different ACs used in HDS* [61]

Carbon	**Elemental Analysis**					**Pore Volume (cm^3g^{-1})**	**Pore size (nm)**	**Surface area (m^2g^{-1})**
	C	H	N	O+S	Ash			
A	94.9	0.5	0.1	4.5	2.4	0.52	1.25	907
B	89.9	0.6	0.2	9.3	0	1.76	0.99	3213

Large differences in CoMo/AC catalytic activity were observed, as they depended on the method of preparation and the nature of the carbon support. The highest activity for

HDS of DBT was observed for catalysts prepared by method II. However, Carbon B with higher surface area and small pore size had lower activity for HDS of the 4,6-DMDBT, own to steric hindrance (Table 7). For all the catalysts studied, the selectivities were similar at the same temperature, but for HDS of 4,6-DMDBT was observed a change in the preferred mechanical pathway, at high temperature the DDS route is preferred and at low temperature the HYD route is dominant. On the other hand for deep HDS of commercial diesel, although the most active catalyst was not used, favorable results for AC support was obtained, therefore it is expected that the 0.05% S specification can be achieved with future studies.

Table 7. *Constant rates for HDS of DBT and DMDBT at 340°C and 2.9 MPa H_2*

Sample	Method of preparation	k_{DBT} x 10^4 $s^{-1}g^{-1}$	$k_{4,6\text{-}DMDBT}$ x 10^4 $s^{-1}g^{-1}$
MC-I-A[a]	Successive impregnation, Mo and then Co	104.7	19-1
MC-II-A[a]	successive impregnation with sulfiding between impregnation	214.5	36
MC-I-B[a]	Successive impregnation, Mo and then Co	124.1	12.2
MC-II-B[a]	successive impregnation with sulfiding between impregnation	193.1	17.5
$CoMo/Al_2O_3$[b]	Commercial catalyst	60	18.6

[a] Co 2 wt%; Mo 10 wt%

[b] Co 3.2 wt%; Mo 13.7 wt%

Bej et al. [62] in 2004, presented an overview of the catalyst supports used in hydrotreating processes and the advances that have been made in the HDS of more refractory molecules. Bej described that for HDS, alumina has been used as a support for impregnated active metals such as (Mo,W) and promoters (Co, Ni). However, there are other supports with potential, such as zeolite, silica-alumina silica, alluminosilicate and activated carbon. Most of the research has been developed around this material and its improvement, followed by silica and to a lesser extent activated carbon. On the other hand, $CoMo/Al_2O_3$ catalysts do not have the same good performance for 4,6 DMDBT as for less refractory molecules such as thiophene, so catalysts with phosphorus, fluorine and lanthanum additives and the use of new supports have been developed.

Lee et al. [63] compared the performance of a nanoporous carbon material, they synthesized it in the laboratory vs. alumina and commercial activated carbon used as a support for a CoMoS catalyst. The materials were prepared as CoMo supports by the successive dry impregnation method. CoMo/nc (nanoporous carbon), CoMo/A (alumina) and CoMo/ac (activated carbon) catalysts were obtained. Subsequently, BET characterization test was performed before and after being prepared as supports, in order to see the influence of porosity and surface area in the process (Table 8), and finally they were applied in HDS reactions of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT).

Table 8. *Physical properties of supports and prepared catalysts* [63].

Catalysts	**Surface area (BET)(m^2/g)**		**Average pore diameter (nm)**		**Pore volume (cm^3/g)**	
	Before [a]	**After** [b]	**Before**	**After**	**Before**	**After**
CoMo (A)	208	156	9.5	11.2	0.49	0.44
CoMo (aC)	1121	591	2.1	2.1	0.59	0.31
CoMo (nC)	728	561	10.8	10.8	2.09	1.51

a Before catalyst preparation (support only)
b After catalyst preparation

The results obtained with respect to catalytic activity in general differ with the type of support used as already recorded in previous studies. They obtained a higher conversion record for DBT for nanoporous carbon, 1.14 times higher than activated carbon and this in turn is 1.35 times higher than alumina. The same effect was obtained for the conversion of 4,6-DMDBT. This is due to the more excellent dispersion of active sites that carbonaceous materials offer. Turnover frequency (TOF) tests were also performed to analyze the intrinsic activity which is defined as the reaction rate per site that chemisorbs. Activated carbon showed a lower value than the other materials especially in 4,6-DMDBT reactions. This was due to the fact that the diffusion of hydrocarbons is limited for CoMo/AC. The pores were reported to measure only 20% of what the reagents measure, with poor penetration to the active sites and much more for refractory molecules. Therefore, nanoporous carbon indicates good performance for HDS and deep HDS, above alumina, which had a low dispersion of active sites and was also above activated carbon especially at 4,6-DMDBT due to its high microporosity despite having a high surface area. This indicates that the catalytic activity is not only dependent on dispersion, also depends on other factors.

In 2011, Liu et al.[64] studied an alumina-activated carbon (AAC) composite as a NiMo catalyst support for hydrodesulfurization (HDS) of a dibenzothiophene (DBT) model compound. The AAC was prepared with granular alumina (215 m^2/g) and activated carbon pellets (1011 m^2/g), once the composite (0.28-0.45 mm) was obtained, NiMo/AAC was prepared by the co-impregnation method, simulating the commercial specifications of catalysts; its analogues NiMo/Al_2O_3 and NiMo/AC were prepared in the same way. HDS catalytic activity testing indicated that NiMo/AAC had 90% conversion while NiMo/Al_2O_3 32% and NiMo/AC 58% at a relatively low temperature of 260 °C; this is attributed to the characteristics obtained by resistance test, BET, XRD and TPR showed the following results. Al_2O_3 and AC showed a microporous structure while ACC showed improved mechanical strength, adequate surface area (160 m^2/g), mesoporous structure with pore size distribution (7 nm) indicated in Figure 12, which gives it facility to transport the reagents, to reach the inside of the pores and to transfer the products to the outside.

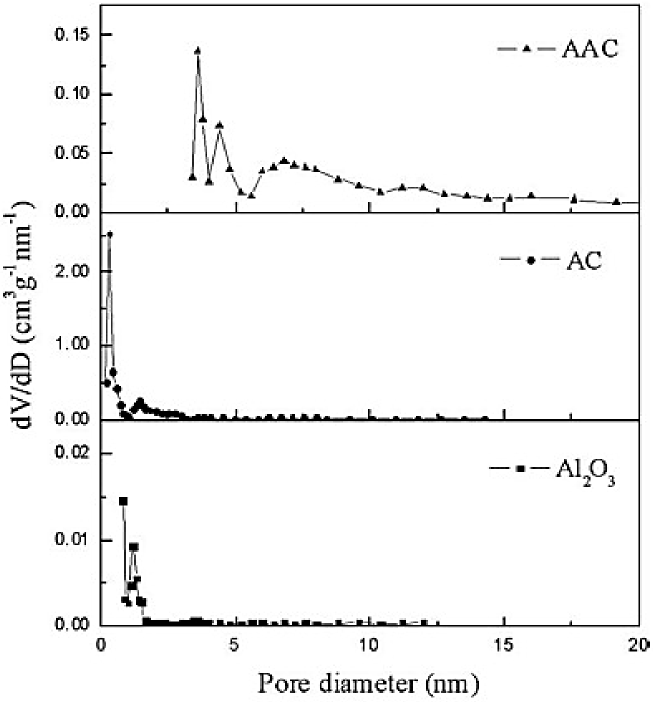


Figure 12. *The pore size distribution of supports Al_2O_3, AC and ACC* [64].

In 2015, Saleh et al.[65] This work reported on the influence of treatment conditions on the waste tire-derived activated carbon for adsorptive desulfurization. The rubber tires were carbonized and activated. The obtained activated carbon (AC) was treated with HNO_3 or NaOH at a temperature range of 30-90 °C. The morphology and surface properties of AC were characterized by surface pH, Boehm's titration, N_2 adsorption–desorption isotherms, Fourier transform infrared spectroscopy, X-ray diffraction, and scanning electron microscope. The AC sample, treated with HNO_3 at 90 °C, possess the highest surface oxygen containing functional groups (2.39 mmol/g), surface area (473.35 m^2/g) and pore volume (0.70 cm^3/g) and the more adsorption capacity to the refractory sulfur compounds. The Boehm's titration experiments indicated that the amount of surface oxygen containing functional groups on the surface of the acid-treated AC increases with treatment temperatures. Acid-treated AC at 90 °C proves to be optimum for adsorptive desulfurization with the order of dibenzothiophene > benzothiophene > thiophene.

In 2018, Umar et al. [66] studied the effect of calcination temperature on hydrodesulfurization activity using mesoporous activated carbon-supported catalysts. A series of AC-supported NiMo catalysts were prepared from waste tires through co-impregnation by excessive moisture and with different calcination temperatures for each sample; 100, 200, 300, and 400 °C. The performance of the catalyst was evaluated in a fuel containing DBT (1000 ppm-S) at 350 °C, 50 MPa during different reaction times, and the results indicated that the catalyst was calcined at 300 °C, NiMo/AC300, obtained the best performance. These differences are due to the degree of dispersion, degree of crystallinity, support-phase metal interaction and structural properties which are influenced by the variation of calcination temperature. In this case NiMo/AC300 has a high degree of dispersion according to XRD; low activation energy according to TDP; the molecules are easily desorbed and the BET results indicate that it has a high surface area (352 m^2/g) with adequate average pore diameter (6 nm). It is also important to mention that all catalysts improved their performance at longer reaction times (Figure 13).

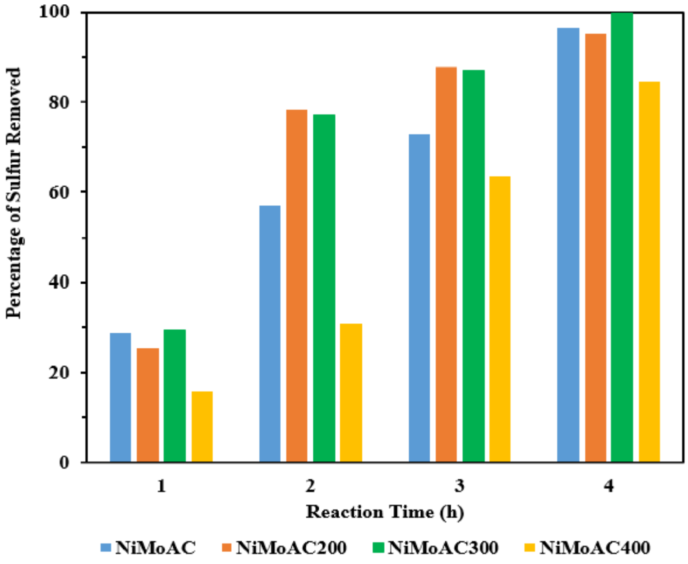


Figure 13. *Graphical representation of the performance of NiMo/AC, NiMo/AC200, NiMo/AC300 and, NiMo/AC300* [66].

In 2020, Kohli et al. [67] studied the effect of Activated Carbon, SBA-15 and Alumina Supports on NiMo Catalysts for Residue Upgrading that contains high asphaltene (22 wt.%), sulfur (5.45 wt.%), and metal contents (Ni + V = 305 wppm). The sequential impregnation method was used to prepare the catalysts supported on SBA-15 (synthesized), commercial AC from Toyo Enginereing Corporation and mesoporous alumina (synthesized). The operational conditions of hydrotreating T= 410 °C, P_{H2}= 10 MPa and time 6 hours.

The catalysts were characterized by N_2 adsorption, XRD and once sulfated TEM. The best results of conversions, yields and activity in HDS, HDM and HDA correspond to $NiMo/Al_2O_3$, because it had uniform pores, larger diameter and pore volume with an adequate surface area for the process, while NiMo/SBA-15 presented high surface areas and small pore diameters that make it prone to coke formation. The NiMo/AC catalyst shows a larger pore distribution than NiMo/SBA-15 but smaller than $NiMo/Al_2O_3$. In addition, according to the XRD spectra, the MoO_3; metal oxide is more dispersed on alumina than on AC, which generates a greater number of active sites and finally, TEM shows a stacking of layers what could be active phase of MoS_2 type II on alumina, giving it a higher hydrotreating activity than the other supports (Figure 14).

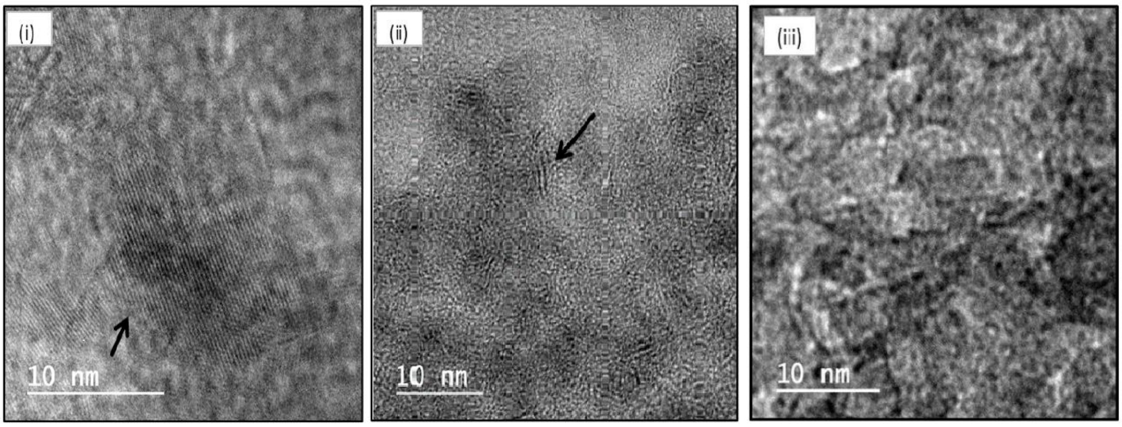


Figure 14. *TEM images of the prepared NiMo catalyst (i)NiMo/AC, (ii) NiMo/Al_2O_3, and (iii) NiMo/SBA-15*[67].

3.2. Avocado seeds

3.2.1. Avocado Current Situation

Avocado or Persea Americana belonging to the Laracea family, is a subtropical stone fruit with a creamy texture and a high content of unsaturated fats, minerals, and vitamins that have become a superfood in great demand. As a result, world production levels have been increasing in recent years, reaching a production of 7 million tonnes in 2019 [68,69]. According to the Food and Agriculture Organization (FAO), most of the world's avocado production and industry is located in the Americas, which accounts for almost 75% of total production, with Mexico, Chile, and Peru leading the way, while Ecuador for the moment represents 0.37% of world production [68,69].

Ecuador has the appropriate climatic conditions for avocado cultivation. Unlike other countries, can produce avocado all year round, with production and harvest peaks fully defined from February to March and from August to September, while other nations produce in a period of only 4 to 5 months of the year [70]. After the 2000s that large-scale cultivation of avocado was established and according to data from the agricultural censuses for the years 2016-2020 production increased, except in 2020 there was a decrease because of the Covid situation (Figure 15) [71]. Production is distributed mainly in the provinces of Imbabura (Chota and Salinas), Carchi (Mira), Pichincha (Guayllabamba), Tungurahua (Patate and Baños) and Azuay (Paute and Gualaceo), Loja, Esmeraldas (Paute and Gualaceo). (Paute and Gualaceo), Loja, Esmeraldas and Manabí [72]. Data from ESPAC and ProEcuador in 2020 show a total production of 20,352 tonnes and exports of 1,157.3 tonnes [73]. However, most of the production is focused on the commercialization of fresh fruit in both the national and international markets.

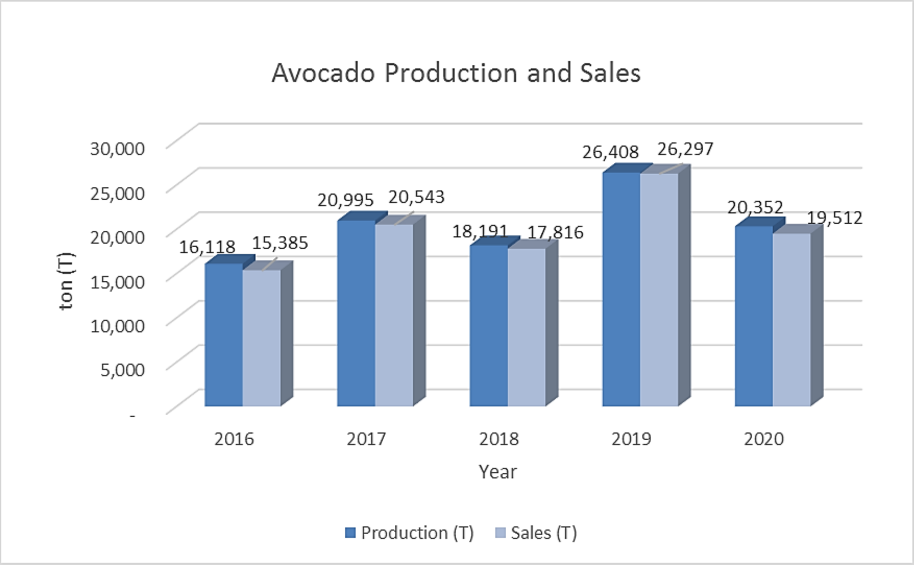


Figure 15. *National avocado production from 2016 to 2020.*

3.2.2. Ecuador avocado market

According to INIAP, the per capita consumption of avocado in Ecuador is approximately 1 kilogram per year, which means that each person consumes that amount of avocado per year; therefore, the national market is seen as an attractive market for its commercialization and to promote projects dedicated to this activity. This product can boost this area of agriculture, so the private and public sectors have implemented a plan to plant and produce avocados on a large scale. In the national market, Fuerte variety is more desirable than Hass variety, mainly because it is cheaper. In Ecuador, the variety produces to exportation is Hass, which has a rough skin and a dark green colour. Hass variety has a higher percentage of fat and the texture of its rind makes it resistant to transportation [74,75].

In 2020, avocado exports generated more than 300 million dollars, and the Ministry of Agriculture and Livestock is promoting its production, above all, as an ideal item for crop diversification. The main avocado importers do not have a high per capita consumption, so the increase in consumption could be greater in the coming years, as it is being incorporated into people's diets and products [71]. World demand is growing by 10% every year. The most demanded variety is Hass and its advantages are its oil content (18 to 20%), its thick and rough rind that makes it resistant to storage and and knocks in the transport of the fruit [74]. Currently, Ecuador is seeking to establish itself in the market with processed products such as butter, avocado oil, and other derivatives [71].

3.2.3. Avocado seed waste

Throughout the avocado value chain, from cultivates to industrialization, a significant amount of organic waste is generated, as it is the pulp that is used the most, while other elements of the fruit such as peel and seed are sent to landfill [76]. For example, in an avocado oil plant, it is estimated that for every 1000 kg of fruit processed, 274 kg of peel and seed are generated [77].

The avocado seed represents 16% of the avocado, and its composition is determined by moisture, ash, protein, sugars, starch and fat., which indicates that it is constituted of carbon (48.3%), hydrogen (7.5%), nitrogen (< 0.5%) and oxygen (43.4%). The quantities may vary depending on the type of avocado [77–79]. In Ecuador, the most commonly consumed varieties are Hass and Fuerte [80]. Table 9 shows the composition of both varieties.

Table 9. *Moisture (%, fresh weight) and chemical composition of different avocado seeds (%, dry weight)* [79].

Variety	Moisture	Ash	Protein	Sugars	Starch	Fat
Hass	54.1	1.2	2.4	3.5	27.5	0.8
Fuerte	50.2	1.3	2.5	2.2	29.6	1.0

3.2.4. Research on avocado seeds in Ecuador

Own to the chemical composition of the seeds, they acquire antioxidant, antimicrobial, antifungal and larvicidal effects that are useful in different industries [81] . In the past, avocado seeds were used to alleviate toothache, to cure dandruff, to soothe skin conditions, to treat hypertension, and as a contraceptive and abortifacient agent [79]. Recent studies indicate that the starch and fibre obtained from the seeds serves as a thickening, gelling agent additive in the food and pharmaceutical industry [82]. Research is also looking at seeds as an alternative for the manufacture of biodegradable polymers for food packaging [83]. Table 10 compiles number of works on avocado seeds in Ecuador.

Table 10. *Research on the use of avocado seed residues in Ecuador*

Study	Number of Research	References
antioxidant and microbial	2	84,85
natural food dye	4	86–89
food coating, biofilm	3	90,91
biopolymer	1	92
nutritional supplement	1	93
textil dye	1	94
antimycotic gel	1	95
adsorbent	1	96

3.2.5. Activated Carbon from Avocado Seeds

Sanchez et al. [97] have produced Granular Activated Carbons (GAC) from avocado seeds, in particular form Hass variety. The material was ground with particle size between 2 and 4 mm. After, it was dried for 24 h at 40 °C. Carbonization process was done heating the material at 10 °C/min to 900 °C under a flowing nitrogen atmosphere. After, 400 ml/min of a steam/nitrogen mixture was injected in the reactor at 1000 °C, for 0-150 min. The amount of carbon obtained represent 19,7 wt.% of the original biomass. N_2 adsorption isotherms display 700 g/m^2 in activated carbons produced at 34-37 wt.% of burn off. The material is essentially mesoporous with a lower contribution of micropores. The produced materials were used to adsorption methylene blue (MB). Adsorption results were modeled according to the Langmuir and Freundlich equations. For the best results, Langmuir qm and Freundlich Kf were 153.8 mg/g and 113.0 mg/g, respectively. This measure belongs to activated carbon with 150 min of residence time. Finally, this material shown a greater performance than commercial activated carbon, which could be used for wastewater treatment applications.

Elizalde-Gonzales et al. [98] prepared different activated carbon samples from avocado seeds. The samples were activated chemically, physically and chemistry-physically. The avocado seeds used were of Hass variety. The seeds were dried at 50 °C for 24 hours and then reduced to a particle size between 1 and 2 mm. The carbonization process was carried out at temperatures at 800-1000 °C. Some of the carbonized samples were activated with H_3PO_4. The results of N_2 adsorption are shown in Table 11. The samples carbonized at 800 °C and 1000 °C do not show a noticeable difference in their surface area. Chemical activation with H_3PO_4 tends to increase the surface area of the material, while activation with nitrogen partially reduces the surface area.

Table 11. *Textural properties of the carbonized samples prepared from avocado naturasorbent AGAP* [98].

Sample	**S_{BET} (m^2 g^{-1})**	**V_P (cm^3g^{-1})**	**% of micropore volume**	**Average pore diameter (Å)**
AGAP-800	143	0.073	93	14.3
AGAP-1000	283	0.147	95	14.3
AGAP-P-800	1069	1.053	53	14.5
AGAP-P-N-800	960	1.023	48	14.4

The FTIR spectra profiles are shown in Figure 16. The profile of the carbonized samples shows a lower number of peaks due to the disappearance of some functional groups. The peak at 3410 reveals that N-H group is present in all samples. Activation with H_3PO_4 produces bands corresponding to $R_3P=O$ phosphine oxides and P-O-C phosphates. In general, carbonized samples do not exhibit basic groups, but abundant phenolic groups. Carbonization and chemical activation with H_3PO_4 promote the formation of carboxylic groups and decrease the amount of other functional groups.

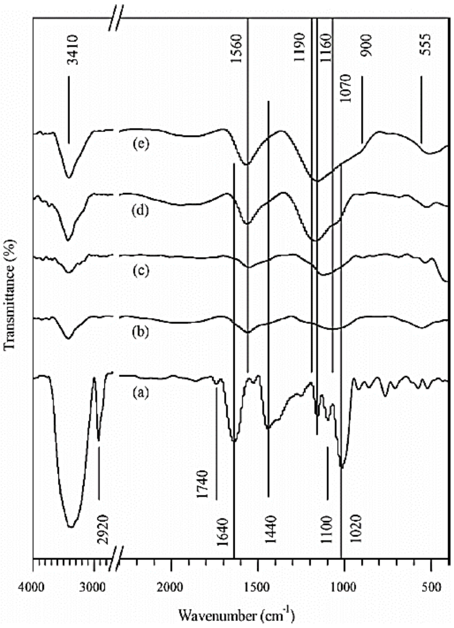


Figure 16. *FTIR spectra of the prepared adsorbents in KBr pellets: AGAP (a),AGAP-800 (b), AGAP-1000 (c), AGAP-P-800 (d) and AGAP-P-N-800 (e)* [98].

Figure 17 shows the removal efficiency of acid and basic dyes. The sample AGAP and AGAP-P-N-800 show higher removal of basic dyes due to the amount of acid groups present on the surface. On the other hand, only AGAP-P-N-800 shows great performance for acid dyes due mostly to the surface area. In conclusion, AGAP1 showed higher adsorption capacity for basic dyes due to its high content of acid groups on the surface. On the other hand, acid dyes were adsorbed better with the samples showing higher surface area, i.e., the H_3P0_4-activated and carbonized samples.

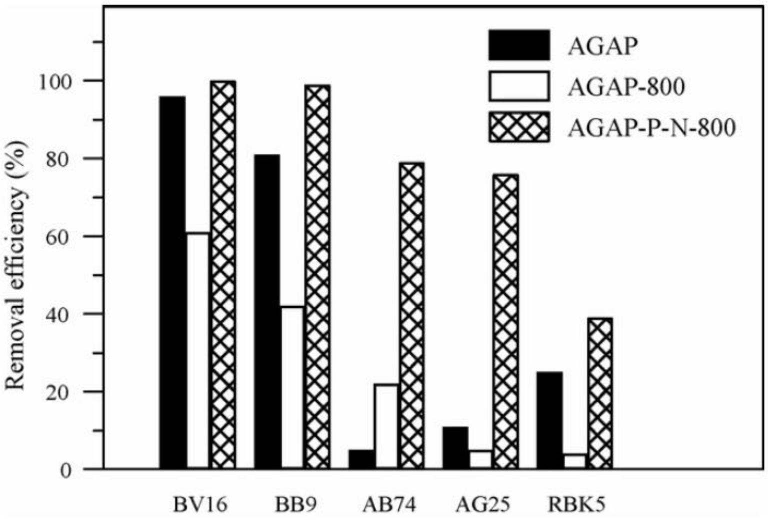


Figure 17. *Comparison of the removal efficiency at 24 °C of non-carbonized AGAP and carbonized AGAP under two different conditions, against basic (BB41, BV16 and BB9),*

acid (AB74 and AG25), and reactive (RBK5) dyes from 400 mg l^{-1} *solutions using adsorbent dosage 0.01 mg m* l^{-1}[98].

Leite et al. [99] used avocado seeds as raw material for producing activated carbons by conventional pyrolysis. Temperature and time were used to set up the essential conditions. The samples were employed to adsorption several emerging organic compounds from aqueous solutions. The samples preparation consists of griding avocado seeds to a grain size no larger than 250 µm. After, this was added to a solution of $ZnCl_2$ and water. The homogeneous paste was subjected to a heating treatment at a range temperature between 500-700 °C. The pyrolysed materials were treated with HCl solution to obtain activated carbon. The surface area was calculated by BET method. These results are shown in Table 12. The values are within the range of 1122 to 1584 m^2/g. In addition, the percentage of mesopores of all samples was between 80 to 87%. Hence this feature means adsorbate molecules could diffuse through the pores. FTIR spectra determined functional groups. The most representative groups include O-H likely from alcohols and phenols, C=O likely from carboxylic acids and esters and CH from aromatic and aliphatic compounds. The total acidity and total basicity was determined by modified Boehm titration, which shown that the acid groups were a little bit higher than the basic groups. Based on the experimental preparation conditions and the analysis of multiple variables, some observations can be made. When the pyrolysis temperature increases from 500 to 700 °C, the surface area of the material decreases. In addition, the increase of pyrolysis time from 30 to 60 min also led to the reduction of the surface area. Increasing the pyrolysis temperature leads to a decrease of the total functional groups present on the surface, as it leads to the release of most of the volatile organic groups. Activated carbon samples were used for the adsorption of 25 emerging organic compounds, among which 10 were pharmaceuticals and 15 phenolic compounds. The carbon prepared at pyrolysis temperature of 700 °C showed the highest adsorption capacity. However, all samples showed to be successful for the adsorption of organic compounds. An analysis between surface chemical properties and adsorption capacity was performed. It was concluded that sorption capacity of the samples decreases as the number of acidic and basic functional groups increases.

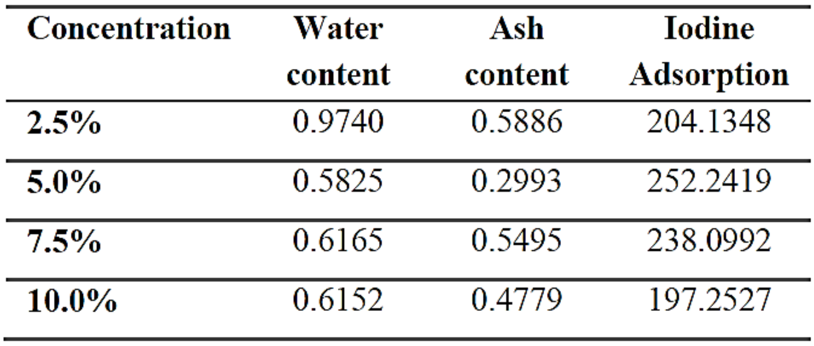
Table 12. *Textural properties of avocado seed activated carbons* [99].

Sample	BET surface area (m^{2}g^{-1})	Total pore volume (cm^{3}g^{-1})	Mesopore volume cm^{3}g^{-1}
ASAC1	1584	0.8469	0.6906
ASAC2	1230	0.6685	0.5847
ASAC3	1370	0.7664	0.6544
ASAC4	1122	0.6002	0.4753
ASAC5	1343	0.7354	0.6000
ASAC6	1300	0.7248	0.5987
ASAC7	1310	0.7232	0.5856

Guntama et al. [78] prepared activated carbon from avocado seeds and used them as a chromic metal adsorbent. The avocado seeds were cut and dried for 2 days. The samples were carbonized at 400 °C for 1 hour. 10 g of carbon was activated with 100 ml of HCl and H2SO4 solution with concentrations of 2.5%, 5%, 7.5% and 10%. The activated samples were dried at 105 °C for 1 hour. 1 g of activated carbon was used for treatment of water contaminated with chromium. The properties of activated carbon are reduced by the amount of water adsorbed on the activated carbon.

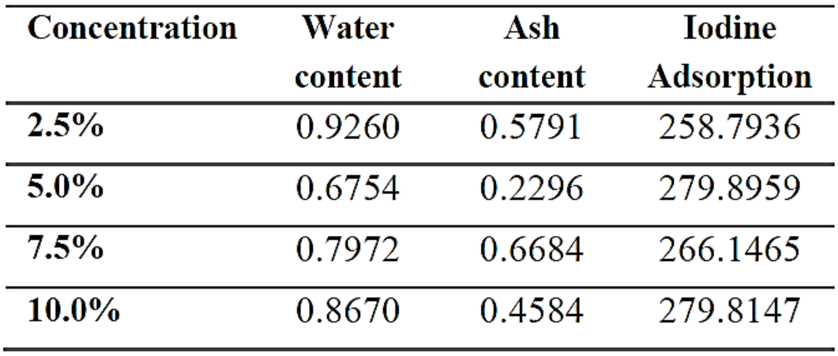
Table 13 shows the adsorption results of the activated carbon with HCl, which shows that the optimum condition is at 5% HCl. On the other hand, Table 14 also indicates that the ideal concentration is 5%. The chromium adsorption values at the 5% concentration are 0.1673 mg/L and 0.1535 mg/L, for HCl and H_2SO_4 respectively.

Table 13. *Characteristics of avocado seed charcoal with HCl activator* [78].



Concentration	Water content	Ash content	Iodine Adsorption
2.5%	0.9740	0.5886	204.1348
5.0%	0.5825	0.2993	252.2419
7.5%	0.6165	0.5495	238.0992
10.0%	0.6152	0.4779	197.2527

Table 14. *Characteristics of avocado seed charcoal with H_2SO_4 activator* [78].



Concentration	**Water content**	**Ash content**	**Iodine Adsorption**
2.5%	0.9260	0.5791	258.7936
5.0%	0.6754	0.2296	279.8959
7.5%	0.7972	0.6684	266.1465
10.0%	0.8670	0.4584	279.8147

CHAPTER 4

CONCLUSIONS

This work is a review about activated carbon supported catalysts used in hydrotreating, especially focused on HDS. An investigation was carried out in the available literature, focusing on the properties of the material as well as the results obtained. Moreover, the possibility of obtaining activated carbon from organic residues, especially from avocado seed was reviewed. Activated carbon supported catalysts have been found to show great potential in hydrotreating, especially HDS and HDM. This is due to surface area, porosity and large surface area of activated carbon, which allows refractory molecules to be processed compared to commercial catalysts.

The calcination temperature influences the structural properties of the catalyst supported on activated carbon. The ideal calcination temperature should be relatively low to avoid sintering problems that decrease the dispersion of active sites. It is also important to mention that all catalysts improve their performance at longer reaction times.

The catalyst preparation method influences the catalytic activity of catalysts supported on activated carbon. Each step in the preparation influences its final properties, such as surface area, pore size distribution, wear resistance and surface chemistry of the carbon materials and thus the amount, dispersion and size of the loaded metal. Consequently, the catalyst must be developed individually for the different applications according to the desired requirements. The most commonly used methods for the preparation of HDS catalysts, the following were used were successive with sulfidation between impregnation and incipient impregnation.

Activated carbon can be manufactured from any solid organic matter, such as coals, wood and agricultural waste. Since their structural properties can be modified as required by the application. No activated carbon obtained from avocado seed is registered for use in HDS. However there is a similarity between the characteristics (surface area, porosity, pore size) of the activated carbon obtained from avocado seeds to use other process and the activated carbon used in the HDS studies.

Although Ecuador represents a small portion of world avocado production, in recent years it has focused on taking advantage of the climatic conditions that allow it to produce avocado in large quantities, in the same way it is starting in the avocado industry with the manufacture of avocado products such as oil, guacamole pulp and cosmetics. In most products, the pulp is what is used the most, leaving the seed and rind as solid waste. For companies, these wastes represent an economic investment since they must focus their efforts on providing adequate treatment. It is worth mentioning that research on the use of avocado residues in Ecuador is very limited, the uses that are currently being studied are as a colorant, source of saponins, tannins. This work has focused on taking advantage of said waste and obtaining value-added products such as activated carbon, without compromising food safety.

SUGGESTIONS

It is recommended to perform the experiments under real operating conditions in terms of duration. The literature recommends experiments from 6 months to one year. In the case of activated carbon, it must be taken into account that it is prone to sintering and is of low packing density, which would cause its performance to decrease over time. On the other hand, it is important that tests are carried out with real feeds since a slight difference in efficiency can be observed with the modeled compounds.

The use of activated carbon is not feasible due to its low packing density and calcination temperatures. Therefore, the use of composites of activated carbon is proposed to overcome the unfavorable characteristics.

Despite the increasing industrialization of avocado in the country, information about the residues and its utilization is limited. Especially as a carbon material, which represents an opportunity for study in the area.

REFERENCES

1. Sahu, R., Jin Song, B., Sun Im, J., Jeon, Y.-P. & Lee, C. W. Journal of Industrial and Engineering Chemistry *A review of recent advances in catalytic hydrocracking of heavy residues. J. Ind. Eng. Chem.* **27**, 12–24 (2015).

2. Escalante, Y. *et al. MCM-41-supported vanadium catalysts structurally modified with Al or Zr for thiophene hydrodesulfurization. Appl. Petrochemical Res.* **9**, 47–55 (2019).

3. Ministerio de Energía y Recrusos Naturales No Renovables. *Informe anual del potencial hidrocarburífero del ecuador*. (2019).

4. Cabrera-munguia, D. A., Rosales-marines, L., Rubio-ríos, A. & Farías-cepeda, L. *The Silicon on the Catalysis : Hydrodesulfurization of Petroleum Fractions*. 1–16 (2019).

5. Uchenna Babalola, F. & Akpoveta Susu, A. *Pre-Treatment of Heavy Crude Oils for Refining. Process. Heavy Crude Oils - Challenges Oppor.* 1–18 (2019) doi:10.5772/intechopen.89486.

6. Alvarez-amparán, M. A. & Cedeño-caero, L. *Analysis and relevance of catalytic processes to sulfur removal from fossil fuels*. **14**, 1–21 (2021).

7. Enríquez, G. & Byun, S. *RESOLUCIÓN No. C 108 -2020*. chrome-extension://oemmndcbldboiebfnladdacbdfmadadm/http://www7.quito.gob.ec/mdmq_ordenanzas/Administración 2019-2023/Resoluciones de concejo/2020/rc-2020-108-exhorto comite inen-diesel.pdf (2020).

8. Rashidi, A. & Mohammadzadeh, F. *Hydrodesulfurization (HDS) Process Based on Nano-catalysts : The Role of Supports*. 193–210 doi:10.1007/978-3-319-60630-9.(2018)

9. Breysse, M., Afanasiev, P., Geantet, C. & Vrinat, M. *Overview of support effects in hydrotreating catalysts*. **86**, 5–16 (2003).

10. Song, C. *An overview of new approaches to deep desulfurization for ultra-clean gasoline , diesel fuel and jet fue*l . **86**, 211–263 (2003).

11. Okamoto, Y. *Effect of support in hydrotreating catalysis for ultra clean fuels*. *Sci. Direct* 1–3 (2003) doi:10.1016/S0920-5861(03)00414-0.

12. Unnikrishnan, P. & Srinivas, D. *Heterogeneous Catalysis*. *Industrial Catalytic Processes for Fine and Specialty Chemicals* (2016). doi:10.1016/B978-0-12-801457-8.00003-3.

13. Sarrazin, P., Baudouin, C. & Martino, G. *Energy-Related Catalysis*. (2008).

14. Speight, J. G. *The Chemistry and Technology of Petroleum*.(2006)

15. Systems, G. E. *Depletion and Decline Curve Analysis in Crude Oil Production.* (2009).

16. Makkee, M. & Diepen, A. Van. *Oil Refining and Petrochemistry crude oil*. 349–376 (2003).

17. Chorkendorff, I. & Niemantsverdriet, J. W. *Concepts of Modern Catalysis and Kinetics*. (2003)

18. Moulijn, J. A. *Chemical process technology*. *Choice Reviews Online* vol. 51 (2013).

19. Eindhoven, T. U. & Magnificus, R. *Hydrotreating Model Catalysts : from characterization to kinetics*. (2001). doi:10.6100/IR548074.

20. Jacques, C. V. *Heterogeneous Catalysis on Metal Oxides.*(2017) doi:10.3390/catal7110341.

21. Kakaei, K., Esrafili, M. D. & Ehsani, *A. Introduction to Catalysis. Interface Sci. Technol.* **27**, 1–21 (2019).

22. Marras, F. Chapter 1 *Recovery and recycling of homogeneous catalysts: silica as temporary or permanent support*. (2010).

23. Group, P. S. *et al.* D*iffusion Processes Affecting the Performance of Heterogeneous Catalysts : Part 1*. **320**, 107–115 (2011).

24. Nicholas P. Cheremisinoff, P. R. *Best Practices in the Petroleum Industry*. (2009).

25. James T. Richardson. *Principles of Catalyst Development*. (1989).

26. Khan, M. R. & Sayed, E. *Sulfur removal from heavy and light petroleum hydrocarbon by selective oxidation*. *Advances in Clean Hydrocarbon Fuel Processing: Science and Technology* (2011). doi:10.1533/9780857093783.3.243.

27. Favennec, J. *Refinery Operation and Management*. vol. 5 (2001).

28. Gary, J. H. *Petroleum Refining.* 741–761. (1994)

29. Bartholomew, C. H. & Farrauto, R. J. *Fundamentals of Industrial Catalytic Processes*. (2006).

30. Lemonidou, A. A. *Catalysis and Refinery*. *Encyclopedia of Life Support Systems (EOLSS)* 60 (2011).

31. Hammond, K. D. & Conner, W. C. *Analysis of catalyst surface structure by physical sorption*. *Advances in Catalysis* vol. 56 (2013).

32. Ozinger, N. *Heterogeneous Catalysis and Solid Catalysts*. (2009).

33. Ertl, G., Knözinger, H., Schüth, F. & Weitkamp, J. *Handbook of Heterogeneous Catalysis*. (2009)

34. Knozinger, H. & Weitkamp, J. *Preparation of Solid Catalysts*. (1999).

35. Debajyoti Bose. *Design Parameters for a Hydrodesulfurization (HDS) Unit for Petroleum Naphtha at 3500 Barrels per Day*. *World Sci. News* (2015).

36. Schuit, G. C. A. & Gates, B. C. Chemistry and Engineering of Catalytic Hydrodesulfurization. *AlChE J.* **19**, 417–438 (1973).

37. Prins, R., Beer, V. H. J. De, Somorjai, G. A., Laboratorium, T. & Beer, V. H. J. De. *Catalysis Reviews : Science and Engineering Structure and Function of the Catalyst and the Promoter in Co — Mo Hydrodesulfurization Catalysts*. 1–41 (2008).

38. Eindhoven, T. U. & Version, D. *Hydrodesulfurization catalysis and mechanism of supported Hydrodesulfurization Catalysis and Mechanism of Supported Transition*

Metal Sulfides. (2020). doi:10.6100/IR531900.

39. Viloria, D. A. & González, E. B. *Study of aluminum – pillared clays as catalyst supports for hydrodesulfurization and catalytic activity* (2021)

40. Tavera García, J. E. *Efecto de la reactivación in situ de un catalizador gastadp NiMoP en la formación de sulfuros metálicos*. (2015).

41. Tye, C. T. *Processing of Heavy Crude Oils - Challenges and Opportunities environment in IntechOpe* (2019). doi:http://dx.doi.org/10.5772/intechopen.89451.

42. Hajjar, Z., Kazemeini, M., Rashidi, A. & Soltanali, S. *Hydrodesulfurization catalysts based on carbon nanostructures :* A review. *Fullerenes, Nanotub. Carbon Nanostructures* **0**, 1–13 (2018).

43. Bej, S. K., Maity, S. K. & Turaga, U. T. *Catalyst : A Review of Recent StudiesSearch for an Efficient 4,6-DMDBT Hydrodesulfurization Catalyst: A Review of Recent Studie*s. **18**, (2005).

44. Marsh, H. & Rodríguez-Reinoso, F. *Characterization of Activated Carbon*. *Activated Carbon* (2006). doi:10.1016/b978-008044463-5/50018-2.

45. Sevilla, U. *Manual Del Carbón Activo*. *Aula.Aguapedia.Org* 1–89 (2011).

46. Kwiatkowski, J. F. *Activated carbon classifications, properties and applications*. (2012).

47. Bandosz, T. J. & Ania, C. O. *Activated Carbon Surfaces in Environmental Remediation*. *Interface Science and Technology* vol. 7 (2006).

48. Furimsky, E. *Hydroprocessing, Carbon-supported Catalysts*. (2008)

49. Nicholas, A. F., Hussein, M. Z. & Zainal, Z. *Activated Carbon for Shape-Stabilized Phase Change Material*. *Synthesis, Technology and Applications of Carbon Nanomaterials* (2019). doi:10.1016/B978-0-12-815757-2.00013-9.

50. Iwanow, M. et al, *Activated carbon as catalyst support: precursors, preparation, modification and characterization.* (2020)

51. Rodriguez, F. *Activated Carbon, Production and Reference Material* (2002).

52. Çuhadar, Ç., *Production and characterization of activated carbon from hazelnut shell and hazelnut husk*. (2005).

53. Bedia, J., Peñas, M. Almudena, G., Rodriguez, J. J. & Belver, C. *Review on Activated Carbons by Chemical Activation with* $FeCl_3$. 1–25 (2020).

54. Kaiser, R. *Carbon molecular sieve*. *Chromatographia* vol. 3 (1970).

55. Miura, K., Nakagawa, H. & Okamoto, H. *Production Of Activated Carbon And Its Catalytic Application For Oxidation Of Hydrogen Sulphide. Carbon N. Y.* **38**, 119–125 (2000).

56. Dias, J. M., Alvim-Ferraz, M. C. M., Almeida, M. F., Rivera-Utrilla, J. & Sánchez-Polo, M. *Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review. J. Environ. Manage.* **85**, 833–846 (2007).

57. Prins, R., Scaroni, A. W. & Solar, J. M. *Hydrodesulphurization activity and coking propensity of carbon and alumina supported catalysts* *. **63**, 1095–1100 (1984).

58. de Beer, V. H. J. *et al. Hydrodesulphurization activity and coking propensity of carbon and alumina supported catalysts* *. **63**, 1095*–1100 (1984).*

59. *Abotsi, G. M. K. & Scaroni, A. W. A Review of Carbon-Supported Hydrodesulfurization Catalysts*. **22**, 107–133 (1989).

60. Rankel, L. A. *Hydroprocessing of Heavy Oil over CoMo/Carbon Supported Catalysts. Energy and Fuels* **7**, 937–942 (1993).

61. Farag, H., Whitehurst, D. D., Sakanishi, K. & Mochida, I. *Carbon versus alumina as a support for Co ± Mo catalysts reactivity towards HDS of dibenzothiophenes and diesel fuel*. **50**, 9–17 (1999).

62. Bej, S. K., Maity, S. K. & Turaga, U. T. *Catalyst : A Review of Recent Studies*. **18**, (2005).

63. Lee, J. J. *et al. Performance of CoMoS catalysts supported on nanoporous carbon in the hydrodesulfurization of dibenzothiophene*. **86**, 141–149 (2003).

64. Liu, F., Xu, S., Chi, Y. & Xue, D. Short Communication *A novel alumina-activated carbon composite supported NiMo catalyst for hydrodesulfurization of dibenzothiophene*. *CATCOM* **12**, 521–524 (2011).

65. Saleh, T. A. & Danmaliki, G. I. *Influence of acidic and basic treatments of activated carbon derived from waste rubber tires on adsorptive desulfurization of thiophenes*. *J. Taiwan Inst. Chem. Eng.* **60**, 460–468 (2016).

66. Cheche, U. A., Alhooshani, K. R., Adamu, S., Thagfi, J. Al & Saleh, T. A. *The Effect of Calcination Temperature on the Activity of Hydrodesulphurization Catalysts Supported on Mesoporous Activated Carbon*. *J. Clean. Prod.* (2018) doi:10.1016/j.jclepro.2018.11.177.

67. Kohli, K., Prajapati, R., Maity, S. K. & Sharma, B. K. *Effect of Silica, Activated Carbon, and Alumina Supports on NiMo Catalysts for Residue Upgrading*. 1–16 (2020).

68. New Zealand Avocado. *World Avocado Market. New Zeal. Avocado* (2019).

69. Statista. *Avocado production worldwide from 2000 to 2019*. https://www.statista.com/statistics/577455/world-avocado-production/.

70. INIAP. *Manual del cultivo del aguacate para los valles interandinos del Ecuador*. (1999).

71. Flores, J. J. Á. *Análisis de la producción de aguacate en el Ecuador y su exportación a mercados internacionales en el periodo 2008 al 2018*. (2018).

72. Martínez, J. I. O. *Evaluación del efecto de tres tiempos de exposición al 1-metilciclopropeno en dos variedades de aguacate* (Persea americana Mill .). (2019).

73. ESPAC. *Encuesta de Superficie y Producción Agropecuaria Continua ESPAC 2020*. *Inec* 61 (2020).

74. Viera, A., Sotomayor, A., Viera, W. *Potencial del cultivo de aguacate (persea americana mill) en Ecuador como alternativa de Comercialización en el mercado local e internacional*. (2016).

75. Manuel, J. & Gavilanez, J. *El aguacate orgánico hass: potencialidad de exportación y estrategias de ingreso a los mercados internacionales*. (2011).

76. García-Vargas, M. C., Contreras, M. D. M. & Castro, E. *Avocado-derived biomass as a source of bioenergy and bioproducts*. *Appl. Sci.* **10**, 1–29 (2020).

77. Salazar-López, N. J. *et al. Avocado fruit and by-products as potential sources of bioactive compound*s. *Food Res. Int.* **138**, 109774 (2020).

78. Guntama, D., Mahardini, I., Purnamasari, R. & Nulhakim, L. *Active Charcoal From Waste of Avocado Seeds As a Chromic (Cr) Metal Adsorbent Using Chloride Acid (Hcl) and Sulfuric Acid (H2So4) Activator*. *J. Community Based Environ. Eng. Manag.* **4**, 57–62 (2020).

79. Dabas, D., Shegog, R., Ziegler, G. & Lambert, J. Avocado (Persea americana) Seed as a Source of Bioactive Phytochemicals. *Curr. Pharm. Des.* **19**, 6133–6140 (2013).

80. INEC—ESPAC. Boletín Situacional. **2017**, (2018).

81. Barbosa-Martín, E., Chel-Guerrero, L., González-Mondragón, E. & Betancur-Ancona, D. *Chemical and technological properties of avocado (Persea americana Mill.) seed fibrous residues*. *Food Bioprod. Process.* **100**, 457–463 (2016).

82. Chel-Guerrero, L., Barbosa-Martín, E., Martínez-Antonio, A., González-Mondragón, E. & Betancur-Ancona, D. *Some physicochemical and rheological properties of starch isolated from avocado seeds. Int. J. Biol. Macromol.* **86**, 302–308 (2016).

83. Domínguez, M. P. *et al. The Avocado and Its Waste: An Approach of Fuel Potential/Application*. *Handb. Environ. Chem.* **34**, 199–223 (2016).

84. Ruiz, S. K. T. *Caracterización bromatológica de la semilla de aguacate (Persea americana) y extracción e identificación de la fracción con mayor actividad antimicrobiana y antioxidante*. (2018).

85. Nahin, C. R. J. & Angéñica, S. M. M. *Evaluación de la actividad antioxidante de la semilla De aguacate (persea americana mill) variedad hass a través del método*

DPPH. (2020).

86. Tituaña, A. C. *Evaluación del uso potencial del colorante extraído de la semilla del aguacate (Persea americana) como producto funcional alimenticio*. 1–90 (2019).

87. Guaña, M. J. R. *Evaluación del pigmento obtenido de la semilla de dos variedades de aguacate (Persea americana var. Hass y Persea americana var. Fuerte) como alternativa de uso en la industria de alimentos*. *Bull. Seismol. Soc. Am.* **106**, 6465–6489 (2016).

88. Alejandro, J. & Mosquera, N. *Aguacate (Persea Americana) para la obtención de tinta para su aprovechamiento en la agroindustria*. (2017).

89. Tayo Cargua, F. E*studio de prefactibilidad de una planta industrial para la producción de yogurt con colorante natural extraído de la semilla del aguacate para los niños en edad escolar*. 1–88 (2020).

90. Chapuel, A. & Reyes, J. *Obtención de una película biodegradable a partir de los almidones de semilla de aguacate (Persea americana Mill) y banano (Musa acuminata AAA) para el recubrimiento de papaya*. *J. Wind Eng. Ind. Aerodyn.* **26**, 1–4 (2019).

91. Verónica-Simancas, S.-R. *Aplicación de un recubrimiento a base de cáscara de piña (ananas comosus) y aceite esencial de semilla de aguacate (persea americana) para conservar queso fresco*. (2019).

92. Vinueza, C. I. A. *Diseño de industria de sorbetes ecológicos con semilla de aguacate en la ciudad de Guayaquil*. (2021).

93. Guerrero Escobar, D. P. *Extracción y evaluación de un colorante natural a partir de la pepa de aguacate para el teñido de las fibras de algodón y poliéster*. 1–97 (2011).

94. Matos, J., Brito, J. L. & Laine, J. *Pretreatment and composition on catalyst reducibility and on ethylene conversion*. **152**, 27–42 (1997).

95. Chunga, A. *Determinación de la acción antimicótica in vitro de un gel elaborado*

a partir del aloe vera y persea americana. 68p (2015).

96. Tapia, E. M. *Textile wastewater treatment filters made up of activated carbon*. (2021).

97. Sánchez, F., Agudín, F. & San Mıguel, G. *Granular activated carbons from avocado seeds. 15th International Conference on Environmental Science and Technology* (2017).

98. Elizalde-González, M. P., Mattusch, J., Peláez-Cid, A. A. & Wennrich, R. *Characterization of adsorbent materials prepared from avocado kernel seeds: Natural, activated and carbonized forms*. *J. Anal. Appl. Pyrolysis* **78**, 185–193 (2007).

99. Leite, A. B. *et al. Activated carbons from avocado seed : optimisation and application for removal of several emerging organic compound*s. 7647–7661 (2018).