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Fluid-dynamic Modeling of Fixed Bed Adsorption Towers for Hydrogen Sulfide Removal from Natural Gas

Trabajo de titulación presentado como requisito para la obtención del título de Petroquímico

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DEDICATION

To my mother for being the person who has accompanied me in my triumphs and failures throughout my life and has taught me to get up every time I fall.

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RESUMEN

El endulzamiento del gas natural es un proceso importante dentro de las operaciones de procesamiento de hidrocarburos, que permite cumplir con las especificaciones de calidad de productos, evitar problemas relacionados con la corrosión de tuberías e instalaciones y cuidar el medioambiente. Este proceso tiene como objetivo la remoción de sulfuro de hidrógeno (H_2S) y dióxido de carbono (CO_2) y se puede llevar a cabo en torres de adsorción en donde un sorbente sólido, basado en óxidos metálicos como principio activo, es puesto en contacto con el gas natural, de tal manera que estos óxidos reaccionan con el H_2S presente en el gas. En este tipo de procesos se debe tomar en cuenta aspectos relacionados al comportamiento fluidodinámico del proceso como la caída de presión que sufre el gas debido a su paso a través del sólido poroso y a la remoción de sulfuro de hidrógeno. En base a esto, en el presente trabajo se desarrolla un modelo fluidodinámico que permite estimar la caída de presión en este tipo de procesos. Para esto se tomó como base la ecuación de Ergun y para cálculos de la densidad y viscosidad del gas se tomó la ecuación de estado de Peng-Robinson (1976) y un ajuste matemático desarrollado por Jarrieh y Handire (2014), respectivamente. Posteriormente, se incluyó en el modelo aspectos de reactividad, considerando la formación de una capa de sulfuro de hierro (Fe_2S_3). Como resultado de la formación de esta capa hay cambios en el diámetro de la partícula y fracción vacía del sólido poroso. Finalmente, se plantearon casos de estudio para poder determinar cómo afectan las propiedades del lecho y las características del sólido en la caída de presión obteniendo como resultado que la porosidad, presión de entrada del gas y diámetro de lecho empacado son las variables que más afectan a la caída de presión y deben ser tomadas en cuenta para la operación de las torres de adsorción. La importancia del modelo desarrollado en el presente trabajo radica en los siguientes puntos: ayuda en el diseño y formulación de sorbentes sólidos, permite el análisis del comportamiento fluidodinámico en torres de adsorción ya instaladas y es una herramienta de apoyo en la planificación de las operaciones de mantenimiento de dichas torres.

Palabras claves: adsorción, gas natural, modelo fluidodinámico, torre de lecho fijo, remoción de H_2S.

ABSTRACT

Natural gas sweetening is an important process within hydrocarbon processing operations, enabling compliance with product quality specifications, avoiding problems related to corrosion of pipes and installations, and taking care of the environment. This process aims to remove hydrogen sulfide (H_2S) and carbon dioxide (CO_2) and can be carried out in adsorption towers where a solid sorbent, based on metal oxides as an active principle, is put into contact with natural gas so the metal oxides present in the solid react with the H_2S present in the gas. Aspects related to the fluid-dynamic behavior of the process such as the pressure drop in the natural gas stream due to its passage through the porous solid and the removal of hydrogen sulfide should be taken into account in this type of process. Based on this, the present work develops a fluid-dynamic model that allows estimating the pressure drop in this type of process. This was based on the Ergun equation and for calculations of the density and viscosity of the gas took the Peng-Robinson Equation of State (1976) and a mathematical adjustment developed by Jarrieh and Handire (2014), respectively. Subsequently, aspects of reactivity were included in the model, considering the formation of an iron sulfide layer (Fe_2S_3). As a result of the formation of this layer, there is a change in the particle diameter and the empty fraction of the porous solid. Finally, case studies were raised to determine how the properties of the bed and the characteristics of the solid affect the pressure drop. Resulting in the porosity, gas inlet pressure and packed bed diameter are the variables that most affect the pressure drop and should be taken into account for the operation of the adsorption towers. The importance of the model developed in the present work is due to the following points: aid in the design and formulation of solid sorbents, allows the analysis of behavior in adsorption towers already installed and helps in the planning of maintenance operations.

Keywords: adsorption, natural gas, fluid-dynamic model, fixed bed tower, H_2S removal.

CONTENT

CHAPTER I

1. INTRODUCTION

Energy demand is constantly increasing according to the years and natural gas represents a large part of this increase. In 2019 natural gas represented a 5% increase in production and consumption worldwide[1]. Therefore, natural gas has an important role in the global economy. In addition, it is profitability due to its great competitiveness in the global market and its efficiency as fuel[2]. In this context, it is important to value natural gas in order to meet the needs of the market.

Natural gas has some pollutants such as carbon dioxide (CO_2), hydrogen sulfide (H_2S) and water. Such contaminants can cause operational problems associated with the corrosion of equipment and pipes, the formation of hydrates, poisoning of catalysts in down-water processes and environmental contamination[3]. Because of this, natural gas sweetening and dehydration processes are necessary in order to remove these contaminants and minimize the presence of them into natural gas.

Currently there are various processes for the removal of H_2S from natural gas, such as: chemical absorption, physical absorption, direct conversion, membranes and adsorption[4]. The use of these methods depends on the characteristics of natural gas, composition, flowrate and operational conditions. Within H_2S removal process adsorption is important for the treatment of gases with flowrates less than 125 million cubic feet standard per day[5] (125 MMSCFD).

This process is carried out by adsorption towers. These towers are vertical columns containing a packed bed which is traversed by natural gas and provides a solid-gas contact surface where hydrogen sulfide adsorption occurs[6]. Sorbent solids are based on metal oxides supported in ceramic, clay or fiberglass. In the industry the most commonly used oxides are iron oxides, zinc oxides and calcium oxides[5].

In Ecuador, the public company responsible for the production of oil and natural gas is Petroamazonas EP, which since 1978 has been in charge of operating oil and natural gas sources in Ecuador. At present, a total of 100 MMSCFD of natural gas from the various production fields are produced at Ecuador[7].

There are two main regions of natural gas production. The first region is the Amistad field belonging to Bloque 6, located in the Gulf of Guayaquil. A percentage of the natural gas produced in this area is intended for the consumption of companies dedicated to the manufacture of ceramics, in specific Edesa S.A and Graiman. The rest of natural gas is intended for the generation of electricity at the Machala plant[8] (Termogas Machala, CELEC EP).

On the other hand, Ecuador's second natural gas production region corresponds to the total fields located in the Ecuadorian East. Currently these do not have fixed consumers, instead the natural gas is used in energy efficiency programs for the generation of electricity inside Petroamazonas EP facilities[9].

The development of this work focuses on analyzing the fluid-dynamic behavior of the natural gas stream as it passes through the packed bed of the adsorption tower. To this end, a mathematical model based on the Ergun equation[10] was first developed. However, this equation does not consider parameters related to the reactivity of gas with the solid bed, since reactivity is an important part in fluid-dynamic analysis must be integrated into the model.

To incorporate reactivity effect into the fluid-dynamic model is considered the core reactivity model with which the changes to the solid bed were calculated after reacting. Once the model was obtained, several case studies were presented in which the variables related to the properties of the gas and the characteristics of the solid bed were changed. This in order to perform an analysis of the effect these characteristics have on gas behavior.

These kind of studies help to analyze the behavior of the adsorption tower to operate it in an optimal way. Specifically, the fluid-dynamic model development in this work will help in the design and formulation of solid sorbents by analyzing the effect of porosity and particle diameter variation. Also, it will allow performance analysis and planning of maintenance operations of installed adsorption towers. This will be achieved by estimating the pressure drop and calculating bed replenishment time within the fluid-dynamic model.

1.1. Problem Approach

Natural gas produced in the fields of eastern Ecuador currently has no final consumers so the economic potential they represent is not valued. An alternative to harnessing this natural gas is the generation of electricity within the Petroamazonas EP facilities[9]. However, this alternative is not optimal as there are companies in demand for this product. It would be better to satisfy the market and increase the value of this gaseous hydrocarbons.

In order to be able to enhance the natural gas from this area it must be subjected to a process called natural gas sweetening in which hydrogen sulfide and carbon dioxide are removed. Because of, H_2S and CO_2 in high quantities decrease the calorific power of the natural gas and they represent pollutants affecting the environment. In addition, removing these components avoids operational problems in corrosion processes of equipment and pipes[3].

One of the technologies used for the hydrogen sulfide removal process in natural gas streams is through packed bed adsorption towers. However, prior to operating these adsorption towers, tools are needed to perform an estimation and analysis of fluid-dynamic parameters depending on natural gas properties and solid bed characteristics.

Ergun equation allows an estimate of important fluid-dynamic parameters and it is applicable to adsorption towers[11]. However, this equation does not take into account parameters about the reaction that occurs between gas and solid, which modifies the important characteristics of the packed bed that serve for further analysis.

In this context, this work aims to analyze fluid-dynamic aspects in packed bed adsorption towers by developing a fluid-dynamic model based on the Ergun equation and including aspects of reactivity between the solid and gas to the fluid-dynamic model with the objective to improve the analysis of the packed bed towers.

1.2. Objectives

1.2.1. General Objective

Analyze the fluid-dynamic behavior in fixed bed adsorption towers for the capture of H_2S in natural gas streams, considering factors related to natural gas properties streams and fixed bed characteristics.

1.2.2. Specific Objectives

- Develop a fluid-dynamic model that incorporates aspects of reactivity for a bed adsorption tower, that allows estimating the variation of pressure across the bed.

- Analyze the effect that the variation of the natural gas properties: composition, H_2S content, pressure, temperature, flow and H_2S specification have on the fluid-dynamic behavior in the adsorption tower.

- Analyze the effect of the variation of the characteristics of the solid bed: adsorption capacity, particle diameter, sphericity, empty fraction or porosity, and packing density on the fluid dynamic behavior in the adsorption tower.

CHAPTER II

2. BACKGROUND AND LITERATURE REVIEW

2.1. Natural Gas

Natural gas is a mixture of light hydrocarbons in gaseous state composed mostly of methane and ethane, propane, butanes, and heavier compounds in small amounts. It also contains water vapor, carbon dioxide, hydrogen sulfide and nitrogen which are considered natural gas impurities, and some heavy metals such as mercury are found as traces[12].

Millions of years ago left-over organic matter traps under layers of rock and was exposed to bacteriological activity, high pressures and temperatures. It is this process that gave rise to what is now known as oil and natural gas. Therefore, they are trapped in rock formations, inside a porous rock that is surrounded by no permeable rocks[13].

The gas reservoirs classification is based in phase diagrams and it can be separate in four categories: retrograde gas-condensate if the gas-oil ratio is between 8,000 and 70,000 standard cubic feet of gas per storage tank barrel of oil (scf/STD), near-critical gas-condensate is closed to retrograde gas-condensate, wet gas if the gas-oil ratio is between 70,000 and 100,000 scf/STD and dry gas if the relation gas-oil is more than 100,000 scf/STD, the only liquid associated with dry gas is water[14].

Natural gas can be classified according liquid content as lean or rich and according to the sulfur content as sour or sweet. Liquid contends refers to the heavy hydrocarbons present in the composition of gas, usually from ethane onwards, the rich gas is one that contain these heavy hydrocarbons in a greater proportion. On the other hand, acid gas refers to the H_2S content, the gas with a negligible amount of H_2S is considered as sweet gas and a sour gas have an unacceptable quantity of H_2S[15].

A gas acid contains more than 4 ppmv (parts per million in volume). When gas from a deposit exceeds this amount it must be subjected to a sweetening process to remove excess H_2S and meet market specifications. Similarly this definition applies to CO_2 content without clutch this is not as undesirable as H_2S[15].

Hydrogen sulfide and carbon dioxide are two of the most relevant compounds in natural gas since their presence in large quantities decreases their calorific power. In addition, these are highly corrosive in the presence of water[3]. Hydrogen sulfide is a toxic gas of a strong odor while CO_2 is an odorless gas that in low concentrations is non-toxic and is easily liquefied by compression[16].

The composition of natural gas varies depending on the area from which it has been extracted, as can be seen in Table 1, Ecuador's natural gas from different deposits shows the Shushufindi Gas Plant, Bloque10, and Shushufindi Field.

Table 1. *Properties of natural gas from some regions in Ecuador*

Composition (mole %)	**Natural Gas Precedence**		
	Shushufindi Gas Plant	**Bloque 10**	**Shushufindi Field**
Methane	39.59	64.21	75.504
Ethane	10.44	7.5	11.339
Propane	24.48	8.47	5.1
iso-Butane	2.11	2.29	0.95
n-Butane	3.93	3.19	1.12
iso-Pentane	0.47	1.87	0.34
n-Pentane	n.d	n.d	0.25
C_6+	n.d	2.26	0.358
Nitrogen	1.65	7.67	0.1
CO_2	17.33	2.51	4.94
H_2S (ppm)	300	300	500
Flowrate [MMSCFD]	25	0.28	2.5
Temperature [°F]	100	80	90
Pressure [psia]	500	65	500

n.d: not determinated

2.2. Corrosion by Carbon Dioxide and Hydrogen Sulfide

Corrosion is a phenomenon, in which a material, usually a metal, wears away due to an electrochemical, chemical or erosion process by interacting with the surrounding medium. Corrosion can be classified as follows[17]:

- *Generalized corrosion:* this type of corrosion occurs on the surface of a material exposed to a corrosive agent and is widespread on the surface of the material.
- *Corrosion by cracks:* this type of corrosion is characterized by an intense attack on cracks that shows the material because the corrosive agent to accumulate in this.
- *Stress corrosion:* due to the mechanical stress that the materials can suffer, small cracks are created in it, which results in the accumulation of corrosive agent that generate the corrosion.
- *Intergranular corrosion:* occurs at the grain edges of the material, giving way to wear and disintegration of the material.

Into the natural gas industry the corrosion in pipes and equips occurs mainly by the presence of acid gases like carbon dioxide or hydrogen sulfide that contain the natural gas[18]. Carbon dioxide corrosion occurs when carbon dioxide forms carbonic acid, Equation (1), in the presence of water and subsequently dissociates into the carbonate and bicarbonate and this species in the surface of the metal (iron) react electrochemically according de Equation (2) to form iron carbonate[18].

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (1)$$

$$Fe + H_2CO_3 \rightarrow FeCO_3 + H_2 \qquad (2)$$

The corrosion by H_2S occurs when hydrogen sulfide dissolved in water undergoes double dissociation forming hydrosulfide ions and sulfide ions. Then, in contact with the surface of the metal, electrochemical reactions occur that end in the formation of iron sulfide[19], as shows the Equation (3).

$$Fe + H_2S \rightarrow FeS + 2H^+ \qquad (3)$$

The overall cost of corrosion in the oil and gas industry worldwide is estimated at USD 1.372 trillion annually according to studies by NACE (National Association of Corrosion Engineers). It can be divided into USD 589 million in facility and surface pipe costs; USD 463 million per year in well fund pipe expenses; and another USD 320 million in corrosion-related capital expenditures. These costs are due to the replacement of pipes and equipment when they are no longer useful due to corrosion[20].

2.3. Natural Gas Sweeting Processes

The sweetening of natural gas corresponds to all activities that are carried out on a natural gas to remove acidic components such as hydrogen sulfide and carbon dioxide[4]. There are different procedures for the removal of acid gases.

2.3.1. Chemical Absorption

Chemical absorption is a process by which it is possible to remove a component of interest from a gas stream using a liquid solvent, it is achieved by the mass transfer of the gas to the liquid solvent[15].

The equipment used for these processes are usually absorption columns, in which the gas and liquid stream in contraflow is introduced. In addition, they usually consist of plates or filling elements inside the same ones that provide a contact surface between the gas and liquid for the transfer of mass. Other commonly used devices are bubbling tanks in which a liquid is at rest in which a gas is bubbling in such a way that when the gas rises, the transfer of matter is given[15].

The chemical reaction between the gas interest compound and the liquid solvent governs this type of process. The reactions of these processes are usually reversible, therefore at the end of the process the liquid solvent can be recovered and used again in the process. For the removal of hydrogen sulfide, the liquid solvents used for excellence are amines due to its low cost, high adsorption capacity and flexibility in design and operation. The most commonly used amines are: monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diglylamine (DGA), methyldietamine (MDEA)[3,15].

Currently the technological trend in chemical adsorption is oriented to process optimization that allow to minimize the consumption of chemical solvents and the establishment of operational conditions that reduce energy consumption. For example, there are studies orientated to the analysis of amine selection to improve de process and also analyze factors like circulation rate and solvent concentration[21].

2.3.2. Physical Absorption

Physical absorption follows the same principle mentioned in the previous section. A compound of interest from a natural gas is removed by a liquid solvent. However, the main difference is that there are no chemical reaction and the process is mainly by transfer of mass of the gas to the liquid. For this reason physical absorption depends mainly on the partial pressure of the compound of interest[22].

Physical adsorption is applicable only for natural gas streams with high pressure and a high concentration of the compound of interest. In addition, this process has an affinity for heavier hydrocarbons than propane[15]. For example, if this process is used with rich gases would represent the loss of heavy hydrocarbons. Therefore, physical absorption is only used in gases whose amount of heavy hydrocarbons is negligible (lean gases).

The liquid solvent usually used in these processes is water. The H_2S removal process takes place in a tower where water enters through the top and gas from the bottom. This process then is complemented by a chemical absorption process in order to remove most of the H_2S present in the gas stream[15] .

Currently the technological trend in physical adsorption is the development of new physical solvents focused on adsorption capacity and reduced regeneration heat. This with the aim of lowering capital and operating costs. However, transport and thermal properties such as viscosity and heat capacity respectively are an important factor for equipment designs and therefore cost of capital[23].

2.3.3. Direct Conversion

In this process, the hydrogen sulfide present in the gas effluent is to remove directly into elemental sulfur. This is achieved reacting directly the hydrogen sulfide present y the natural gas stream.

First hydrogen sulfide is absorbed into an iron chelate solution where sulfide is ionized, then oxidized to elemental sulfur by reducing ferric to ferrous ions. The solution is then regenerated by an oxygen stream that transforms the ferrous ion to ferric[4].

2.3.4. Membranes

Membrane separation refers to a process in which a component of interest is physically separated by a membrane. These membranes can have a pore size of 5 microns to 100 microns and the separation of the component of interest depends mainly on the partial pressure of this. In addition, the hydrogen sulfide, carbon dioxide and water presents in the gas stream are high diffusers than hydrocarbons, therefore they can easily cross a membrane than hydrocarbons[15].

One of the most commonly used standard membranes is cellulose acetate. These membranes without thin to maximize mass transfer. However, a support layer is needed to provide mechanical strength. One of the disadvantages of this process is that the methane losses are close to 10%[24].

2.3.5. Adsorption

The adsorption process is a surface phenomenon, where atoms, ions or molecules are retained on the surface of a solid. Such solids are known as adsorbent and are specific to a substance being able to retain it and separating it from gaseous or liquid solutions. The substance retain in the surface of the solid is known like adsorbate[6].

This process is carried out in adsorption towers, which contain a porous solid packaging inside (adsorbent), and when making contact with the gas is able to retain on its surface the hydrogen sulfide present in it, giving way to a chemical reaction[22].

2.4. Sorbents

Sorbents or adsorbents are mainly made up of metal oxides such as iron oxide, zinc oxide, calcium oxide or magnesium oxide[5]. These are supported on an inert material such as fiberglass or ceramic. Metal oxides have high selectivity for acidic gases such as hydrogen sulfide.

The most commonly used sorbent in the industry is one that contains iron oxide due to its high adsorption capacity and its natural abundance. However, zinc oxide has a higher adsorption capacity than iron oxide, but the latter is the most used because it is less expensive than zinc oxide[2]. Actually, these sorbents can be found like commercial products, one example of these is the product called Sulfatreat® (produced by Schlumberger company), based on iron oxide supported on silicates and presented in the form of small granules of regular shape and size[3]. This commercial product is used in the gas natural industry to remove hydrogen sulfide; the typical characteristics as show in the following table.

***Table 2**. Characteristics of Sulfatreat® solid sorbent*[25]

Sulfatreat	
Particle diameter [in]	0.07
Empty fraction [-]	0.3
Packed density [lb/ft]	93
Adsorption capacity [lbH_2S/lb]	0.235

This type of products can be used in Ecuador's natural gas. The INEDITA project aims to enhance natural resources (ferruginous and titaniferous sands) available in Ecuador, through the development of potential applications within the hydrocarbon processing and refining industry[26].

2.4.1. Types of Adsorption

- *Physical adsorption*: occurs when the adsorbate is retained on the surface of the adsorbent by Van der Waals-type interactions without the formation of chemical bonds[27] .
- *Chemical adsorption*: occurs when there is the formation of a chemical, covalent or ion bond, between the adsorbate and adsorb[27].

Considering an iron oxide-based sorbent, the typical chemical reactions that can be found with hydrogen sulfide are as follows[28]:

$$4\,H_2S_{(g)} + Fe_3O_{4(s)} \rightarrow 4\,H_2O_{(l)} + S_{(s)} + 3\,FeS_{(s)} \qquad (4)$$

$$6\,H_2S_{(g)} + Fe_3O_{4(s)} \rightarrow 4\,H_2O_{(l)} + 2\,H_{2(g)} + 3\,FeS_{2(s)} \qquad (5)$$

$$3\,H_2S_{(g)} + Fe_2O_{3(s)} \rightarrow 3\,H_2O_{(l)} + 3\,Fe_2S_{3(s)} \qquad (6)$$

2.5. Adsorption Process in Natural Gas Fields

The sweetening of natural gas occurs in contact towers which contain packaging filled with a fixed bed. Natural gas enters the top of the tower and circulates continuously, passes through the solid and it reacts with hydrogen sulfide contained in the gas stream. This reaction give a product that can be retained on the surface of the solid and finally the sweet gas leaves the tower by the bottom[6]. Figure 1 shows a scheme of this process.

The sweetening process is carried out before dehydration and usually prior to a separation of liquids from natural gas in a separator, and is passed by a filter that retains any foreign particles such as gravel, sand and other solid impurities[12].

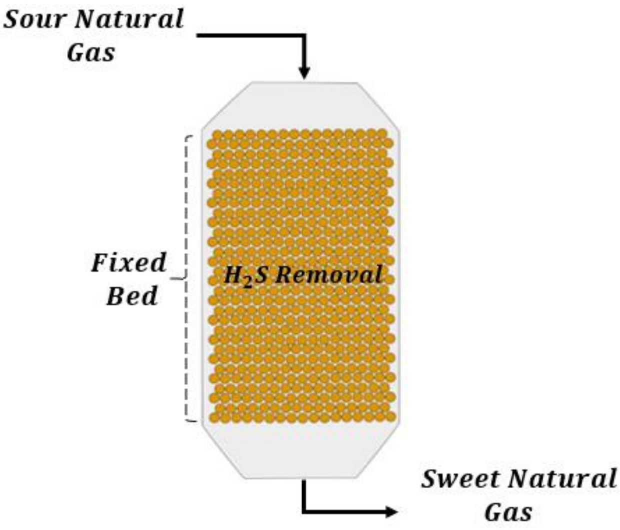


Figure 1. *Adsorption tower of natural gas sweeting*

The behavior of the fixed bed in the adsorption process can be explained as follows. Such as show in Figure 2, at the beginning of the process, the bed is completely free of hydrogen sulfide the gas begins to circulate constantly and the upper layers of the bed begin to react with hydrogen sulfide (a). Once these upper layers are worn out the adsorption process migrates to the layers below them until they are worn out and the adsorption zone changes again (b) and (c).

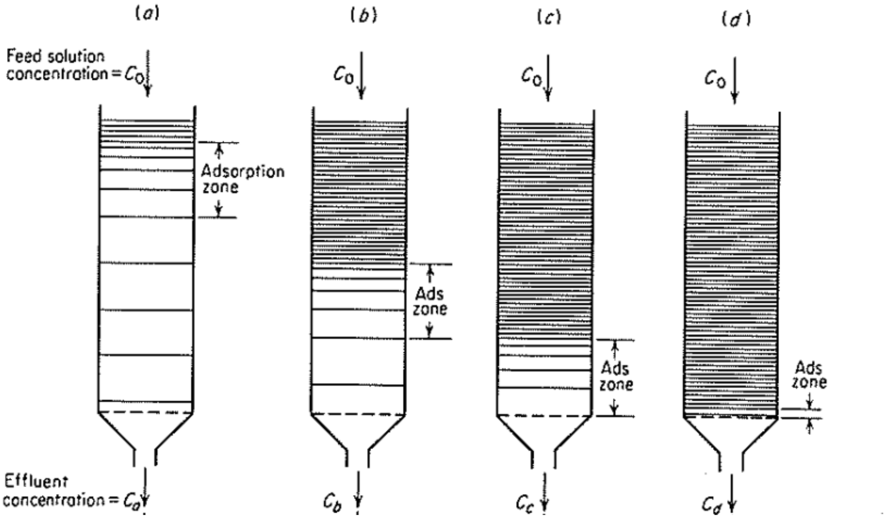


Figure 2. *Diagram of fixed bed evolution during H_2S adsorption*[24]

This adsorption zone moves from the top of the bed to the bottom. When the adsorption zone reaches the bottom the H_2S output concentration increases rapidly until equal to the input amount (d). This indicates that the bed has been worn and needs to be replaced.

2.6. Factors that Influence the Fluid-dynamic Behavior of the Fixed Bed Adsorption Towers

The analysis of fluid-dynamic aspects in a fixed bed adsorption tower is of capital importance as it allows to know basic aspects such as the pressure drop across the adsorption tower and the replacement time of the solid bed[27]. Among the aspects to consider we have the following:

2.6.1. Characteristics of Solid Beds

- *Particle diameter*: it is a measure of the particle size, however in fixed bed the particles will not always be perfectly spherical nor all particles will be the same size, so an equivalent diameter must be obtained.

- *Sphericity*: the sphericity of a particle refers to both its geometry resembling a sphere, it can be obtained as the relationship between the outer surface of the sphere with the same volume of the particle and the surface of the particle according to the following equation[29].

$$\varphi = \frac{A_s}{A_p} \quad (7)$$

where:

φ: esphericity
A_s: sphera surface
A_p: particle surface

Figure 3 shows an example of the sphericity difference of a particle, where (a) correspond a particle with a perfect sphericity, (b) correspond a particle with moderate sphericity and (c) a particle with less sphericity.

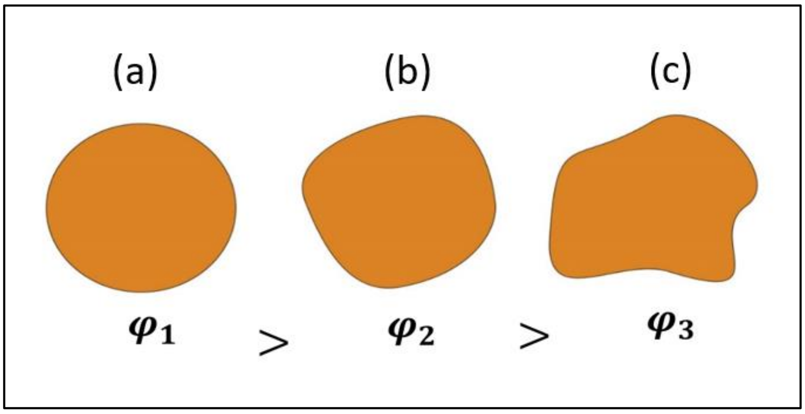


Figure 3. *Sphericity comparison of particles*

- *Empty fraction or porosity*: a porous medium is a solid or group of solids with enough space around or between them so that a fluid can pass through them[27]. Therefore, the empty fraction corresponds to the hollow area of the porous medium. This factor is one of the mainly characteristic of the fixed bed due to it allow the flow of gas in the adsorption towers as show in Figure 4.

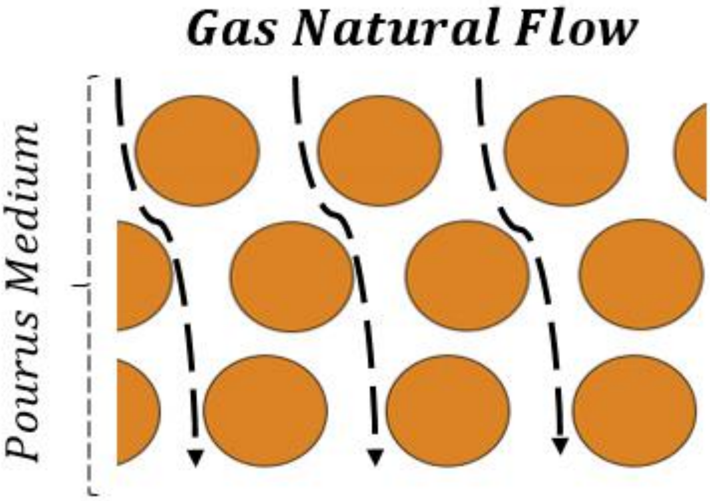


Figure 4. *Natural gas flowing through the porosity of fixed bed*

- *Packaging density*: the density of the packaging refers to the amount of material per volume unit, however this packing density considers the volume of fraction empty.

- *Solid adsorption capacity*: this is the amount of adsorbate that the solid can retain, i.e. the maximum adsorbate mass ratio that can be retained between the total mass of the packaging.

2.6.2. Natural Gas Properties

- *Composition*: the composition of natural gas plays an important role in fluid-dynamic analysis since the density and viscosity of the gas depends on the composition of the gas. In addition, the amount of adsorbate it contains will depend on the amount of packaging required and therefore the height of the bed.

- *Pressure*: like composition, it is an important factor when determining the density and viscosity of the natural gas.

- *Temperature*: it is a fundamental parameter when calculating the density and viscosity of the gas. In addition, the temperature affects the removal of adsorbate as low temperatures decrease the rate of the reaction of the adsorbate with the sorbent.

- *Flowrate:* the velocity of natural gas affects the H_2S removal process at a low rate there is less turbulence and therefore a mass transfer lower.

2.7. Ergun Equation

Ergun equation allows estimate the pressure drop of a gaseous current passing through a solid bed in dependence on the factors seen in the previous section. Ergun's equation is as follows[11]:

$$\frac{dP}{dz} = -\frac{G}{\rho D_p}\left(\frac{1-\emptyset}{\emptyset^3}\right)\left[\frac{150(1-\emptyset)\mu}{\varphi^{3/2} D_p} + \frac{1.75G}{\varphi^{4/3}}\right] \qquad (8)$$

where:

$P: pressure$

$\emptyset: empty\ fracci\acute{o}n;\ 1-\emptyset = \frac{Solid\ volume}{Total\ volume}$

$D_p: particle\ diameter$

$\mu: gas\ viscocity$

$z: fixed\ bed\ heigth$

$\rho: gas\ density$

$G: \rho * u = mass\ velocity\ per\ area$

$\varphi: esfericity$

Apply the Ergun equation at the case of the adsorption towers, is possible estimate the pressure drop across the fixed bed, but it is necessary know some properties of the gas like density and viscosity. Also, this properties of the gas can be calculated from the composition, temperature and pressure data. Add more, is important to mention that this equation not take account the reaction that exist between de gas and solid, only delineates the pass of gas through a porous solid.

2.8. Theoretical Reactivity Models

Reactivity models describe how the non-catalytic reaction process occurs between a solid particle and a fluid. Solid-fluid reactions are heterogeneous reactions that are represented as follows[30]:

$$A_{solid} + B_{fluid} \rightarrow C_{solid} \ / \ C_{fluid} \ / \ C_{solid} + D_{fluid} \qquad (9)$$

Solid particles do not change in size during the reaction if it contains a high degree of inert material or when it forms a consolidated solid product. On the other hand, the particle tends to change size if this forms an unconsolidated solid product, non-stick ash, or when pure solidness is used.

These types of reactions are widely used in the industry. As for example for obtaining metal oxides, obtaining carbon sulfide, obtaining sodium cyanide among others. Also, this kind of reactions occur in to de adsorption towers for sweeting of natural gas. Given the wide range of these cases it is necessary to study a theoretical model that allows to represent this reaction process.

2.8.1. Progressive-Conversion Model (PCM)

This model describes the process of the following, a reactant gas enters and reacts throughout the particle at all times, most likely at different rates at different locations within the particle. Thus, solid reactant is converted continuously and progressively throughout the particle. Figure 5 is show a scheme of this process[30].

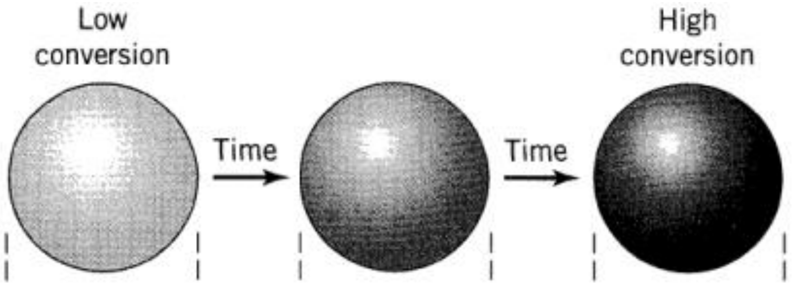


Figure 5. *Evolution of the solid particle according to Progressive-Conversion Model*[30]

2.8.2. Shrinking-Core Model (SCM)

The SCM describes that reaction occurs first at the external skin of the particle. The zone of reaction then moves into the solid, leaving behind completely converted material and inert solid. Thus, at any time there exists an unreacted core of material which shrinks in size during reaction. Figure 6 shows that there are a region without react, this correspond at the center of the sphere[30].

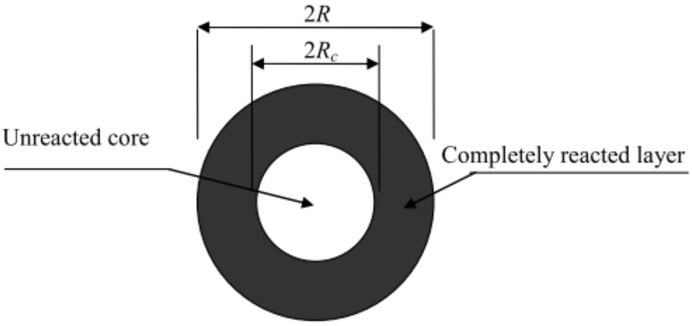


Figure 6. Diagram of the solid particle according to Shrinking-Core Model[30]

CHAPTER III

3. METODOLOGY

To perform fluid-dynamic analysis of the hydrogen sulfide adsorption towers, first, a model was built based on the Ergun equation for calculating the pressure drop across the solid bed. For this, it was necessary to incorporate equations for the calculation of the density and viscosity of the gas. For the calculation of density the Peng-Robinson equation of state[31] was taken while for the calculations of viscosity a mathematical adjustment made by Jarrahian and Heidaryan[32] was taken into account.

Once the model was made based in the Ergun equation, parameters associated with the reactivity between hydrogen sulfide and the solid were integrated. To do this, the chemical reaction that occurs between iron oxide and hydrogen sulfide, the unreacted nucleus reactivity model and unit cell parameters of iron oxide and hydrogen sulfide was taken into account. Figure 7 shows a schematic representation of the methodology developed in this study.

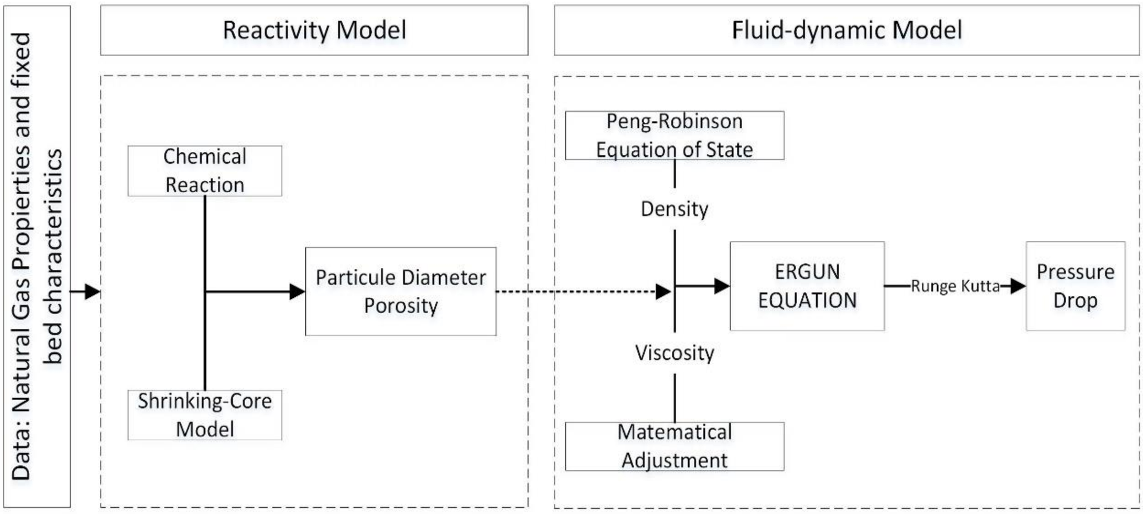


Figure 7. *Methodology diagram*

Subsequently, 2500 studies cases were established in which the properties of the gas and the characteristics of the solid bed were varied in order to obtain data for further analysis.

3.1. Model Premises

For develop of the fluid-dynamic model the following premises are take account:

3.1.1. Fluid-dynamics Analysis

- The calculation of the pressure drop is performed taking the Ergun equation as a reference.
- The Peng-Robinson equation of state (PR EoS)[31] is used to calculate the natural gas density.
- The mathematical adjustment of Jarrahian and Heidaryan[32] is taken to calculate the natural gas viscosity.
- Sphericity is considered as a factor that describes the geometry of the particle.

3.1.2. Reactivity Model Premises

- For the calculations performed for the spent bed, the reaction is considered: $3H_2S + Fe_2O_3 \rightarrow Fe_2S_3 + 3H_2O$.
- The product of the chemical reaction is considered to be distributed evenly over the entire surface of the solid bed particles.
- Non-reversible reaction.
- Relative humidity keeps the solid moist and favors the diffusion of H_2S.
- The reaction of the packed bed with H_2S is given by packing sections which progressively wear out, that is to say, the packing wears out one section at a time.

3.2. Natural Gas Density Calculation

First proceeded to estimate the density that the natural gas stream using the Peng-Robinson equation of state[31]. From this, is possible obtain the molar volume and therefore the density. For this it is necessary to know data about the composition (y_i), pressure (P) and temperature (T) of natural gas. The Peng-Robinson equation is the following:

$$P = \frac{RT}{v-b} - \frac{aT}{v(v+b)+b(v-b)} \qquad (10)$$

This equation can be rearranged as a cubic polynomial, Equation (11), in which the roots are the compressibility factor (Z) and then obtain the molar volume using Equation (14):

$$Z^3 - (1-\mathrm{B})Z^2 + (\mathrm{A} - 3B^2 - 2\mathrm{B})\mathrm{Z} - (\mathrm{AB} - B^2 - B^3) = 0 \qquad (11)$$

where:

$$A = \frac{aP}{R^2T^2};\ \ B = \frac{bP}{RT};\ \ Z = \frac{Pv}{RT} \qquad (12); (13); (14)$$

In this way the problem is re-found to find the factors a and b according to the following equations:

$$a = \sum_i \sum_j y_i y_j a_{ij} \qquad (15)$$

$$b = \sum_i y_i b_i \qquad (16)$$

First, proceed with the calculation of b. For this is necessary to know the composition y_i of each component of natural gas and calculate b_i for each component of natural gas as follows:

$$b_i = 0.07780 \frac{RT_c}{P_c} \qquad (17)$$

Where T_c and P_c correspond to the critical temperature and pressure of each component and R is the universal gas constant. Once b_i has been obtained from each natural gas component, proceed to calculate b using Equation (16)

Then, to calculate the factor a you need to know a_{ij} by the following equation:

$$a_{ij} = \left(1 - d_{ij}\right) a_i^{1/2}\, a_j^{1/2} \qquad (18)$$

Where d_{ij} a binary interaction coefficient is determined empirically The following equation is used for the calculation of each component's a_i coefficient:

$$a_i = a_i(T_c) \cdot \propto (T_r, \omega) \qquad (19)$$

Where $a_i(T_c)$ is calculated from the critical temperature and pressure of each component using the following equation:

$$a_i(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c} \qquad (20)$$

Alpha, $\propto$, is obtained from the following equation:

$$\propto^{1/2} = 1 + k\left(1 - T_r^{1/2}\right) \qquad (21)$$

Where T_r corresponds to the reduced temperature obtained by dividing the actual gas temperature for its critical temperature, for each component. To get k the following equation is followed:

$$k = 0.37464 + 1.5422\omega - 0.26992\omega^2 \qquad (22)$$

Where ω is a constant of each compound called the acentric factor. Knowing this data can be performed in accordance with Equation (15) for the calculation of factor a. Table A.1 and Table A.2 (Appendix A) show the critical properties and binary interaction coefficients for each of the components considered in the study.

Once the factors a and b are known, the cubic polynomial raised in Equation (14) whose roots respond to the compressibility factor Z from which the molar volume can be resolved:

$$v = \frac{PZ}{RT} \tag{23}$$

And by dividing the average molecular weight of the gas for the molecular volume the density is obtained according to the following equation:

$$\rho = \frac{\overline{PM}}{v} \tag{24}$$

3.3. Calculation of the Viscosity of Natural Gas

For the calculation of natural gas a mathematical adjustment made by Jarrahian and Heidaryan (2014) were taken which propose a simple method for calculating the viscosity of natural gas current[32]. The equation for the calculation is as follows:

$$\mu = \mu_{1atm}\left[1 + \frac{A_{11}}{T_{pr}^{5}}\left(\frac{P_{pr}^{4}}{T_{pr}^{20} + P_{pr}^{4}}\right) + A_{12}\left(\frac{P_{pr}}{T_{pr}}\right)^{2} + A_{13}\left(\frac{P_{pr}}{T_{pr}}\right)\right] \tag{25}$$

It depends on the viscosity to one atmosphere (μ_{1atm}), pressure (P_{pr}) and temperature (T_{pr}) pseudo-reduced and A_i are empirical constants. Table A.3 (Appendix A) shows the data of these empirical constants.

The following equation is used for the calculation of viscosity to an atmosphere:

$$\mu_{1atm} = \mu_{1atm}^{uncorrected} + \Delta\mu_{N_2} + \Delta\mu_{CO_2} + \Delta\mu_{H_2S} \tag{26}$$

where:

$$\mu_{1atm}^{uncorrected} = \left(A_1\gamma_{gMix}^{A_2}\right)(T - 459.67) + A_3 + A_4 Log\left(\gamma_{gMix}\right) \tag{27}$$

$$\Delta\mu_{N_2} = y_{N_2}\left(A_5\, Log\left(\gamma_{gMix}\right) + A_6\right) \tag{28}$$

$$\Delta\mu_{CO_2} = y_{CO_2}\left(A_7\, Log\left(\gamma_{gMix}\right) + A_8\right) \qquad (29)$$

$$\Delta\mu_{H_2S} = y_{H_2S}\left(A_9\, Log\left(\gamma_{gMix}\right) + A_{10}\right) \qquad (30)$$

Where γ_{gMix} is the specific gravity of the gas that is calculated as follows:

$$\gamma_{gMix} = \frac{M}{w_{air}}\sum y_i Mw_i \qquad (31)$$

M corresponds to the average molecular weight of the gas, w_{air} is the molecular weight of the air and y_i is the molar composition of the gas.

Pseudo-reduced pressure and temperature are then calculated as follows:

$$P_{Pr} = \frac{P}{P_{Pc}} \qquad (32)$$

$$T_{Pr} = \frac{T}{T_{Pc}} \qquad (33)$$

Where P_{Pc} and T_{Pc} are pressure and psedocritical temperature that are obtained from the following equations:

$$P_{Pc} = \frac{P^{**}_{pcMix}T^{**}_{pcMix}}{T^{**}_{pcMix} + y_{H_2S}\left(1 - y_{H_2S}\right)\left(120\left(y_{CO_2} + y_{H_2S}\right)^{0.9} + \left(y_{CO_2} + y_{H_2S}\right)^{1.6}\right) + 15\left(y^{0.5}_{H_2S} + y^{4}_{H_2S}\right)} \qquad (34)$$

$$T_{Pc} = T^{**}_{pcMix} - 120\left(\left(y_{CO_2} + y_{H_2S}\right)^{0.9} + \left(y_{CO_2} + y_{H_2S}\right)^{1.6}\right) + 15\left(y^{0.5}_{H_2S} + y^{4}_{H_2S}\right) \qquad (35)$$

where:

$$P^{**}_{pcMix} = \left(1 - y_{N_2} - y_{CO_2} - y_{H_2S}\right)P^{*}_{pcHC} + y_{N_2}P_{cN_2} + y_{CO_2}P_{cCO_2} + y_{H_2S}P_{cH_2S} \qquad (36)$$

$$T^{**}_{pcMix} = \left(1 - y_{N_2} - y_{CO_2} - y_{H_2S}\right)T^{*}_{pcHC} + y_{N_2}T_{cN_2} + y_{CO_2}T_{cCO_2} + y_{H_2S}T_{cH_2S} \qquad (37)$$

To obtain P^{*}_{pcHC} and T^{*}_{pcHC} the following equation are used:

$$P^{*}_{pcHC} = 671.1 + 14\gamma_{gHC} - 34\gamma^{2}_{gHC} \qquad (38)$$

$$T^{*}_{pcHC} = 120.1 + 429\gamma_{gHC} - 62.9\gamma^{2}_{gHC} \qquad (39)$$

and;

$$\gamma_{gHC} = \frac{\gamma_{gMix} - \left(M_{N_2}y_{N_2} + M_{CO_2}y_{CO_2} + M_{H_2S}y_{H_2S}\right)/M_{air}}{1 - y_{N_2} - y_{CO_2} - y_{H_2S}} \tag{40}$$

3.4. Numerical Solution to Ergun Equation

Given that the density and viscosity of the gas are in dependence on the pressure and these are calculated with complex procedure the differential equation of Ergun cannot be solved analytically so that a numeric method is chosen, the numerical method used is Runge-Kutta fourth order.

The Runge-Kutta fourth order method provides a solution to first-order differential equations $\frac{dy}{dx} = f(x, y)$ and as a result yields a table of the solution function with y values corresponding to x specific values[33]. However, is necessary to know the range of x, the value of y for a point x. For this, the method determines constants in such a way that the equation is as follows:

$$x_{i+1} = x_i + h \tag{41}$$

$$y_{i+1} = y_i + \frac{1}{6}h(K_1 + 2K_2 + 2K_3 + K_4) \tag{42}$$

where constants are determined in the following ways:

$$K_1 = f(x_i, y_i) \tag{43}$$

$$K_2 = f\left(x_i + \tfrac{1}{2}h, y_i + \tfrac{1}{2}K_1h\right) \tag{44}$$

$$K_3 = f\left(x_i + \tfrac{1}{2}h, y_i + \tfrac{1}{2}K_2h\right) \tag{45}$$

$$K_4 = f(x_i + h, y_i + K_3h) \tag{46}$$

and h correspond to:

$$h = \frac{x_n - x_i}{N} \tag{47}$$

Applying the Runge-Kutta method to the Ergun equation the results obtained are a table with the values of pressure that correspond at a specific height and could be represented graphically as shows in Figure 8.

For the value of N an arbitrary value of 100 was taken, which are the sections in which the height of the packaging is divided, in addition for each point the calculation of the density and viscosity of the gas must be performed as the pressure changes.

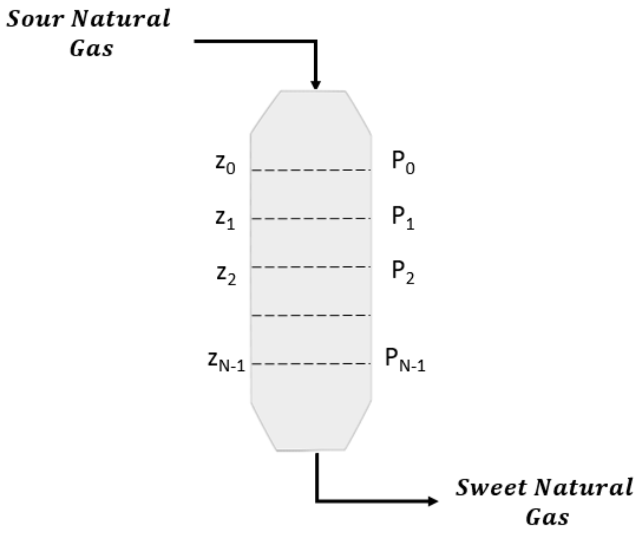


Figure 8. *Results obtained by the Runge-Kutta method apply at Ergun equation*

3.5. Fluid-dynamic Model Input Data and Case Studies

When the equations and calculations required for the model are set, the input data required by the model is shown in Table 3. This data corresponds to the characteristics of natural gas as its composition and operating conditions. In addition, the characteristics of the fixed bed are required.

Table 3. *Input data of the fluid-dynamic model*

Natural Gas Stream		**Fixed Bed**	
Composition	y_i	Fixed bed height	z
H_2S concentration	$y_{o\ H_2S}$	Fixed bed diameter	D_{emp}
Pressure	P	Particle diameter	D_p
Temperature	T	Empty fraction or Porosity	$\emptyset$
Flowrate	Q_G	Sphericity	φ
H_2S specification	$y_{f\ H_2S}$	Packed density	ρ_{emp}
		Adsorption capacity	CA_{emp}

The output data delivered by the model are the ones shown in Table 4, the most important are the pressure drop and fixed bed replenishment time, since these data are predictive and help when operating the adsorption tower.

Table 4. *Output data from de fluid-dynamic model*

Natural Gas Stream		**Fixed Bed**	
Density	ρ	Pressure drop	ΔP
Viscosity	μ	Packing duration time	t_{emp}
Gas Velocity	u	H_2S mass removed	$m_{H_2S\ T}$
Residence Time	τ		

To test the model a base case was raised, for this the properties of the gas from the Shushufindi Field shown in Table 1, and the characteristics of the commercial solid sorbent Sulfatreat shown in Table 2 were used as data. In addition, a packing diameter of 120 inches and a diameter height ratio of 3 inches were considered

Subsequently, 2500 case studies were raised based on the base case and from this the characteristics of the bed were changed and the properties of natural gas were varied in order to analyze how these affect the pressure drop of natural gas. As shown in Table 7 the cases were varied within a certain range and in the case of natural gas composition the gas from Bloque 10 and the gas plant shown previously in Table 2 was taken as references.

Table 3. *Case studies for the analysis of the fluid-dynamic model*

Properties		Base Case	Minimum	Maximum
Natural gas stream	**Composition**	Shushufindi	Bloque 10	PG
	H_2S content [ppm]	300	150	450
	Pressure [psia]	500	50	750
	Temperature [°F]	80	60	100
	Flow rate [MMPCED]	25	2.5	100
	H_2S specification [ppm]	4	2	10
Solid	**Adsorption capacity**	0.2	0.05	0.8
	Particle diameter [cm]	0.5	0.1	1.5
	Sphericity [-]	1	0.5	1
	Empty fraction or Porosity [-]	0.4	0.2	0.7
	Packing density [lb/ft^3]	75	50	100
	Packing diameter [in]	120	12	132
	Height/Diameter ratio	3	2	4

3.6. Complementary Calculations

1. Packing duration time calculation:

$$t_{emp} = \frac{m_{H_2S\,T}}{Q_{H_2S}} \qquad (48)$$

where:

$$Q_{H_2S} = \frac{Q_G\,(y_{o\,H_2S} - y_{f\,H_2S})\,PM_{H_2S}}{v_e} \qquad (49)$$

2. Calculation of linear gas speed:

$$u = \frac{4 \cdot Q_G}{\pi \cdot D_{emp}^2} \qquad (50)$$

3. Residence time:

$$\tau = \frac{z}{u_g} \qquad (51)$$

Parameter 1 refers to the time when the bed stopped removing H_2S from the natural gas stream. This parameter is of importance as it allows the realization of operational bed planning, that is, it helps to plan the time in which the bed should be replaced and maintenance of the tower.

CHAPTER IV

4. REACTIVITY MODEL PROPOSAL

Since all the equations shown in Chapter III only consider the dynamic fluid appearance, it is necessary to develop a model that contemplates aspects of the reaction between the solid and the gas.

Analyzing from the engineering point of view, what happens in the solid bed, as shown in the Figure 7. First the H_2S molecules around the solid (a) are adhere to the surface of the solid (b) and subsequently the reaction between iron oxide and hydrogen sulfide occurs (c).

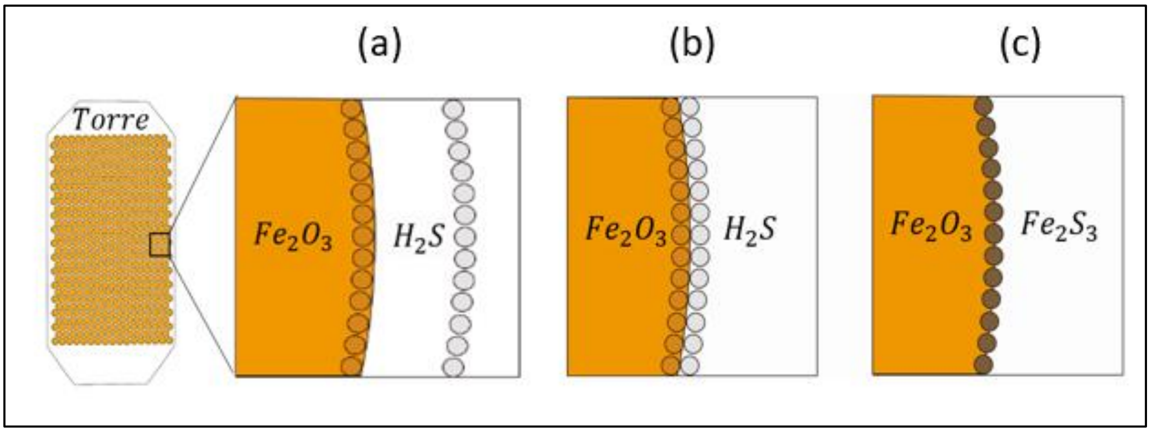


Figure 9. *Adsorption of H_2S in the surface of a particle and reaction with Fe_2O_3*

The volume of the unit cell of iron oxide Fe_2O_3 considering a R$\bar{3}$c [167] structure changes when it reacts and it is converted to iron sulfide Fe_2S_3 with a R$\bar{3}$c [167] structure. Know that the volume of unit cells of Fe_2O_3 is 105.430 Å[34] and the volume of Fe_2S_3 is 140.782 Å [35] is possible calculate the relation between both as show in the Equation (52).

$$f_{\Delta V} = \frac{V_{Fe_2S_3}}{V_{Fe_2O_3}} = 1.335 \qquad (52)$$

The ratio between the two volumes indicates that the volume of the particle increases at the end of the reaction. Therefore, the particle diameter increase due to consumption in the reaction of iron oxide and subsequently to the incorporation of the iron sulfide product. In addition, since the diameter of the particle increase the empty fraction should decrease.

Figure 10 shows a comparison between the reacted bed and unreacted bed. Because of the incorporation of Fe_2S_3 at the surface of particles the ratio r_1 is higher than ratio r_2. Add more, the distance between the particles d decreased due to incorporation of Fe_2S_3.

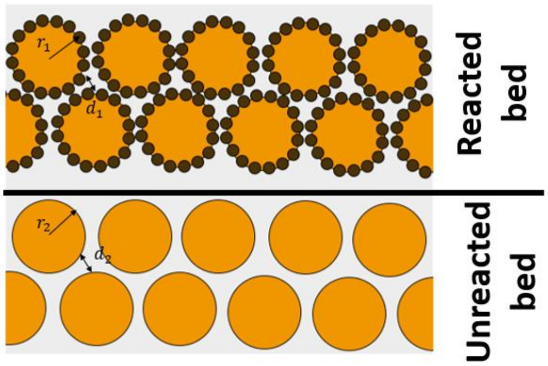


Figure 10. *Comparison between reacted and unreacted bed*

4.1. Particle Diameter Variation Calculation

To know what the change in diameter in the particle was first it is necessary to know what amount in mass of hydrogen sulfide was adsorbed by each particle in the packaging considering that the distribution is uniform:

$$m_{H_2S\,p} = \frac{m_{H_2S\,T}}{n_p} \qquad (53)$$

where:

$$m_{H_2S\,T} = V_{emp} \cdot \rho_{emp} \cdot CA_{emp} \qquad (54)$$

$$n_p = V_{emp}\frac{(1-\emptyset)}{V_p} \quad (55)$$

Subsequently, the mass of iron oxide that reaction per particle is calculated, Equation (51), and the volume corresponding to it, Equation (52), considering the reaction raised in the premises.

$$m_{Fe_2O_3\,p} = \frac{1}{3}\cdot\frac{PM_{Fe_2O_3}}{PM_{H_2S}}\cdot m_{H_2S\,p} \quad (56)$$

$$V_{Fe_2O_3\,p} = \frac{m_{Fe_2O_3\,p}}{\rho_{Fe_2O_3}} \quad (57)$$

Where the coefficient 1/3 corresponds to the stoichiometry ratios.

To obtain the particle volume variation due to the reaction the following equation is followed:

$$\Delta V_p = V_{Fe_2O_3\,p}(f_{\Delta V}-1) \quad (58)$$

The variation of the particle radius is then calculated by dividing it for the surface area of the particle, Equation (59), and finally the diameter of the particle is find Equation (60).

$$\Delta r_p = \frac{\Delta V_p}{A_{sp}} \quad (59)$$

$$D_{fp} = D_p + 2\Delta r_p \quad (60)$$

4.2. Empty Fraction Change Calculation

The calculation of the new empty fraction stars by the following equation:

$$\emptyset_f = 1 - \frac{V_{fp}}{V_{emp}} \quad (61)$$

Where V_{fp} corresponds to the total volume of bed particles after the reaction. Knowing that the total volume of the particles is equal to the total volume of the particles before the reaction plus the particle volume variation:

$$V_{fp} = V_{tp} + n_p{}^{\circ}\Delta V_p \qquad (62)$$

Therefore;

$$\emptyset_f = 1 - \frac{V_{tp} + n_p{}^{\circ}\Delta V_p}{V_{emp}} \qquad (63)$$

Reordering we have to:

$$1 - \frac{V_{tp}}{V_{f\ emp}} + \frac{n_p{}^{\circ}\Delta V_p}{V_{emp}} \qquad (64)$$

Where, $\frac{V_{tp}}{V_{f\ emp}}$ is the empty fraction before the reaction, therefore:

$$\emptyset_f = 1 - \emptyset_o + \frac{n_p{}^{\circ}\Delta V_p}{V_{emp}} \qquad (65)$$

4.3.Integration of Fluid-dynamic Model with H_2S Reactivity Model Proposal

To integrate the reactivity to the fluid-dynamic model was required to divide the packed bed into three main zones: reacted bed zone, H_2S removal zone and unreacted bed zone. Each of this zones have different characteristics as show the Figure 11.

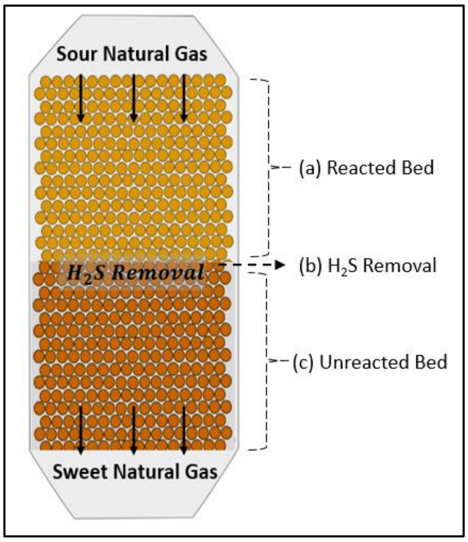


Figure 11. *Fixed bed divided in reacted bed zone, adsorption zone and unreacted bed zone.*

Reacted bed zone: in this area of the bed the reaction between the gas and the solid is already considered to have been carried out and the calculations of the Ergun equation in this region are given considering the following aspects:

- Particle diameter has increased due to reaction, therefore D_{fp} diameter is used for the calculus.
- Empty Fraction has decreased due to the reaction, therefore $\emptyset_f$ void fraction is used for the calculus.
- The amount of moles of H_2S remains the same as at the input.

H_2S removal zone: in this area is where the reaction is occurring. Therefore, pressure drop is calculated as a result of removing the moles of hydrogen sulfide from de natural gas, for this the Equation of Peng-Robinson is used for this are considered the following aspects:

- Not considered fluid-dynamic aspects.
- The amount of H_2S moles are reduced to the natural gas output specification.

Unreacted bed zone: in this area it is considered that the reaction between the gas and the solid has not yet occurred. Therefore, calculations are carried out with the Ergun equation, considering the following aspects:

- Particle Diameter has not been increased due to the reaction by which the diameter D_p is used for the calculus.
- Empty Fraction has not decreased due to reaction, therefore void fraction $\emptyset$ is used for the calculus.
- The number of moles of H_2S remains constant to de output specifications.

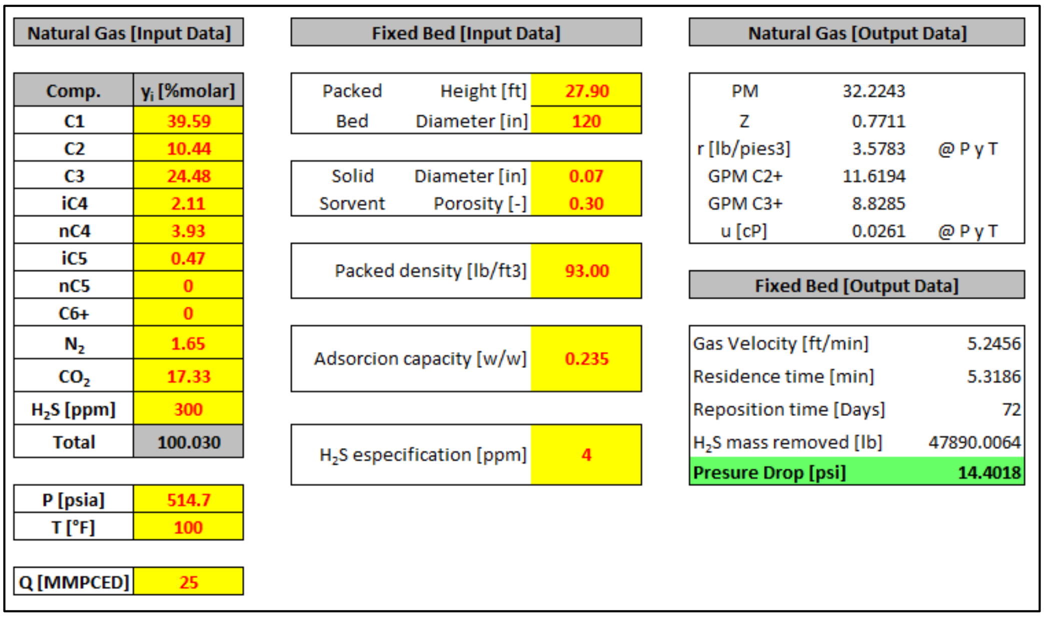
CHAPTER V

5. RESULTS

Below, there are the results obtained after developing the fluid-dynamic model and analyzing the data obtained from the case studies. The first results are the model which is proof in the base case to obtain an estimation of the pressure drop and then it was compared with a data provided by Schlumberger company for the same case. Then, the case studies data are analyzed trough graphics.

5.1. Fluid-dynamic Model and Base Case

As shown in Figure 12, the fluid-dynamic model data corresponds to the properties of the gas and properties of the fixed bed of base case, where the replenishment time indicates the number of days that the adsorption tower can operate satisfying the H_2S output specifications for natural gas.



Natural Gas [Input Data]

Comp.	y_i [%molar]
C1	39.59
C2	10.44
C3	24.48
iC4	2.11
nC4	3.93
iC5	0.47
nC5	0
C6+	0
N_2	1.65
CO_2	17.33
H_2S [ppm]	300
Total	100.030

P [psia]	514.7
T [°F]	100

Q [MMPCED]	25

Fixed Bed [Input Data]

Packed	Height [ft]	27.90
Bed	Diameter [in]	120

Solid	Diameter [in]	0.07
Sorvent	Porosity [-]	0.30

Packed density [lb/ft3]	93.00

Adsorcion capacity [w/w]	0.235

H_2S especification [ppm]	4

Natural Gas [Output Data]

PM	32.2243	
Z	0.7711	
r [lb/pies3]	3.5783	@ P y T
GPM C2+	11.6194	
GPM C3+	8.8285	
u [cP]	0.0261	@ P y T

Fixed Bed [Output Data]

Gas Velocity [ft/min]	5.2456
Residence time [min]	5.3186
Reposition time [Days]	72
H_2S mass removed [lb]	47890.0064
Presure Drop [psi]	**14.4018**

***Figure 12**. Capture of the fluid-dynamic model with the case base data*

The most important result presented by the fluid-dynamic model is the pressure drop across the adsorption tower (Figure 13). In the first instance it can be seen that the pressure drop estimated by the model without the adsorption of H_2S follows the same linear tend and is less than the pressure drop of the H_2S reactivity model proposed in this study.

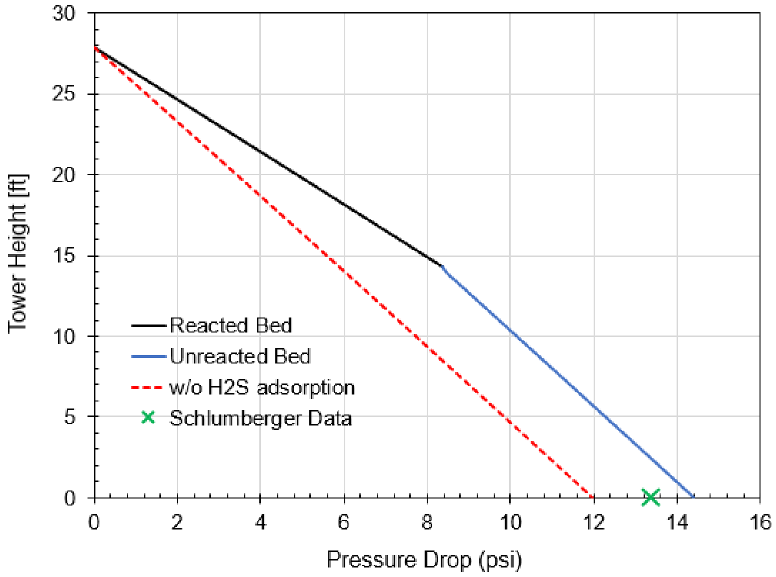


Figure 13. Comparison of pressure drop for base case

Moreover, the pressure drop of the model that includes the H_2S adsorption is shown, in this it can observe three zones (as shown in reactivity model proposal, Figure 11). The first corresponds to the pressure drop of the bed that reacted with the H_2S, it can be seen that it has a different linear trend to the model without H_2S adsorption. This is because of the change in particle diameter and empty fraction due to hydrogen sulfide removal reaction, also this different trend indicates that in the zone of the reacted bed the pressure drop is higher.

The adsorption zone corresponds to the region on the chart where there is a sudden change in trend. This is due to the abrupt disappearance of H_2S molecules from the gas phase resulting from the chemical reaction of sulfides formation[5]. The last region corresponds to the bed without reacting, the trend is linear and equal to that of the model without H_2S adsorption.

The pressure drop estimate by de model is compare with a data provided by Schlumberger company for the same case, and it correspond to value of 13.35 psi[25] as show in the

Figure 13. The value calculated by de model without reaction corresponded to 11.93 psi a value that approximate. However, the value closer at the Schlumberger data is the value calculated with the H_2S model that correspond to 14.40 psi. Therefore, the reactivity model proposed in this study gives a better approximation.

The increase in pressure drop is given by the removal of H_2S molecules of natural gas and the increment of the particle diameter and the decrease in the empty fraction of packed bed. Therefore, is expected that the pressure drop estimated with H_2S adsorption model is higher in all cases. This can be to prove in Figure 14 that plots the pressure drop results of case studies considering H_2S adsorption versus pressure drop without considering H_2S adsorption. As it can see, the pressure drop estimated considering H_2S adsorption is greater for all cases. This prove that the increase in particle diameter and the decrease of the empty fraction due to the reaction in the bed favor the pressure drop.

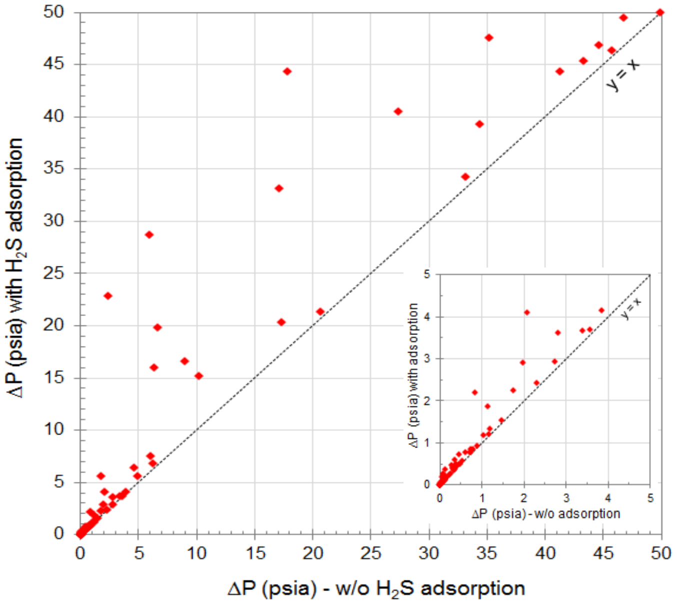


Figure 14. *Comparison of the case studies with and without reactivity*

5.2. Influence of Natural Gas Properties

In order to better analysis of the data obtained from de case studies, the results are arranged at the follow: the pressure drop is classified like “low pressure drop” (<5 psi), “mean pressure drop” (5-100 psi) and high pressure drop (>100psi). Generally, a pressure drop less than 5 psi is the expected in this type of natural gas sweetening processes[15]. Similarly, relative importance is established as the ratio between the number of cases that meet specific conditions. For example, the number of cases that considerate a value of 0.3 for empty fraction divided for the number of the total cases.

Natural gas source: as can be seen in Figure 15 (a), there is a predominance for cases with low pressure in all natural gas currents. However, the same Figure indicates that natural gas from Bloque 10 is the one with the most cases where the pressure drop is less than 5 psi followed by Shushufindi Field and finally by the Shushufindi Gas Plant. The preference for medium and high pressures is going the other way, with the Shushufindi Gas Plant with the most cases in favor.

It is important to emphasize that the natural gas from Bloque 10 has less amount of heavy compounds than the Shushufindi Field and the Shushufindi Gas Plant. This indicates that the pressure drop would can be favored when the heavier hydrocarbons is presented into natural gas streams.

Natural gas flow: as can be seen in the Figure 15 (b), there is a strong preference that indicates lower flow rates favor cases where the pressure drop is less than 5 psi. While higher flow rates favor cases where the pressure drop is medium and high. For an adsorption tower of fixed dimensions (diameter and height), increases in the natural gas flowrate indicates that there is greater mass per unit of cross section, which increases the friction between the molecules when crossing the bed, advantaging the pressure drop.

Input and output H_2S concentrations: as can be seen from the Figure 15 (c) and (d), the relationship between H_2S concentration and pressure drop affect to a small extent. This is because the low amounts of H_2S present in the gas are not fluid-dynamic significant. From an engineering point of view, adsorption processes are recommended to treat natural gas streams with H_2S concentrations below 500 ppmv[15].

Operating Pressure: corresponds to the pressure at which the gas enters the adsorption tower. In the Figure 15 (e) you can see a strong preference that favors cases of low pressure drop as the inlet pressure is higher.

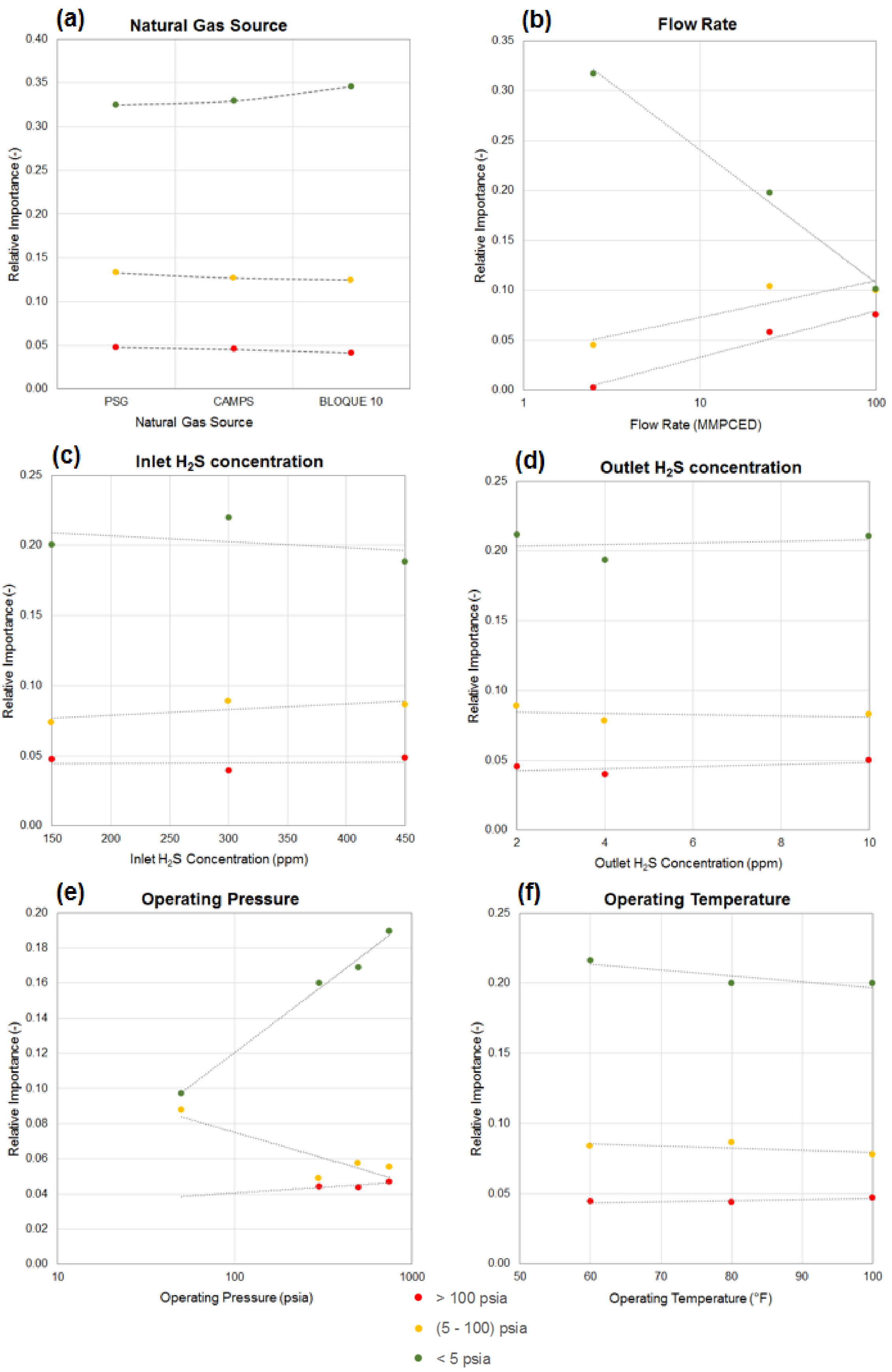


Figure 15. *Operating Conditions vs. fluid-dynamic performance*

Operating temperature: The Figure 15 (f) can be observed cases of low pressure drop predominate in the temperature range shown. In addition, there is a slight preference that favors cases of low pressure drop as the temperature decreases.

5.3. Influence of Adsorbent Characteristics

H_2S adsorption capacity: Figure 16 (a) shows that cases with low pressure drop are best favored than cases of medium and low pressure drop. In addition, cases with low pressure follow a preference that indicates that for lower adsorption capabilities this case is favored. This is because the adsorption capacity is directly related to the amount of H_2S that can be extracted, the more H_2S is extracted from the gas the greater the pressure drop.

Particle size: Figure 16 (b) shows the influence of the particle diameter on pressure drop. It can be seen that for larger diameters cases with pressure drop less than 5 psi are favored. While for small diameters the cases that are favored are those of medium and high pressure drop. This is due to the interaction between the gas and the solid. The larger particle size, more space is going to exist for the gas to pass through the adsorption tower.

Shape factor or sphericity: Figure 16 (c) shows how the form factor influences pressure drop. It can be noted that low pressure drop is favored with particles whose geometry is more similar to that of a sphere. On the other hand, for cases with a medium and high pressure drop, a clear preference cannot be observed. The form factor influences in this way as for more spherical particles the gas will have less resistance for its passage through it. particles sphericity depends on the manufacturing process (e.g. pelletizing) and the mechanical resistance of sorbents[2].

Empty fraction or porosity**:** this is one of the fundamental aspects in an adsorption package, as can be seen in Figure 16 (d), the larger empty fraction cases with low pressure drops are favored. This means that at a higher empty fraction the pressure drop is smaller. This is because a larger fraction of vacuum indicates that there is more space for the gas to pass through the packaging freely.

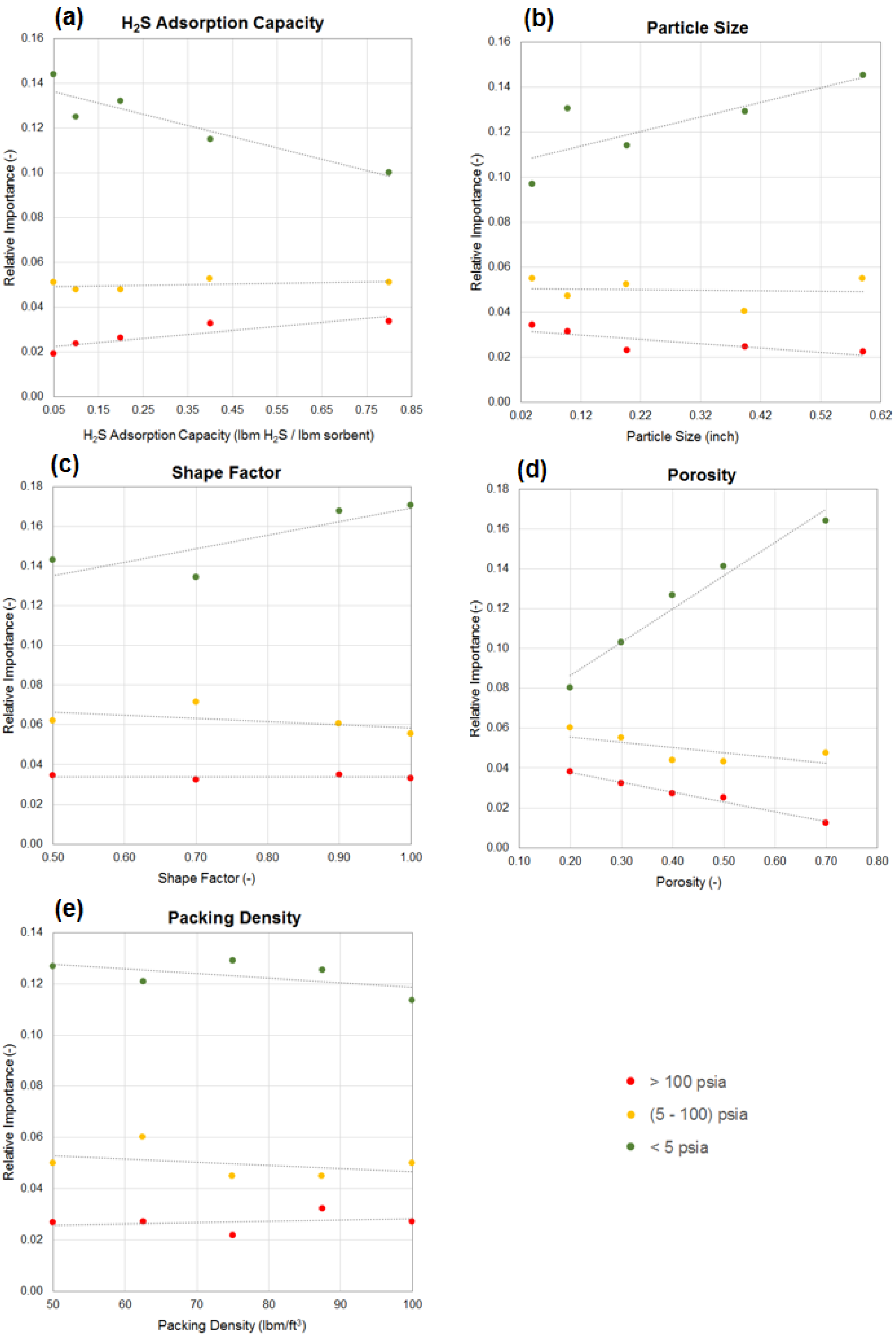


Figure 16. *Sorbent properties vs. fluid-dynamic performance*

Packing density: Figure 16 (e) shows how the packing density affects pressure drop. It shows that cases of drop below 5psi are favored for lower packing densities. This is directly related to the amount of particles in the packaging, so the more particles there are more resistance will put in so that the gas can flow, which results in a greater drop in pressure.

In addition, one can have factors that correspond to sizing, these are the vessel diameter and the ratio diameter - height. As Figure 17 (a) shows there is a strong trend for cases of pressure drop less than 5 psi being favored as the diameter increases while for cases of medium and high pressure drop are favored when the diameter decreases.

Figure 17 (b) shows the ratio diameter - height, where it is seen that for cases of pressure drop less than 5 psi are favored when the lower the diameter height ratio, this means that the lower the height of the tower there will be a lower pressure drop. Cases of medium and high pressure are favored the lower the height of the tower. Finally, there are many variables that affect the fluid dynamic behavior of an adsorption tower and it is important to take them into account at the time of the tower's operation.

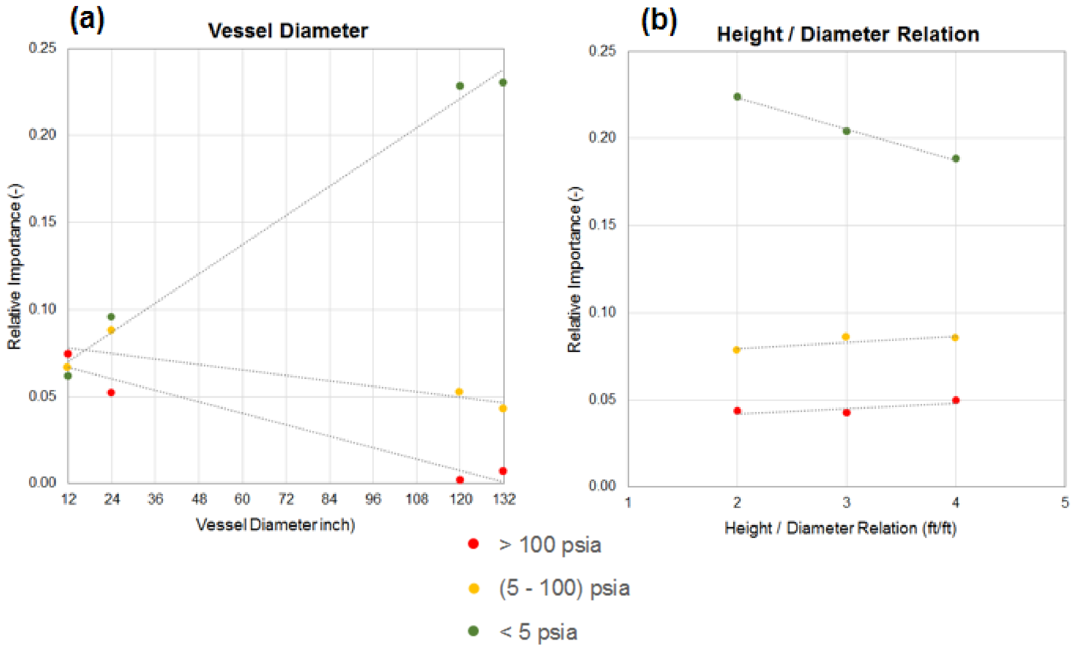


Figure 17. *Vessel sizing vs. fluid-dynamic performance.*

CHAPTER VI

6. CONCLUSIONS AND RECOMMENDATIONS

Analysis of the case studies showed how the properties of the gas and the characteristics of the fixed bed influence the drop in pressure of the fixed bed. However, there are factors in both gas and the fixed bed that influence more strongly than others. These predominant factors are: natural gas inlet pressure, natural gas flow, fixed bed porosity and fixed bed packaging diameter.

The inlet pressure is inversely proportional to the pressure drop, the flow of the natural gas is directly proportional to the pressure drop, the porosity is inversely proportional to the pressure drop in the bed and the fixed bed packing diameter inversely proportional. Therefore, these are the aspects that should be taken into account in the process of natural gas sweetening by means of adsorption towers from the fluid- dynamic point of view.

Other factors that also significantly influence pressure drop are: form factor, particle diameter, adsorption capacity, and height of solid bed packaging. However, these factors affect to a lesser extent than those mentioned above. The trend of this is as follows: the particle diameter is inversely proportional to the pressure drop, the adsorption capacity is directly proportional to the pressure drop, the form factor is inversely proportional to the pressure drop and the bed height is directly proportional to the pressure drop. These aspects should also be considered in the sweetening of natural gas by adsorption towers.

The factors that affect the pressure drop to a lesser extent are the temperature that affects the temperature proportionally and the composition of the natural gas that affects inversely proportional to the pressure drop. In addition, the concentration of H_2S at the gas inlet and the H_2S specification, from a fluid-dynamic point of view, are very low concentrations compared to hydrocarbons and these have little influence.

Finally, in an adsorption tower the pressure drop does not exceed 5 psi, the following should be considered: that the geometry of the particles be spherical and with non-small particle diameters, in addition to having a high porosity and being arranged in a high diameter packaging and the ratio of height to diameter is small. As for the properties of gases are for those that have a little heavy hydrocarbon content, and large flows.

Taking into account the conclusions, the recommendations are aimed at deepening the study about the effect of the concentration of H_2S on the natural gas stream in the pressure drop. In addition, it is an important recommended in future studies to take into account the influence of saturation water present in the gas as well as the formation of water in the H_2S reaction and the packed bed.

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APPENDIX A:

Physical Properties and Physical Constants

Table A.1: *Critical properties of typical natural gas compounds*[36]

	Tc (K)	Pc (MPa)	ω [-]
C_1	190.564	4.599	0.0115
C_2	305.32	4.872	0.0995
C_3	369.83	4.248	0.1523
iC_4	408.14	3.648	0.1808
nC_4	425.12	3.796	0.2002
iC_5	460.43	3.381	0.2275
nC_5	469.7	3.37	0.2515
nC_6	507.6	3.025	0.3013
N_2	126.2	3.4	0.0377
CO_2	304.21	7.383	0.2236
H_2S	373.53	8.963	0.0942

Table A.2: *Binary interaction parameters for the Peng-Robinson state of equation*[37]

	C_1	C_2	C_3	iC_4	nC_4	iC_5	nC_5	nC_6	N_2	CO_2	H_2S
C_1	--	-0.0026	0.014	0.0256	0.0133	-0.0056	0.023	0.0422	0.035	0.0919	0.085
C_2	-0.0026	--	0.0011	-0.0067	0.0096		0.0078	-0.01	0.05	0.1322	0.085
C_3	0.014	0.0011	--	-0.0078	0.0033	0.0111	0.0267	0.0007	0.08	0.1241	0.075
iC_4	0.0256	-0.0067	-0.0078	--	-0.0004				0.09	0.12	0.06
nC_4	0.0133	0.0096	0.0033	-0.0004	--		0.0174	-0.0076	0.09	0.1333	0.06
iC_5	-0.0056	0	0.0111	0	0	--			0.095	0.122	0.06
nC_5	0.023	0.0078	0.0267	0	0.0174	0	--		0.095	0.122	0.06
nC_6	0.0422	-0.01	0.0007	0	-0.0076	0	0	--	0.1	0.11	0.06
N_2	0.035	0.05	0.08	0.09	0.09	0.095	0.095	0.1	--	-0.017	0.18
CO_2	0.0919	0.1322	0.1241	0.12	0.1333	0.122	0.122	0.11	-0.017	--	0.1
H_2S	0.085	0.085	0.075	0.06	0.06	0.06	0.06	0.06	0.18	0.1	--

Table A.3: *Coefficients for calculating the viscosity using the Jarrahian and Heidaryan correlation*[32]

Coefficients	Value
A1	8.9775×10^{-6}
A2	-3.0481×10^{-3}
A3	1.0188×10^{-2}
A4	-2.9137×10^{-4}
A5	7.8189×10^{-4}
A6	3.8356×10^{-2}
A7	7.2996×10^{-4}
A8	5.8921×10^{-2}
A9	1.3683×10^{-3}
A10	2.2820×10^{-2}
A11	7.8634×10^{0}
A12	-9.0016×10^{-6}
A13	2.7814×10^{-1}