



A STUDY ABOUT CO₂/CH₄ SEPARATION USING POLYMERIC MEMBRANES

Elísio Fernandes de Almeida Quintino

Júlia de Andrade Stock

Graduation Project presented to the Petroleum
Engineering Course at Escola Politécnica,
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a partial fulfillment of the requirements for
the degree of Engineer.

Advisor: Regis da Rocha Motta

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FULFILLMENT TO OBTAIN THE DEGREE OF PETROLEUM ENGINEER.

Evaluated by:

Regis da Rocha Motta, Ph.D.

Thereza Cristina Nogueira de Aquino, D.Sc.

Eng^o Bernardo Cascon Neves

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Quintino, Elísio Fernandes de Almeida
Stock, Júlia de Andrade

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Preciso admitir que tenho a inegável incapacidade de transformar sentimentos em palavras. É como pintar um pôr-do-Sol apenas em tons de cinza: fica evidente que não se dispunha de cores suficientes, das cores certas, daquelas que retratariam a absoluta verdade fidedigna na tela. É assim que me sinto quando procuro as palavras em minha paleta. De todo modo, tentarei pincelar alguns borrões.

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Júlia de Andrade Stock

*"Jag gick i ett kvarter idag
Som en gång var min hela värld
Allting var ju enklare då
Men ingenting kan bli vad det var"
– Andreas Grega, "Mammas Gata"
med Promoe, Timbuktu och Supreme*

*"The value of a college education
is not the learning of many facts
but the training of the mind to think."
–Albert Einstein*

Abstract of the Graduation Project presented to Escola Politécnica/UFRJ as a partial fulfillment of the requirements to obtain the degree of Petroleum Engineer.

A STUDY ABOUT CO₂/CH₄ SEPARATION USING POLYMERIC MEMBRANES

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Júlia de Andrade Stock

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Advisor: Regis da Rocha Motta

Course: Petroleum Engineering

This work has two main objectives. The first one is to present an overview of the usage of polymeric membranes for CO₂/CH₄ separation. First, it is presented the need for this separation, focusing in the fact that high concentrations of CO₂ are expected in the pre-salt reservoirs in Brazil. Subsequently, different methods for the separation are presented in a comparative way, in order to give to the reader a broader sense about the state of the art in the technology for separations of gases. The technology of polymeric membranes is then discussed in more details, with attention to the physics that model the phenomena of selective permeation of gases through membranes. Technical description of the usage of membranes in separation systems and its equipment is also explored. The discussion about the membrane technology, which is the first objective of this work, gives enough comprehension of the subject to make it possible to develop the second objective, which is the development of a simple membrane system simulator. This simulator aims to represent a membrane separation system and it will be built using a procedure of reverse engineering: analyzing history data from the operation of a separation system and obtaining functions by data fitting in order to model the unknown parts of the physics behind the membrane systems. This procedure is useful when an enterprise wants to make decision about the operation of a membrane system but does not want to depend on the know-how kept by the membrane seller.

Keywords: Membranes, CO₂/CH₄ separation, Pre-salt reservoirs, Reverse engineering.

Resumo do Projeto de Graduação apresentado à Escola Politécnica/ UFRJ como parte dos requisitos necessários para a obtenção do grau de Engenheiro de Petróleo.

UM ESTUDO SOBRE A SEPARAÇÃO DE CO₂/CH₄ USANDO MEMBRANAS POLIMÉRICAS

Elísio Fernandes de Almeida Quintino

Júlia de Andrade Stock

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Orientador: Regis da Rocha Motta

Curso: Engenharia de Petróleo

Esse trabalho tem dois objetivos principais. O primeiro é apresentar o uso de membranas poliméricas para a separação de CO₂ e CH₄. Primeiro, é apresentada a necessidade dessa separação, focando no fato de que altas concentrações de CO₂ são esperadas nos reservatórios do pré-sal no Brasil. Subsequentemente, diferentes métodos para a separação são apresentados de maneira comparativa, a fim de dar ao leitor uma visão mais ampla acerca do estado da arte na tecnologia de separação de gases. A tecnologia de membranas poliméricas é então discutida em maiores detalhes, com atenção para a física que modela os fenômenos de permeabilidade seletiva de gases através de membranas. Uma descrição técnica do uso de membranas em sistemas de separação e seus equipamentos também é apresentada. A discussão sobre a tecnologia de membranas, que é o primeiro objetivo desse trabalho, dá compreensão suficiente sobre o assunto para possibilitar o desenvolvimento do segundo objetivo, que é o desenvolvimento de um simulador simples de um sistema de membranas. Esse simulador tem como objetivo representar um sistema de separação usando membranas e será construído usando um procedimento de engenharia reversa: analisar históricos de dados da operação de um sistema de separação e obter funções por ajuste de dados a fim de modelar a parte desconhecida da física por trás dos sistemas de membranas. Esse procedimento é útil quando uma empresa deseja tomar decisões acerca da operação de um sistema de membranas mas não quer depender do *know-how* mantido pelo vendedor de membranas.

Palavras-chave: Membranas, Separação CO₂/CH₄, Reservatórios do pré-sal, Engenharia reversa.

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1 INTRODUCTION

1.1 Research Objectives

The present work has two main objectives. The first one is to briefly present the technology of separation of gases using membranes, with mentions to its necessity in the petroleum industry and comparison with alternative technologies. This first part aims to be informative on its own and also to justify the need and furnish material for the second part, which is a study about simulation applied to the usage of systems of membranes in order to improve the quality of decisions related to these systems. An industry case study will be used as the background of the whole development, namely the project of FPSO Cidade de Paraty's separation system based on membranes technology, by the enterprise SBM.

Separation using membranes is an upcoming technology that has started to be widely applied for CO₂/CH₄ separation. When considering offshore structures and reservoirs containing high levels of carbon dioxide, the application of this technology was found to be very favorable, since it is an efficient system with relatively simple operation even under motion conditions. The industry case study considered here was originated from the fact that SBM is an offshore specialized company, producing vessels that will operate on pre-salt reservoirs, which implies that these vessels may have to deal with high CO₂ content in the production streams. Thus, the membrane technology is a clear and immediate option to be applied in SBM's projects.

One of the key motivations for the development of simulation methods is the fact that the knowledge about membrane specific technology aspects may be kept as an industrial secret by membrane separation systems' producers, in order to aggregate value to their product. In this case, the company that is buying the equipment has access only to history data regarding the upstream and downstream streams, and the membrane devices remain as a "black box". It can be profitable to these companies to be able to, given data from the production and separation, simulate different cases that are similar to the ones that produced the data, performing in this way sensitivity analysis, and calculate optimal operational variables in order to optimize this and other membrane

arrangements, thus becoming less dependent on the membrane supplier's confidential know-how. These features can be reached by use of a membrane system simulator.

Part of the information necessary to calculations was extracted from confidential data from the mass balance diagram of the membrane system of FPSO Cidade de Paraty. They were then analyzed and extrapolated to a more embracing situation, producing curves that will be used on our testing case. Since these data were obtained from an industry case, we believe that the study to be carried on can be of good use for further developments in the area.



Figure 1: FPSO Cidade de Paraty (SBM Archives)

1.2 Research Context

1.2.1 *The need for CO₂/CH₄ separation*

The composition of natural gas, whether it is produced from a condensed field or from free gas, may vary substantially from source to source. Although its desirable components are hydrocarbons, it also contains impurities such as water, small particles

and acid gases. Those contaminants may represent a threat during the production process; hence, it becomes necessary to remove them. [4]

Due to its high volume, gas is traditionally transported through long and highly pressurized pipes. Therefore the occasional presence of any quantity of acid gases may become dangerous as it will induce a corrosive environment. Analyzing the case of carbon dioxide, it is well known that, when in presence of water, it presents a relevant corrosive potential due to the formation of carbonic acid, fact that demands CO₂ removal from these streams.

It is also important to notice that CO₂ is an inert gas and therefore doesn't add heating value to the produced and transported gas, which leads to a waste on the pipeline capacity. Furthermore, the advent of LNG technologies exposes the gaseous mixture to extreme conditions of temperature and pressure, which may lead to dry ice formation (and possibly compromise the performance of the equipment) when CO₂ is present in sufficient quantities.

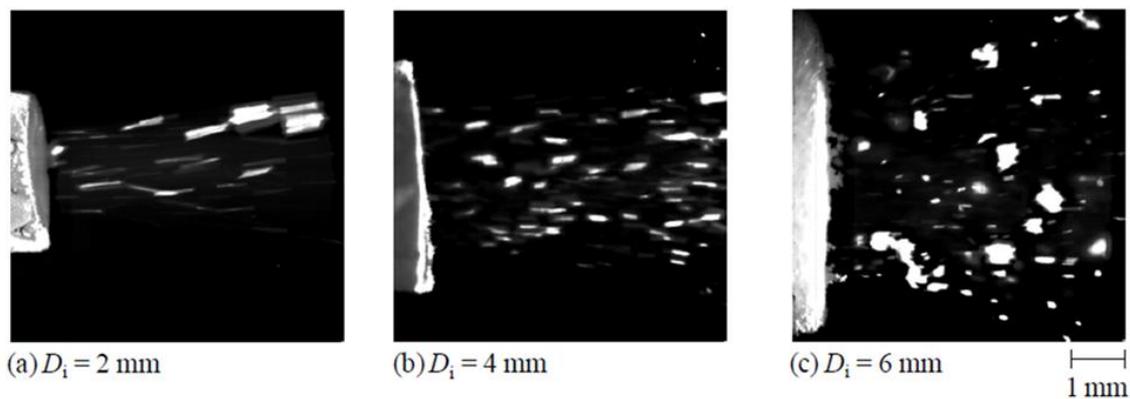


Figure 2: Dry ice formation on different diameter pipes introducing a blockage risk [18]

CO₂ extraction from natural gas is also motivated by the emergence of new Enhanced Oil Recovery techniques, in which the supercritical form of CO₂ is injected in the well with the intention of reducing oil's viscosity and consequently decreasing its resistance from flowing. It is a very suitable technique for reservoirs where water injection is not a convenient technique due to capillarity effects or when increase on the recovery rate is required. Besides, permanent CO₂ sequestration rises as a promising

field, as it offers the potential to provide a permanent sink for CO₂ industrial emissions. [6]

1.2.2 Membranes technology overview

The concept of membrane separation was originally proposed by Graham in 1866 as initially the majority of membranes research was directed towards reverse osmosis. Gas separation membranes were first commercialized in 1977. During the 1980s and 1990s, Cynara, Separex and Generon led to substantial innovations on membrane materials, which have improved the gas separation efficiency and membrane durability, making gas separation using membranes commercially competitive. [15]

Membranes act as filters to separate one or more gases from a feed mixture and to generate a specific gas rich permeate or a specific gas retentate (or Non-Permeate). It is based on the principle that some gases permeate the membrane more rapidly than others, since the permeation rate for a given gas component will be dependent on its molecular size, its solubility in the membrane polymer and operational conditions. The permeation rate will be dependent mostly on the differential partial pressures through the membrane, membrane's permeability and the area exposed to the flow on each side.

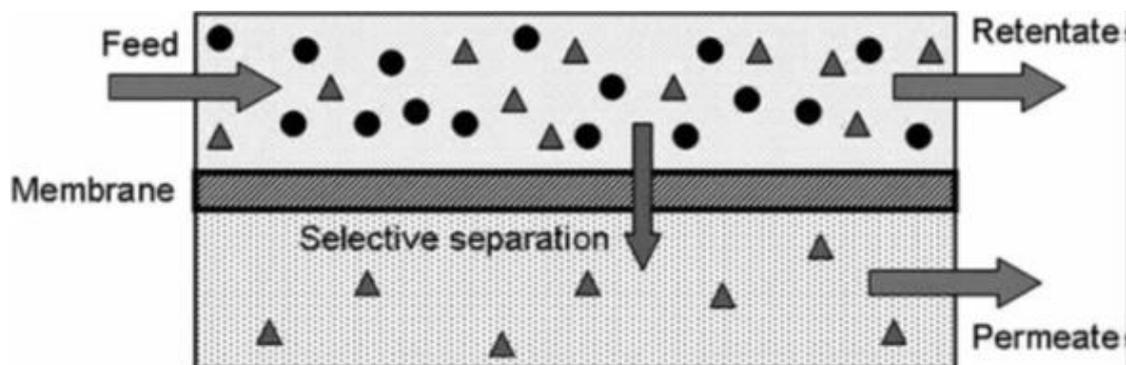


Figure 3: Scheme of membrane gas separation [15]

The first CO₂/CH₄ separation membranes were based on cellulose acetate and derivatives. They were characterized by a thin, dense and selective layer that would separate both gases by the difference in their permeation coefficient through the membrane. However, the practical application of the concept proved to be challenging, since the membranes were very fragile due to their composition and thickness, lacking

the mechanical strength necessary for any industrial process. In order to change this scenery, a different membrane (now asymmetric) was developed; it consisted on the already proposed thin and dense layer supported by a less dense, porous layer. In this configuration, the dense layer participates in the separation as the selective material, whereas the porous layer provides sufficient mechanical resistance and increases the area exposed to flow on the permeate side, which will enhance gas permeation.

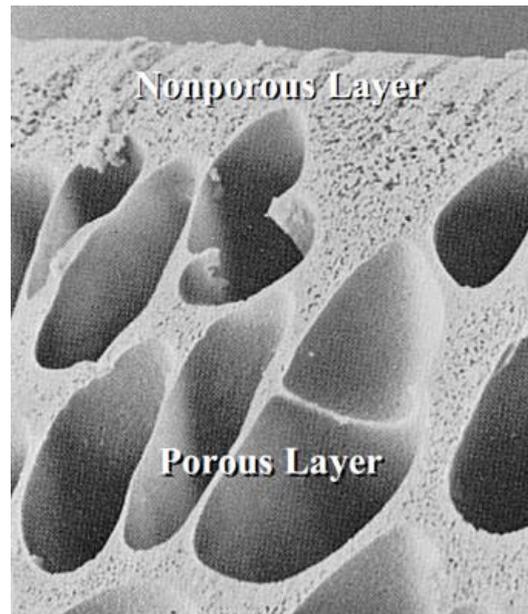


Figure 4: Asymmetric membrane structure [4]

The first membrane systems to separate carbon dioxide from natural gas were introduced by Grace Membrane Systems (a division of W.R. Grace), Separex (now part of UOP), and Cynara (now part of Natco). These companies used the previously mentioned anisotropic cellulose acetate membrane, produced using the Loeb-Sourirajan technique (involving precipitation of a casting solution by immersion in a non-solvent bath).

However, a further development of CO₂ permeable materials is beginning to challenge traditional polymeric membranes. Although cellulose acetate membranes are still widely used, newer membranes such as the polyimide membranes (made by Medal, a division of Air Liquide) are starting to be industrially produced and commercialized. One of the reasons for that is that the flux through Cellulose Acetate membranes decreases substantially with the time, due to the plasticization (reaction between CO₂

and the polymeric chain) and compaction of the material (low mechanical strength). In fact, the presence of a differential pressure through the membrane will induce the collapse of the pores, decreasing the exposed area to flow, which will affect membrane's performance. Since polyamide membranes are less reactive and more resistant, cellulose acetate is slowly being replaced by them. [1]

In order for membranes to be used in a commercial separation system, they must be packaged in a manner that supports the membrane and facilitates handling of the two product gas streams. These packages are generally referred to as elements or bundles. The most common types of membrane elements in use today for natural gas separation are the spiral-wound type and the hollow-fiber type. [5]

1.2.2.1 Membrane elements

Spiral-wound elements (Figure 5) consist of one or more membrane leaves. Each leaf contains two membrane layers separated by a rigid, porous, fluid-conductive material called the permeate spacer. The spacer facilitates the flow of the permeate gas, an end product of the separation. Another space, the high pressure feed spacer, separates

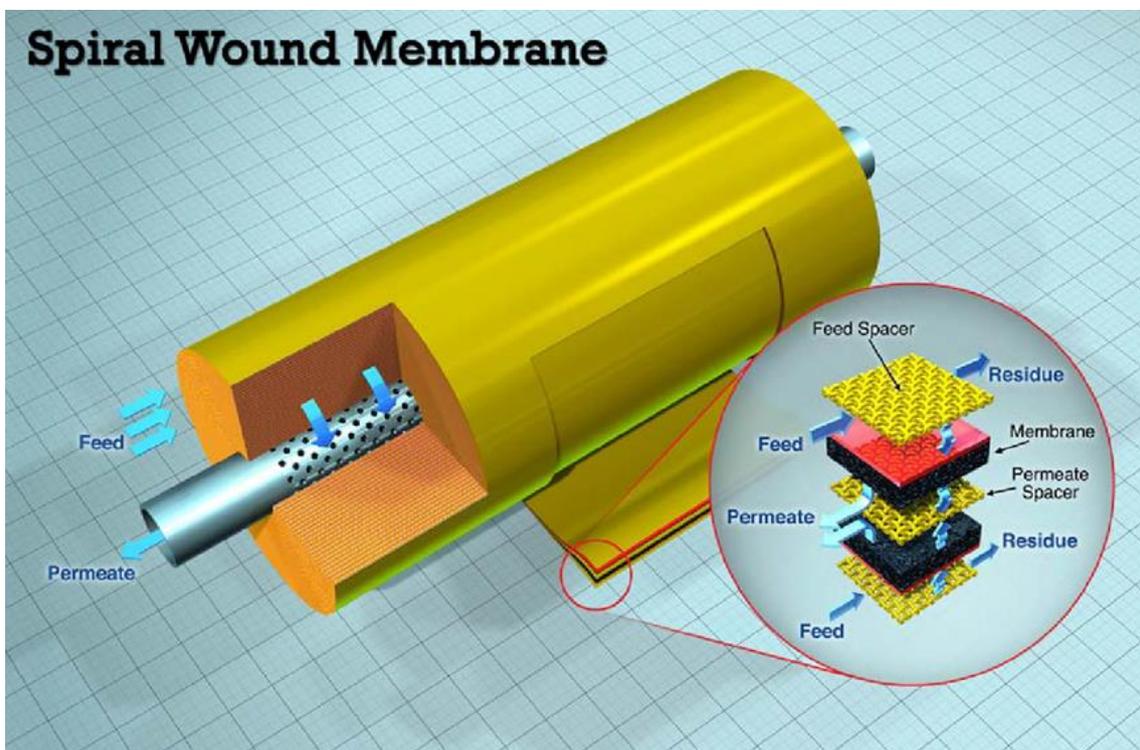


Figure 5: Scheme of the spiral-wound membrane (Courtesy of ProSep)

one membrane leaf from another and facilitates the flow of the high pressure stream linearly along the element. The membrane leaves are wound around a perforated hollow tube, known as the permeate tube, through which permeate is removed. The membrane leaves are sealed with an adhesive on three sides to separate the feed gas from the permeate gas, while the fourth side is open to the permeate tube. [5]

The operation of the spiral-wound element can be best explained by means of an example. In order to separate carbon dioxide from a natural gas, the feed mixture enters the pressure vessel (tube) at high pressure and is introduced into the element via the feed spacer. The more permeable CO_2 and H_2O rapidly pass through the membrane into the permeate spacer, where they are concentrated as a low pressure gas stream. This low pressure CO_2 gas stream flows radially through the element in the permeate spacer channel and is continuously enriched by additional CO_2 entering from other sections of the membrane. When the low pressure CO_2 reaches the permeate tube at the center of the element, the gas is removed in one or both directions. The high pressure residual gas mixture remains in the feed spacer channel, losing more and more of the carbon dioxide and being enriched in hydrocarbon gases as it flows through the element, and exits at the opposite end of the element.

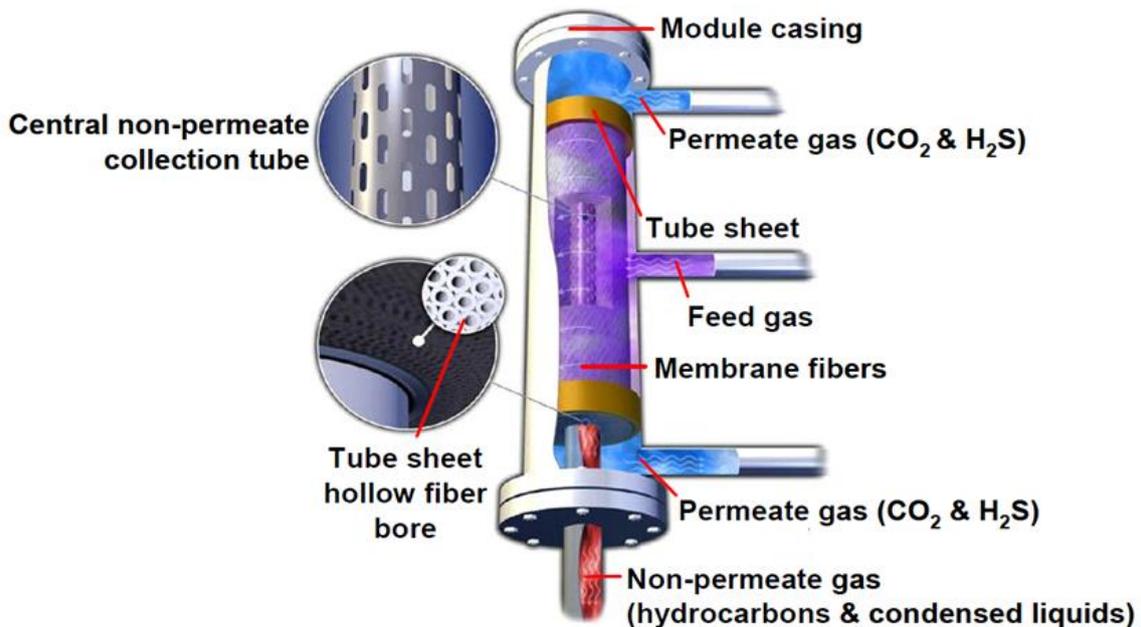


Figure 6: Scheme of the hollow-fiber membrane (Courtesy of Cameron Limited)

The membrane system consists of membrane elements connected in series and contained within pressure tubes. A rubber U-cup attached to the element serves to seal the element with the inner diameter of the pressure tube, thereby forcing the feed gas to flow through the element. The pressure tubes are mounted in racks on a skid.

To construct hollow fiber elements, very fine hollow fibers are wrapped around a central tube in a highly dense pattern. The feed natural gas flows over and between the fibers and the fast components permeate into the middle of the hollow fiber. The wrapping pattern used to make the element is such that both open ends of the fiber terminate at a permeate pot on one side of the element. The permeate gas travels within the fibers until it reaches the permeate pot, where it mixes with permeate gas from other fibers. A permeate pipe allows the collected gases to exit the element. An illustration is shown in Figure 6.

Types of Membranes	ADVANTAGES	DISADVANTAGES
Hollow Fiber	<ul style="list-style-type: none"> • Greater amount of membrane surface area within a given volume. • Ability to operate effectively in the presence of heavy hydrocarbons 	<ul style="list-style-type: none"> • Limited maximum operating pressure • Strength reduces with increasing CO₂ concentration
Spiral Wounds	<ul style="list-style-type: none"> • Able to withstand relatively high pressures • Minimum permeate pressure drop 	<ul style="list-style-type: none"> • Hydrocarbon condensation may not be easily removed and liquid accumulated inside reduces the productivity of the membrane

Table 1: Comparison between different membrane elements [10]

As the feed gas passes over the fibers, the components that do not permeate eventually reach the center tube in the element, which is perforated like the spiral-wound permeate tube. In this case, however, the central tube is for residual gas collection, not permeate collection. Many optimizations are possible for either element configuration. For hollow fibers, an important parameter is adjusting fiber diameter – finer fibers give higher packing density while larger fibers have lower permeate pressure drop and so use the feed-to-permeate-side pressure drop driving force more

efficiently. While each element type has its own advantages, the mechanism for gas separation is independent of the membrane configuration.

While each membrane has its own pros and cons, in order to a better comparison Mat Isa [10] introduced the scheme illustrated in Table 1.

1.2.3 Alternative techniques

Membranes technology is one among several others that may be used in order to remove acid gases from natural gas streams; therefore, in order to better evaluate a membrane technique one should be informed about the alternative systems and be aware of the conditions that will justify choosing one over the other.

A wide variety of acid gas removal technologies are available. They include:

- Absorption Processes (Chemical and Physical)
- Cryogenic Processes
- Adsorption Processes

Similarly, selecting an acid gas treating scheme hinges on many factors, such as:
(Adapted from: [9] - Concentration and degree of removal desired for the impurities (acid gases))

- Feed pressure and temperature
- Presence of heavier hydrocarbons
- Feed rate
- Relative economics of suitable processes
- Energy costs
- Production location

- Capital versus operation costs
- Reliability
- Others

On an **Absorption Process** a component of gaseous phase is contacted with a liquid in which it is preferentially soluble. It is usually carried out in a counter current tower (column), through which liquid descends and gas ascends.

The reverse process is employed when it is needed to remove the absorbed gases from the solvent for the purpose of recovery of the gas, or the solvent or both. In physical absorption, the desired gas component being absorbed (absorbate) is more soluble in the liquid solvent (absorbent) than other components in the gas phase but does not interact chemically with the absorbent; whereas in chemical absorption the absorbate reacts chemically with the absorbent or a component within the absorbent.

Among main absorption processes, chemical absorption with amines stands out as the traditional technique used when removing CO₂ from CH₄. For this reason the technique will be further detailed in the next section, where a comparison will be made between amine and membrane CO₂ extraction.

When considering the method's disadvantages, the corrosive potential of amine's solutions may lead to corrosion of the unit. Depending on the inhibitor used, it may cause a high tendency for foaming and solid suspension. In an offshore environment, the volume occupied by the equipment and its sensitivity to ship's motions may be added to the disadvantages list.

Regarding **Cryogenic Fractionation**, it is a technique that uses very low temperature (-73.30 °C) for purifying gas mixtures in the separation process. While the method is used commercially to liquefy and purify CO₂ from streams that have high CO₂ contents (typically greater than 50-70%), it has not been applied to large scale CO₂ capture from flue gas due to their low concentration of CO₂, which makes the application of this technique not economical.

Cryogenic Separation has the advantage that the CO₂ can be obtained at relatively high pressure as opposed to the other methods of recovering CO₂. This advantage may, however, be offset by the large refrigeration, and consequent energy costs, required. Moreover, the tendency for blockage of process equipment is high and cryogenic fluids may be flammable and toxic and special materials are required due to the extreme conditions achieved.

Finally, **Adsorption Process** is described as the adhesion or retention of selective components of feed gas stream brought into contact to the surface of certain solid as the result of the field force at the surface. As the surface of an adsorbing material may exhibit different affinities for the various components of a fluid, it offers a straightforward means of purification as well as potentially useful method of bulk separation.

Depending on the nature and strength of surface forces, adsorptive gas separation can be divided into two types: physical adsorption and chemisorptions, where chemisorptions can be considered as the formation of a chemical bond between the sorbate (element to be extracted from the mixture) and the solid surface. Such interactions are strong, highly specific and often not reversible. In physical adsorption the forces are weaker (a combination of Van der Waals force and electrostatic force), therefore the adsorbent is more easily regenerated

The primary requirement for an economic adsorption separation process is an adsorbent with sufficient selectivity, capacity and service life. Since adsorption is a surface phenomenon, an adsorbent should have high surface area to volume ratio. The main advantage of physical adsorption methods is its low energy requirements for the regeneration of the sorbent material with short period of time associated to the change in pressure. [13]

As it is a method mainly used for purification processes, and the present case requires a bulk extraction, the technique is not indicated.

1.2.4 Membranes X Amines

Initially, membranes were restricted to either small natural gas streams or those with very high CO₂ content, such as in enhanced oil recovery CO₂ floods. However, as the technology evolved, it became better known and more competitive.

As the technique settles into the market, it becomes more important to compare it with the well-established ones (amine technology), evaluating the relative strengths and weaknesses of the each process.

Many alkalonamines are most widely used as the chemical solvent gas treating process for acid gas removal in natural gas and petroleum processing industries. These processes use a solvent in an aqueous solution. The common amine based solvents used for the absorption process are monoethanolamine (MEA), diethanolamine (DEA) and methyldietanolamine (MDEA) that reacts with the acid gas (CO₂ and H₂S) to form a complex or bond.

As discussed above, the method's disadvantages include a high tendency for foaming and solid suspension, the system's sensitivity to ship's motion and the large space required by the installations.

The table below (Table 2) looks at some key areas for comparison.

	Amines	Membranes
User Comfort Level	Very Familiar	Becoming Familiar
Hydrocarbon Losses	Very Low	Depend Upon Operational Conditions and Initial and Final CO ₂ Concentration
Energy Consumption	Moderate to high	Low (for one-phased plants)
Operating Costs	Moderate to high	Low (for one-phased plants)
Maintenance Costs	Low to moderate	Low (for one-phased plants), although misuse cause irreversible damage
Ease of Operation	Relatively Complex	Relatively Simple

Table 2: Comparison between Amines and Membrane techniques (Adapted from [5])

In another dimension, membranes can be coupled with a solvent to capture desired gases (such as CO₂). This process is known as membrane gas absorption. In

such process, the CO₂ diffuses between the pores in the membrane and is then absorbed by the solvent. The membrane maintains the surface area between gas and liquid phases. This technique will be advantageous when CO₂ presents a low partial pressure (not the present case), due to the small driving force for separation.

This technique does not use the permeation coefficient of the gas through the membrane as the separation factor; it functions rather as a barrier between liquid and gas permeability through the pores. This physical separation between liquid and gas flow eliminates transport problems such as foaming and channeling.

1.3 Membranes technology and sustainable development

When introducing new technologies in a global market it is not only important to evidence a product's contribution to the industry immediately involved. In order to secure a long-lasting profitable future of an unconventional technique one must make sure it may be considered a sustainable technology.

When touching the subject of sustainable development it is important to be aware of the broad definition of the concept. Although words such as "green" or "eco-friendly" may have been used to define the early beginning of sustainable technologies, the current definition has grown very much outside the ecological sphere, enclosing economic and social concepts to it. Nowadays a technology is not only judged over its efficiency, cost and other performance-oriented issues, its environment impact and its future social consequences are just as important.

Those three spheres (economical, environmental and social) are interconnected and the result of this process can be seen with much more complex analysis of a new project's consequence. Surely, we live in a capitalist world, and for this reason the economic sphere may at times prevail over the others, however there is no doubt that both of the other elements still carry considerable weight.

Regarding relatively recent membranes technology, it is possible to identify research trends oriented to all three parameters. It is very naive to assume that the oil industry interest on the technique considers its advantages related to environmental and

social concepts, since even though some slight benefits may be noticed, it is clear that the industry's focus is directed towards profit increase and the creation of value.

The membranes technology applied to CO₂ rich oil production wells will enable an efficient gas separation into two primary streams, a first, methane rich flow and a second carbon dioxide rich one. In the studied case, the later stream is used to Enhanced Oil Recovery techniques that will extend the life of an oil reservoir by improving oil flow, flow properties and/or its interaction with the rock.

Gas injection EOR methods are based on the theory that the injection of gas into the oil-bearing layer under reservoirs conditions and high pressure will promote a decrease on oil viscosity and therefore facilitate its displacement. A very good oil recovery can be guaranteed if the pressure is higher than the minimum miscibility pressure, which is function of temperature and crude oil characteristics.

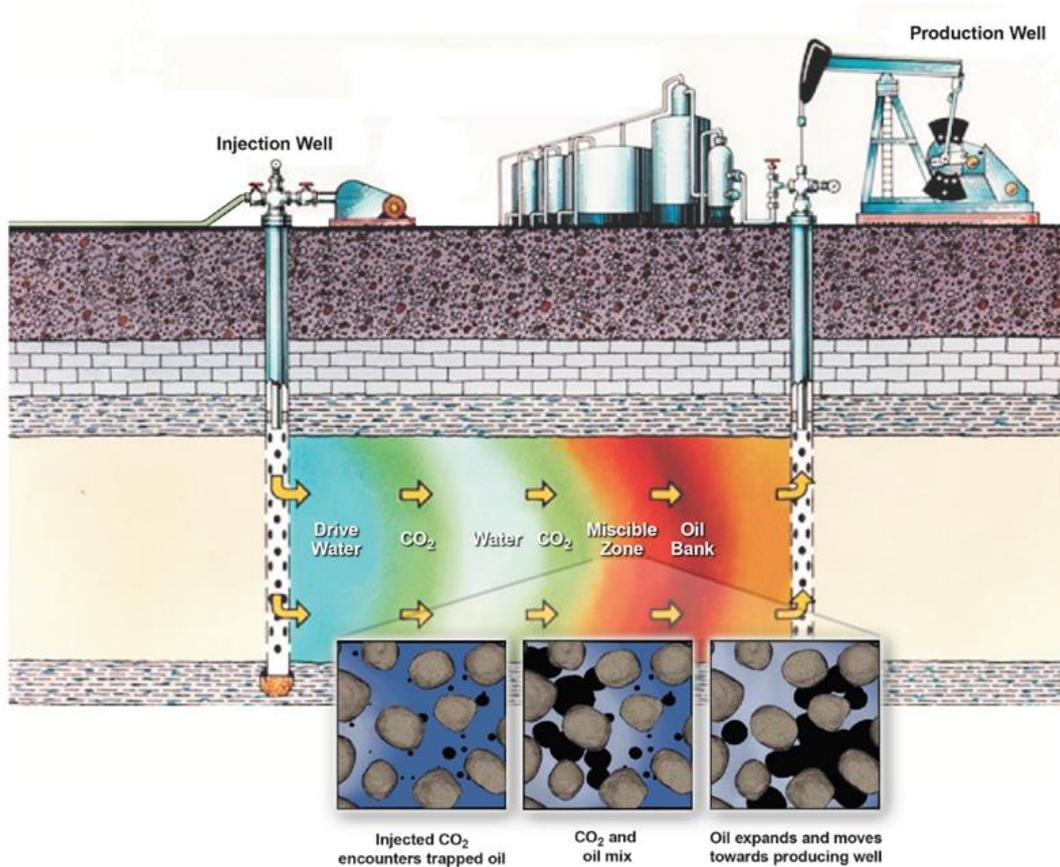


Figure 7: Cross-section illustrating how carbon dioxide and water can be used to flush residual oil from subsurface rock formation between wells. [14]

The injected CO₂-gas for EOR applications has typically purity from 95% to 99% (vol.). CO₂ is compressed, dried and cooled, before being transported and injected into the formation. In a classical EOR-CO₂ flooding, CO₂ is introduced into the field through injection wells, typically drilled around the producer well. Once the oil is mobilized, through miscible or immiscible processes, it has to be transported to the production well.

The WAG (water-alternating-gas) process, in which water and CO₂ are alternated in small slugs until necessary CO₂ slug size is reached, is the most common method employed. This approach helps to mitigate the tendency for the lower viscosity CO₂ to finger its way ahead of the displaced oil, since once the injected CO₂ breaks through the producing well, any gas injected afterwards will follow that path, reducing the overall efficiency of the injected fluids to sweep the oil from the reservoir rock.

Part of the injected CO₂ (30 to 70%) returns with the produced oil and is usually recompressed and re-injected into the reservoirs. Remaining CO₂ stays permanently sequestered into the reservoir.

The possibility of a permanent CO₂ storage induced a great amount of research investment in the area. Due to well-known malefic effects of high amount of atmospheric CO₂ (global warming, glacial melt, oceans acidification, etc.) techniques are being developed in an attempt to detain the process. In this context, geological sequestration has become a promising alternative. Figure 8 illustrates the general CCS (carbon capture and sequestration) process and shows a typical depth at which CO₂ would be injected.

CCs will reduce emissions from large stationary sources of CO₂, which include coal- and natural gas- fired power plants. There is where an opportunity may lay, on post-combustion CO₂ capture.

Compared to oil and gas, coal is the lowest cost method of producing electric power and it is relatively abundant in large energy-consuming nations, such as China. For these reasons, it is clear that coal will continue to be used to produce a large percentage of world's electric power.

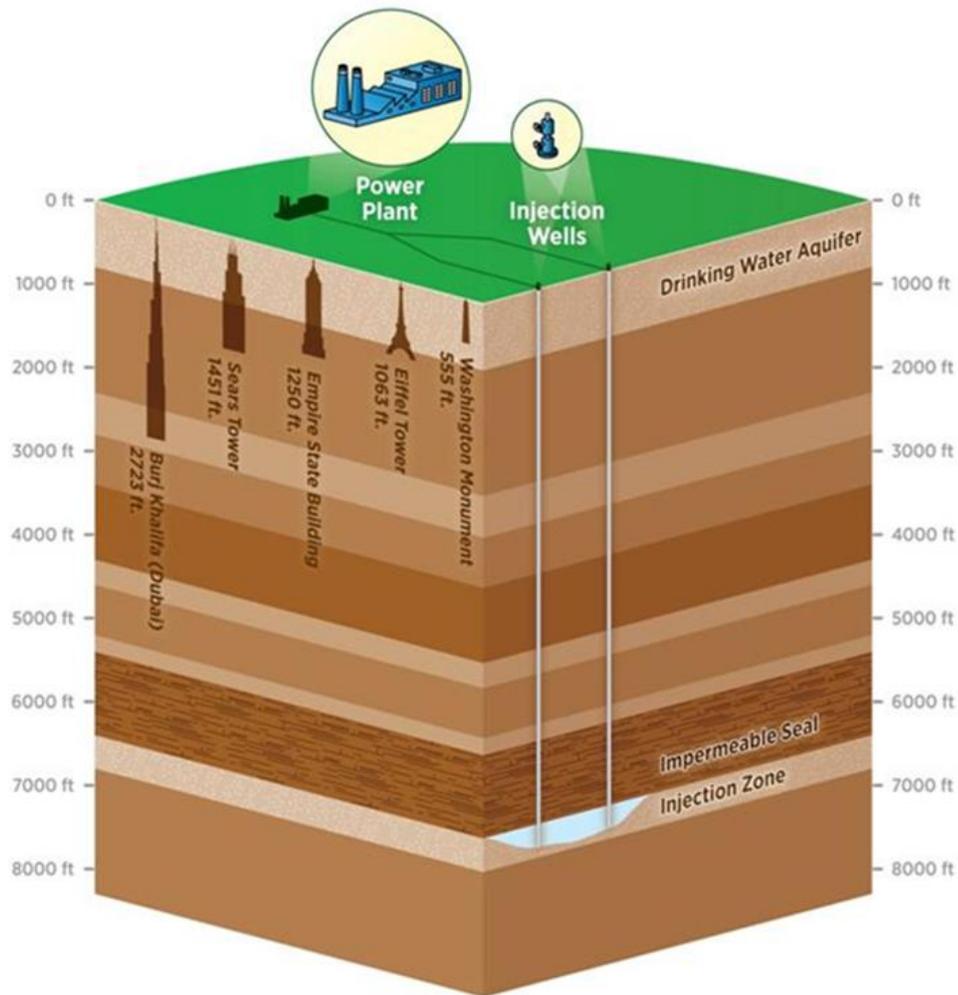


Figure 8: General CCS process and CO₂ injection typical depth. [14]

When considering this case, separation of CO₂ from flue gas streams is a difficult application for any separation technology. The problems are low CO₂ concentration, low pressure of the feed gas, coupled with huge gas flows. The enormous volumetric flow rate of a power plant flue gas stream means plants with very large membrane areas are required. Since the composition of the stream is different from the one on oil wells, the couple that needs to be separated is no longer CO₂/CH₄, but CO₂/N₂. Nevertheless, separating CO₂ and N₂ is a relatively easy separation for membranes, and high CO₂/N₂ selectivities have been developed. Therefore, this is not the principal problem preventing adoption of post-combustion membrane systems for CO₂ treatment. The more difficult problem to overcome is the scale of the process and the very large, expensive, energy-consuming compression equipment needed.

Ultimately, the competitiveness of a membrane flue gas CO₂ capture process hinges on membrane cost and reliability issues, demonstration and acceptance of large vacuum/compression equipment, and efficient integration with power facility systems. These issues will require close collaboration between membrane developers and the power industry, as well as successful demonstrations of membrane plants of progressively larger size in the field.

2 STATE OF THE ART

2.1 Molecules Transport in Membranes

2.1.1 *Characterizing transport in membranes*

Since membrane separation is based on the molecular behavior of each component of the feed gas, an analysis of molecular behavior throughout the separation appears to be useful to promote a better understanding of the process. [8]

There are five possible mechanisms for membrane separation:

- Knudson diffusion
- Molecular sieving
- Solution-diffusion separation
- Surface diffusion
- Capillary condensation

Being molecular sieving and solution-diffusion transport the mainly ones used mechanisms on gas/gas separation.

Knudson separation is based on a gas molecules passing through pores small enough to prevent bulk diffusion. Separation is based on the difference in the mean path of the gas molecules due to collisions with the pore walls, which is related to the molecular weight.

Molecular sieving relies on size exclusion to separate gas mixtures. Pores within the membrane are of a carefully controlled size relative to the kinetic (sieving) diameter of the gas molecule. This allows diffusion of smaller gases at a much faster rate than larger gas molecules.

Surface diffusion is the migration of adsorbed gases along the pore walls of porous membranes. The rate of surface diffusion is determined by the level of interaction between the adsorbed gases and pore surface. Thus, molecules diffuse along the pore walls relative to the strength of this interaction, achieving separation.

Capillarity condensation is an extension of surface diffusion. When the vapor pressure is low enough, adsorbed gas can undergo partial condensation within the pores. This condensed component diffuses more rapidly through the pore than gases, causing separation of the condensable gas.

Solution-diffusion separation is the mechanism actually used with polymeric CO₂/ CH₄ separations, and therefore will be explained in detail at the next section.

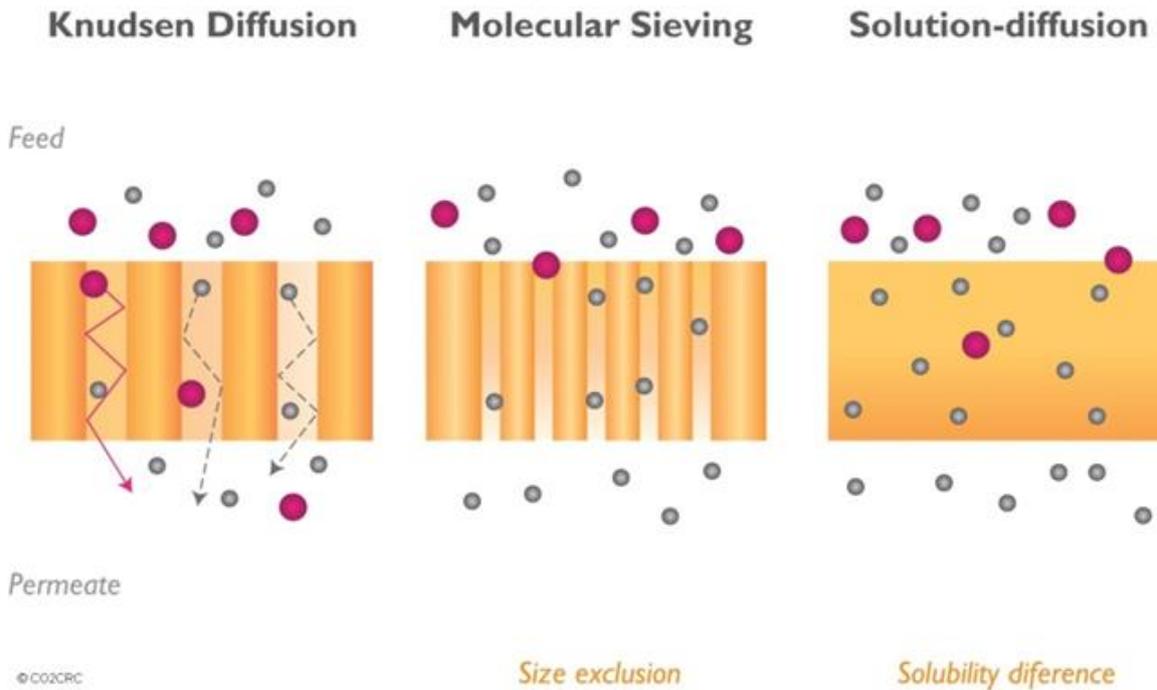


Figure 9: Schematic representation of three of the different possible mechanisms for membrane gas [15]

2.1.2 Permeation theory

When describing solution-diffusion processes, it is commonly accepted that the principal mechanisms are identified in the following order (Figure 10):

Sorption (at the Feed Gas/Membrane interface)

Diffusion (through the Membrane)

Desorption (at the Membrane/Permeate Gas interface)

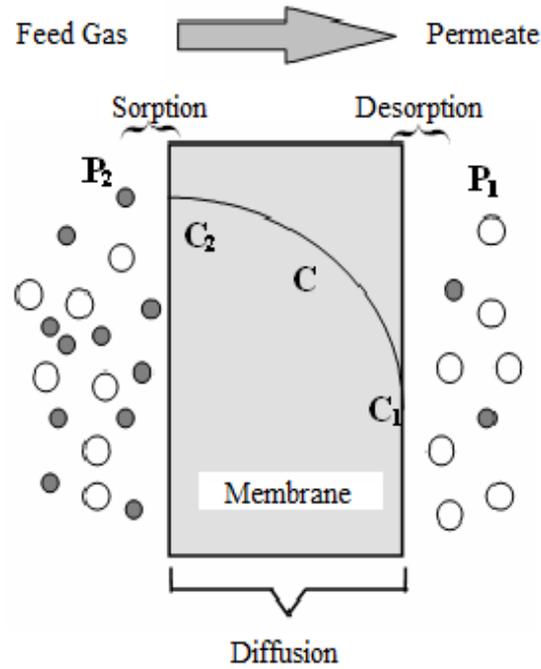


Figure 10: Sorption and diffusion mechanisms [2]

Since the processes of sorption and desorption are opposite phenomena they can be equationated together (adapted Henry's Law) as function of CO_2 /membrane material condensability [8]:

$$J_S = S_i \cdot (C_F - C_P) \quad \text{Equation 2.1}$$

Being J_S the molar flux due to (de)sorption mechanisms; S_i the condensability factor between the membrane material and the feed gas; C_F the CO_2 concentration at the feed gas; C_P the CO_2 concentration at the permeate gas.

Moreover, the diffusion process is described by Fick's Law and is equationated as follow:

$$J_D = \frac{D_i}{\gamma} \cdot (C_F - C_P) \quad \text{Equation 2.2}$$

Being J_D the molar flux due to diffusion; D_i the diffusion coefficient of the membrane material - it is a function of different operational variables being very much affected by the operating temperature; γ the membrane's thickness; C_F the CO_2 concentration at the feed gas; C_P the CO_2 concentration at the permeate gas.

Considering both phenomena independent, we may have the total molar flux equation as follow:

$$J_T = J_S + J_D \quad \text{Equation 2.3}$$

$$J_T = S_i \cdot (C_F - C_P) + \frac{D_i}{\gamma} \cdot (C_F - C_P) \quad \text{Equation 2.4}$$

$$J_T = \frac{S_i \cdot D_i}{\gamma} \cdot (C_F - C_P) \quad \text{Equation 2.5}$$

Multiplying both sides by the membranes area, we end up with the molar flow through the membrane:

$$J_T \cdot A = F_T = \frac{A \cdot S_i \cdot D_i}{\gamma} \cdot (C_F - C_P) \quad \text{Equation 2.6}$$

Equations 2.5 and 2.6 clearly show dependence between the mass flow and (de)sorption and diffusion coefficients, therefore we will find that the total mass flux will depend on the most demanding of these two phenomena.

On a separation application of membranes, it is not only important to analyze the gases' individual permeation rate. In order to adequately measure a membrane's ability to separate two gases i and j, the ratio of their permeability ($\alpha_{i/j}$) must be analyzed; this parameter is called membrane selectivity, and can be written as:

$$\alpha_{i/j} = \frac{P_i}{P_j} = \frac{D_i S_i}{D_j S_j} \quad \text{Equation 2.7}$$

The ratio D_i/D_j is the ratio of the diffusion coefficients of the two gases and can be viewed as the mobility selectivity, which indicates the relative motion of individual molecules of the two components. The mobility selectivity is proportional to the ratio of the molecular kinetic size of the two permeants. The ratio S_i/S_j is the ratio of the sorption coefficients, which indicates the relative concentration of the components i and j in the membrane material. The sorption selectivity is proportional to the relative condensability of components i and j.

On CO₂ separation with polymeric membranes mobility selectivity D_i/D_j

always favours the permeation of small molecules (such as water (kinetic diameter of 2.65 Å) and carbon dioxide (kinetic diameter of 3.30 Å)) over larger ones (such as methane (kinetic diameter of 3.80 Å)). [15]

In order to evaluate membranes performance in a gas separation, two characteristics may be considered: the above mentioned permeability (specifying the mass flow rate the material is able to reach) and its selectivity (the membrane's preference to pass one gas species and not another).

Unfortunately, high CO₂ permeability does not correspond to high selectivity when polymeric materials are regarded. In fact the relationship between those two factors tends to be inversely proportional, admitting either one or the other. Achieving this combination is a constant goal for membrane's scientist.

In order to better define technological limits on the trade-off between permeability and selectivity Robeson described an Upper Bound function (Figure 10: Robeson's trade-off curve for carbon dioxide/natural gas pair [13]). It is important to notice that this boundary evolves together with technology, and is therefore always being optimized.

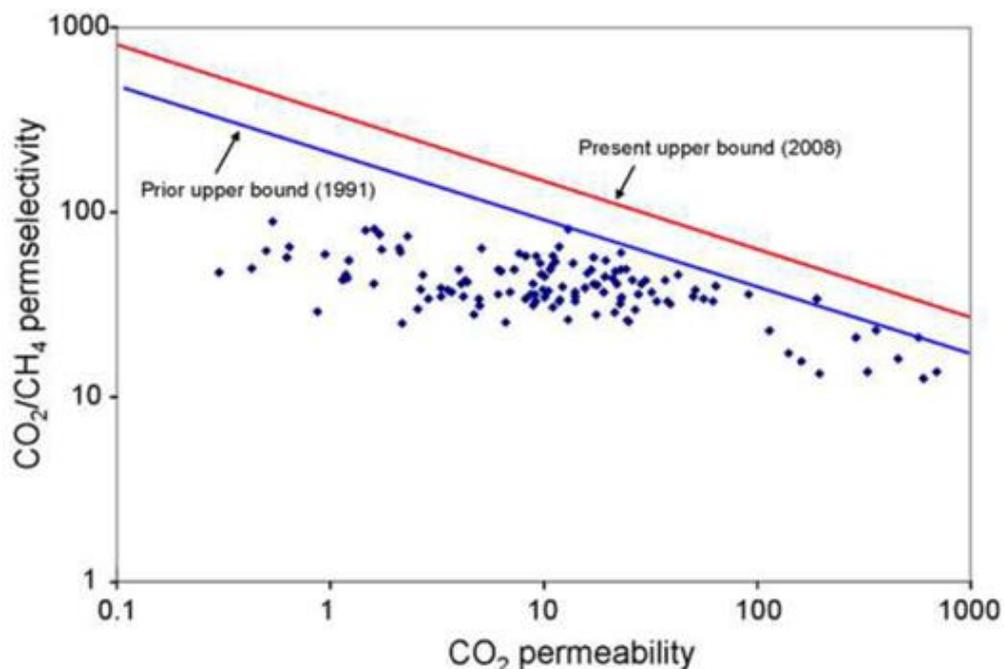


Figure 11: Robeson's trade-off curve for carbon dioxide/natural gas pair [13]

2.1.3 Thermodynamic aspects

A thermodynamic analysis of the feed gas is found to be necessary in order to assure proper membrane functioning. A dew point analysis is particularly important in order to foresee liquid formation in the membrane due to the increased heavy hydrocarbons concentration.

The problem of liquid condensation on the membrane surface is illustrated in Figure 10. This figure shows an example of two natural gas phase envelope curves. [8]

The dew-point temperature is dependent on the pressure and the concentration of heavy hydrocarbons in the gas mixture. In the example, the feed gas (A) is at 55 °C, comfortably above the dew point of the feed, which is approximately 35 °C. When the gas is processed by a membrane, carbon dioxide and some methane is removed from the feed side to the permeate side. Because membranes are relatively impermeable to heavier hydrocarbons, these components are retained and concentrated in the residue gas. This increase in heavy hydrocarbon concentration in the gas causes the phase envelope to shift to higher temperatures; the dew point of the residue gas (B) is, in this case, increased to around 50 °C.

In addition to the movement of the dew point line, the system will also present a cooling tendency. The depressurization of the permeate gas (passing from a ≈ 50 bar to ≈ 2 bar) will induce a temperature reduction by the Joule-Thompson effect that will be transferred to the high pressure side through thermal diffusion. In the case analyzed the non-permeate gas will reach temperatures 10- 15 °C below the feed gas. Therefore, in this case the combination of these effects is sufficient to bring the gas into the two-phase region of the phase envelope. Condensation of hydrocarbon at the end of the non-permeate portion of the membrane train would then likely occur. Condensation of this type may damage the membrane permanently (when reacting with membrane's material) and reduce its performance (by decreasing relative area of contact).

When occurred to spiral-wound membrane elements, the condensation of heavy hydrocarbons is especially prejudicial as the internal structure of the element encumbers liquid's drainage. Hollow-fiber modules will be less severely damaged since, due to its vertical positioning and the horizontal gas flow, liquid may be accumulated and occasionally drained through the bottom. Condensate formation will be more harmful

when the feed gas contains traces of water and/or aromatic hydrocarbons since they easily react with the polymer forming the membrane (traditionally cellulose acetate).

In order to prevent those difficulties, a pre-treatment system may be employed. It must have a wide safety margin and be highly flexible to cope with unexpected circumstances. The heavy hydrocarbon content of a feed gas can vary widely from initial pre-start-up estimates and also from month to month during the plant's life. Large variations are seen even between different wells in the same area. For this reason a reliable pre-treatment system must take this variation into account and must be able to protect the membranes against all kinds of contaminants that may possibly be encountered. [4]

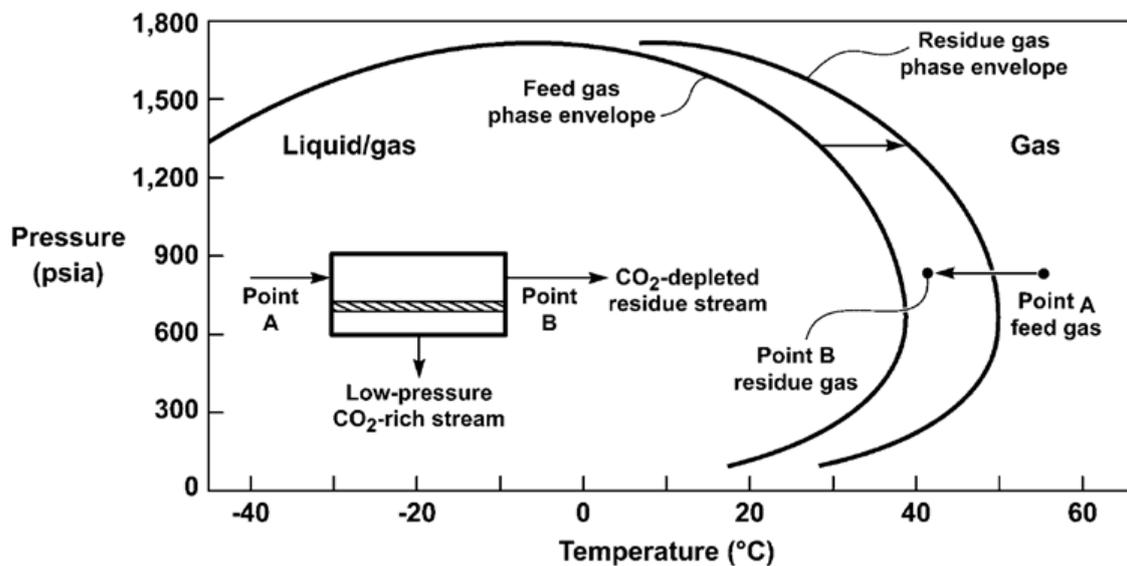


Figure 12: Graph showing the change in the phase envelope of CO₂ containing natural gas during processing of the gas by CO₂ selective membrane [8]

2.2 Separation Polymers

2.2.1 Overview

Current membrane carbon dioxide separation plants use a very limited number of membrane materials, of which cellulose acetate is probably the most common (Table 3).

Company	Principal Gas Separation	Natural	Membrane Type	Module	Membrane Material
Medal (Air Liquide)	H ₂ (National Energy Technology Laboratory, 2010)		Hollow Fibre		Polyimide
W.R. Grace	CO ₂		Spiral-wound		Cellulose Acetate
Separex (UOP)	CO ₂		Spiral-wound		Cellulose Acetate
Cynara (Natco)	CO ₂		Hollow Fibre		Cellulose Acetate
ABB/MTR	CO ₂ , hydrocarbons	N ₂ , C ₃₊	Spiral-wound		Perfluoro Polymers Silicone Rubber
Permea Product)	(Air Water		Hollow Fibre		Polysulfone

Table 3: Principal suppliers of Membrane Natural Gas Separation Systems [8]

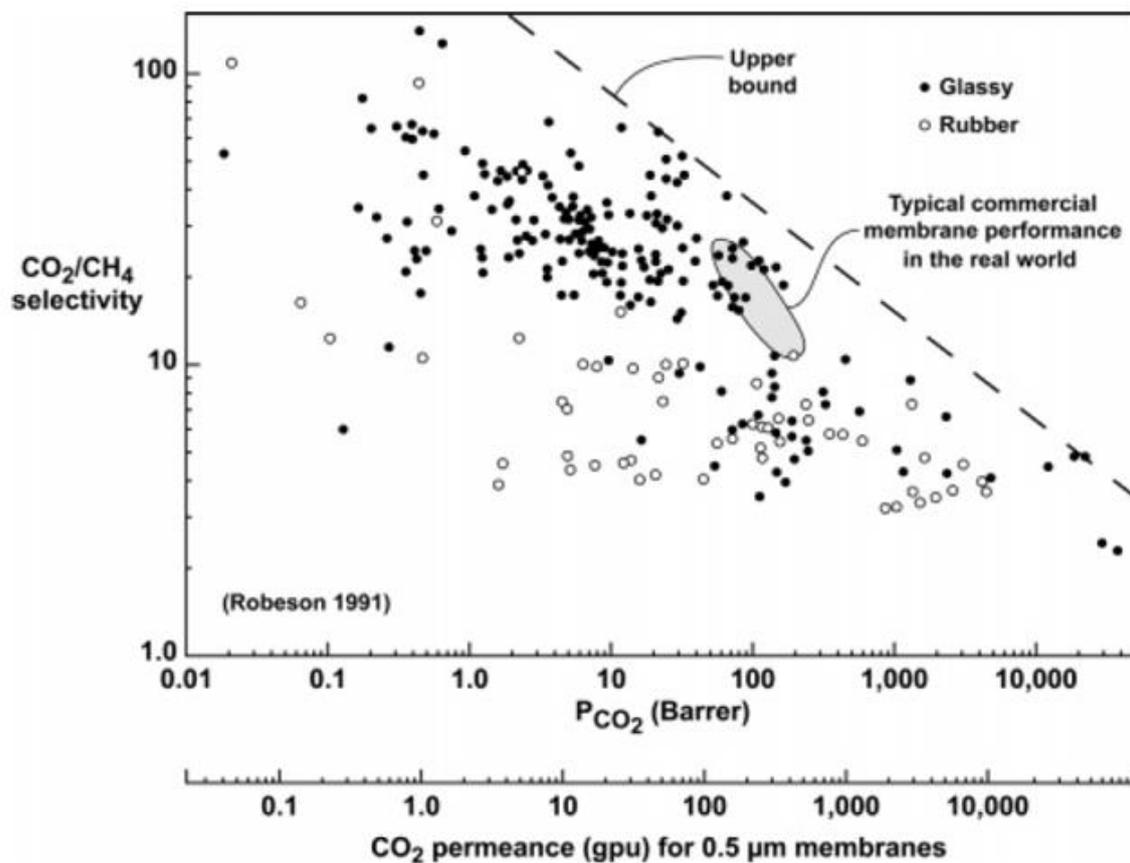


Figure 13: Robeson's plot of CO₂/CH₄ selectivity versus membrane permeability (permeance). [8]

When analyzing the typical material used to build industrial membrane's, it has been discovered that they would present a very fair behaviour, when contemplating permeability and selectivity. This result surprised many researchers who pointed to

literature data that showed the availability of much-better membrane materials (Figure 13).

In addition, commercial membranes that are presently in use have half the selectivity showed in the plot. Since Figure 11 measurements are obtained from the ratio of pure-gas permeability plotted against carbon dioxide permeability. When applied with natural gas, impurities will promote a shift towards weaker performance, reflecting the effect of water, carbon dioxide, and heavy hydrocarbons. Anyhow this is a situation that will be faced by any membrane in use and therefore should not be considered a comparative downside.

2.2.2 Vitreous X Rubbery polymers

Amorphous polymeric membranes may be classified as rubbery or glassy membranes, depending on its operating temperature relative to the glass transition temperature of the polymer. It is a very important parameter to analyse the mobility of sorbed molecules, which is mainly dependent on the free volume (Figure 14) of the polymer and on the degree of rigidity of the chains.

In polymer materials, diffusion coefficients decrease as the molecular size increases, since large molecules interact with more polymer segments chain than do small molecules. In the other hand the sorption coefficients for a particular gas pair is relatively constant for all amorphous polymers. Thereby it is safe to say that gas selectivity will be very dependent of the diffusive conditions.

Moreover, depending on the kind of polymer the membrane is made of, a different transport commands. As a general rule one can say that sorption transport is the more demanding movement on rubbery polymers, while glassy polymers will select preferably through diffusion movements.

When the operational temperature is above T_g , polymer is in a rubbery state. In this state, it tend to have a higher free volume (high specific volume) and more flexible chains. This configuration does not impose a resistance for molecular diffusion, as the chains can adjust to the molecular flow relatively easy; consequently the effect of molecular size of the permeating gases on relative mobility is reduced. Therefore, the

main selection promoted by rubbery membranes will be on the sorption coefficients, which is facilitated as molecular size increases.

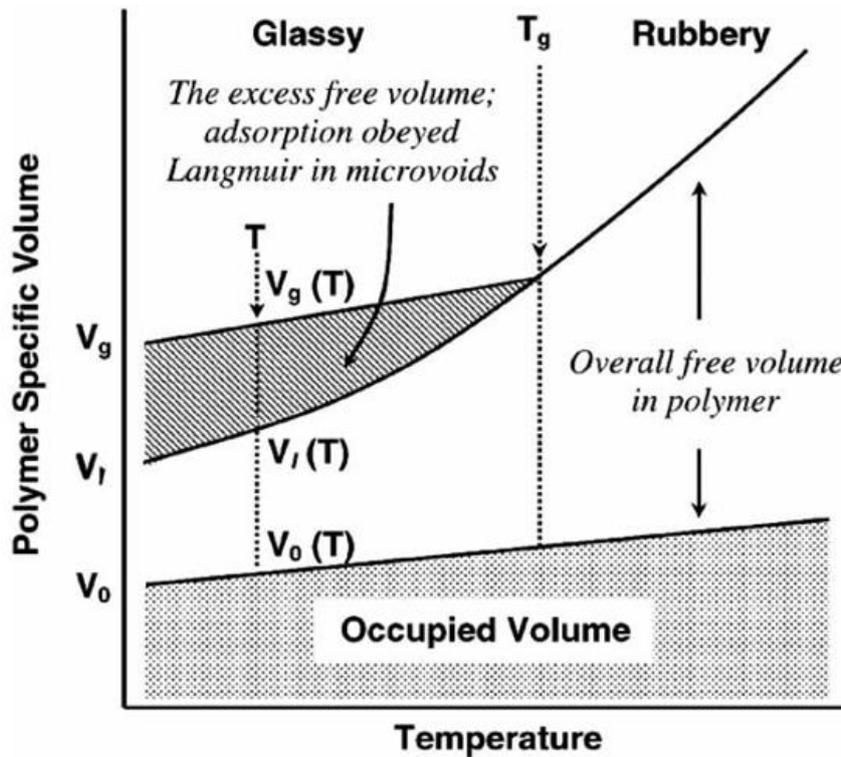


Figure 14: Schematic representation of the relationship between the polymer specific volume and temperature in an amorphous polymer [15]

However if the operational temperature is below glass transition temperature (T_g), the polymer is at a vitreous state. This implicates a relevant reduction on intern free volume and the formation of rigid and often brittle chains, and the effect of differences in size of the permeating gases on their relative mobility is large, favoring small molecules diffusion. In other words, the diffusive coefficient (and therefore molecular size) will prevail on determining gas selectivity.

2.2.2.1 Plasticization and physical ageing in glassy polymers

The deterioration in membrane separation performance under field conditions is primarily due to the action of CO_2 and higher hydrocarbon contaminants present in natural gas. Large hydrocarbons are highly condensable and have high solubility in the hydrocarbon polymers. Upon sorbing into a polymer, these higher hydrocarbons can act

as plasticizers, increasing polymer chain mobility by increasing the free inside volume and decreasing the size-sieving ability (or diffusivity selectivity) of the polymer.

When discussing CO₂ plasticizing effect it is very difficult to make a prediction on selectivity behaviour. That is due to the use of pure gas for experimental purposes. At the laboratory an increase feed pressure should result in an increase in CO₂/CH₄ selectivity, as CO₂ plasticizes the polymer, increasing its diffusivity and hence its permeability.

However, in the mixed gas experiments, CO₂-induced plasticization influences to a greater extent the diffusion of CH₄ than that of CO₂, and this causes a decrease in the overall selectivity. Higher hydrocarbon-induced plasticization can further decrease the selectivity.

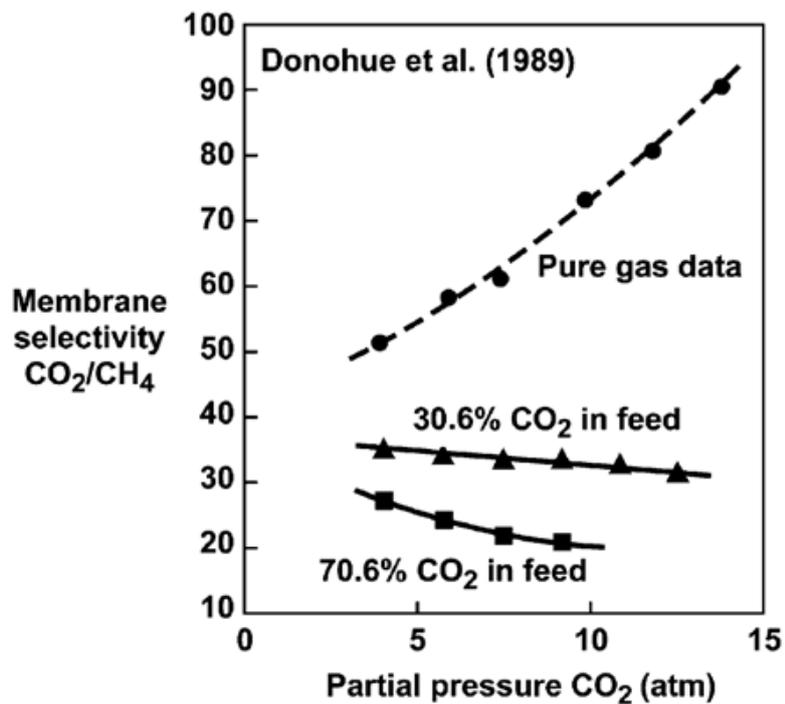


Figure 15: Difference of selectivity calculated from pure gas measurements and gas mixtures for acetate cellulose membranes. [8]

A decrease in CO₂/CH₄ selectivity results in more of the desired methane product appearing in the low pressure permeate stream from the membrane unit, which either forces the use of a second membrane stage to recover the permeated methane and repressurize it to pipeline conditions (expensive) or results in larger losses of methane from the separation system. Both of these options increase the cost of purifying the gas.

Several strategies have been used to overcome membrane plasticization, being pre-treatment the most common one.

Finally, when working with those glassy materials one must be very attentive to physical aging. This is because the polymers used in CO₂-selective membranes are in a nonequilibrium state and, over time, the polymer chains can slowly relax into a preferred higher-density-lower-permeability form. This type of aging effect can reduce membrane permeability significantly over the average 2-5-year life of a membrane used in natural gas service.

2.3 Other Materials

2.3.1 Composite membranes

Polymers that exhibit good CO₂/CH₄ separation performance (selectivity and flux) may not be ideally suited for providing mechanical support and long-term chemical stability. Therefore a membrane has usually either very good separation properties or very good mechanical resistance. Composite membranes result of the attempt to uncouple performance and strength properties. The membrane consists of three layers: a nonwoven fabric that serves as the membrane substrate (the support web); a tough, durable, solvent-resistant microporous layer that provides mechanical support without mass transfer resistance; and a nonporous, defect-free selective layer that performs the separation. (Figure 14)

This configuration allows each of the layers to be independently chosen to optimize their function: the selective layer for high flux and selectivity, and the support layers for mechanical and chemical stability that will not influence the separation.

Composite membranes are structured trying to use materials that are impervious to hydrocarbon exposure intending a better performance even in the presence of condensates and a reduction of costs on gas pre-treatment. Furthermore the packing configuration of this new membrane is spiral-wound.

Finally, although it is clearly a very promising new technology, it is still on its preliminary fase of manufacturing, not being available at an industrial scale.

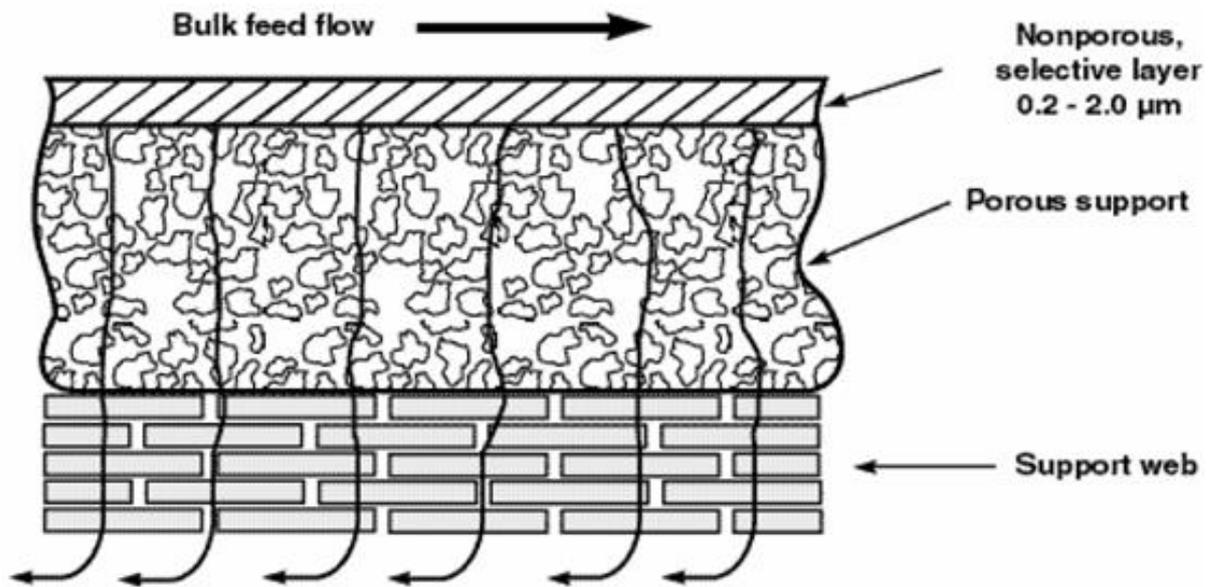


Figure 16: Cross-section of a MTR composite membrane [7]

2.3.2 Facilitated transport membranes

Facilitated transport membranes rely on a chemical reaction occurring between the gas of interest and a component of the membrane (carrier). The reacted species is readily carried across the membrane, whereas diffusion of non-reactive gases is inhibited. The active carrier is generally basic in nature, given that carbon dioxide is acidic. The driving force for gas transportation remains the partial pressure difference across the membrane; however the facilitator carrier increases both the permeability and selectivity of the membrane through the increased loading.

The facilitator carrier can be either fixed-sited within the polymeric matrix or mobile. An illustrated schematic of a fixed-sited carrier, polyvinylamine, can be seen at Figure 15.

The first facilitated transport membranes patent was awarded to General Electric in 1967. This related to cellulose acetate films swollen by the inclusion of an aqueous carbonate solution. Carbon dioxide readily dissolves and reacts with water to form the bicarbonate anion. Carbonate acts as a carrier by increasing the amount of carbon dioxide absorbed. Hence, this reaction occurs on the feed side of the membrane and the bicarbonate anion transports through to the permeate side, where the reverse reaction occurs and carbon dioxide is released.

However, one of the restrictions of facilitated transport membranes is their inability to operate at high feed temperatures due to evaporation problems.

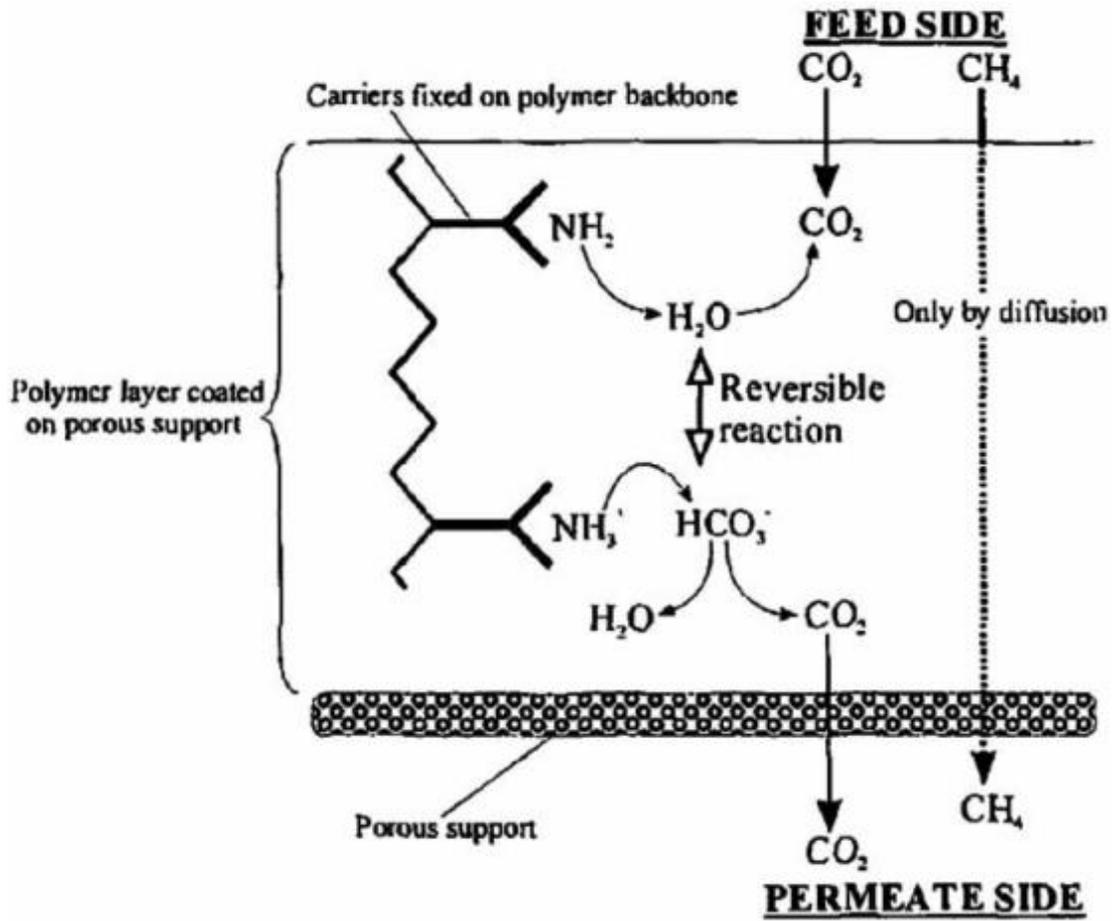


Figure 17: Fixed carrier facilitator transport membrane for CO_2/CH_4 separation [15]

3 CASE MODELING

3.1 Considerations

In order to model a membrane separation system, it is necessary to define a set of considerations that will be taken into account when formulating the equations to be used. Since the technology of membranes is still a matter of deep study and most technical details are classified by its developers, effort was carried in order to design an acceptable model of membrane separation system and to incorporate the information available from the industry case, so the present study could approach the reality as much as possible.

One important consideration is that our model will treat only CO₂/CH₄ separation, which means that the composition of a stream will consist of only these two gases. Furthermore, we consider steady-state conditions, in the sense that the molar flow rates and pressures of the streams do not change with time, or at least are kept constant for the moment. These two considerations simplify a lot the development of the model and at the same time seem not to change qualitatively the problem, in the sense that the model developed in this work can easily be adapted to more complex conditions regarding these two considerations.

Trying to simulate a real situation in the industry, where the membrane systems' producer may want to sell the whole separation systems and not want to reveal technical details about the membranes themselves, the interaction between membrane and gases is considered to be a set of unknown functions. In fact, this is what happens with our industry study case. It is possible to measure pressures, concentrations and flow rates of the different streams considered in the process, but the behavior of the membrane that will reflect the degree of separation is unknown. This situation was presented in the introduction of this work, and the approach used to deal with it will be presented in the appropriate section.

3.2 The membrane separation system

The membrane separation system aims to receive a production stream, called **Feed Stream**, with specific pressure, flow rate and concentration of gases, and produce a stream with higher concentration of desirable gases, namely hydrocarbons, being this stream called **Non-permeate Stream** and presenting its own values of pressure, flow rate and concentrations. A third stream, called **Permeate Stream**, is formed by the flow which permeated the membranes, and is expected to present lower concentrations of hydrocarbons and this higher concentration of CO₂. The quantities of hydrocarbons and other gases in each downstream flow are functions of the behavior of the membrane, its interaction with each of the gases and, as we are going to see in more details, the concentrations, and thus partial pressures, of the gases in the upstream and downstream flows.

In order to have a better comprehension of the process, some numbers from our industrial example are commented. The process gas stream has a total inlet flow of about 5.7 MMSCMD (Million Metric Standard Cubic Meter Per Day). The CO₂ concentration in the feed gas ranges from 4% to 61%. The gas processing design capacity of the unit is different for different CO₂ concentrations in the feed. The gas for the membranes feed is pre-treated in the molecular sieve dehydration unit in order to avoid liquid water formation in the membranes, followed by mechanical refrigeration unit for hydrocarbon dew point control so as to condense and separate eventual aromatics compounds which would damage the membranes when in liquid phase. The process design parameters for the membrane system are provided in the following table:

Conditions	Design Basis
Gas Flow	5.7 MMSCMD
Pressure	52.5 bar
Temperature	23.5 – 30.4 °C (design case dependent)
Feed Gas CO ₂	4 mol% - 61 mol%
Feed gas moisture (max)	1 ppmv (parts per million per volume)
Feed gas HC dew point	10 °C @ 53 bar
Permeate pressure	2.5bar
Non-permeate pressure (min)	48 bar
Non permeate CO ₂ (max)	3 mol%

Table 4: Process design parameters (courtesy from Cameron)

The membrane elements installed in the housings remove the CO₂ rich permeate gas from the feed gas so that the CO₂ concentration in the non-permeate gas is less than 3 mol%. The CO₂ rich permeate gas is produced at a pressure of 2.5 bar and the non-permeate gas is delivered at a pressure of 48 bar minimum.

3.2.1 Membrane separation stages

The simplest system of membranes can be visualized as a unique stage, where one can identify one feed stream, one permeate stream and one non-permeate stream. Arrangements of such stages can lead to more complex systems, to be commented below. Each stage contains a certain number of membrane modules inside of it. These modules are the inseparable units that are placed together in order to perform the separation of gases. One of the objectives of the modeling studied in the present work is to observe how the number and organization of modules inside different stages can impact the performance of the separation system.

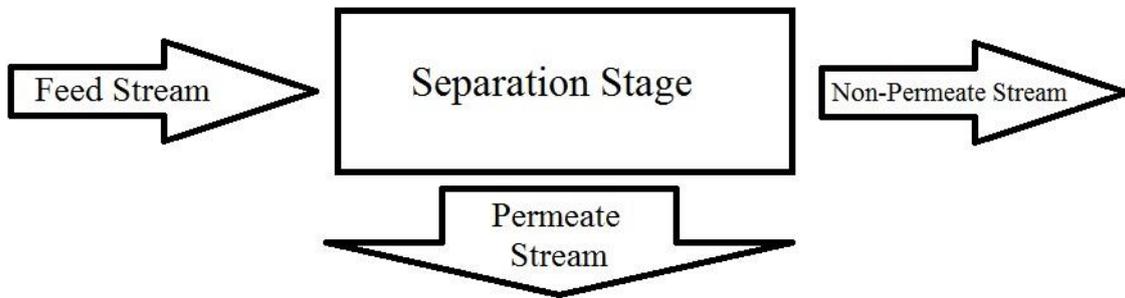


Figure 18: Separation stage scheme (Authors)

For each of the streams above, we will define variables that will be used in the process of modeling the physics of the system. First, P_F , P_P and P_{NP} are the absolute pressures measured in the feed, permeate and non-permeate streams respectively. The reasoning regarding the subscripts will be maintained, what implies the definitions of the molar flow rates Q_F , Q_P and Q_{NP} and the concentrations C_F , C_P and C_{NP} of CO₂. Since only two gases are considered, the concentration of CH₄ is obtained as 1 minus the concentration of CO₂. Furthermore, N will represent the number of membrane modules in a given stage.

Two mass balances are applied to the above situation. First, the total molar flow must be conserved. This leads to:

$$Q_F = Q_{NP} + Q_P \quad \text{Equation 3.1}$$

Second, since no chemical reaction is considered to happen inside the membrane module, the molar flow of one of the gases must also be conserved. This leads to:

$$C_F Q_F = C_{NP} Q_{NP} + C_P Q_P \quad \text{Equation 3.2}$$

Further relations are needed in order to represent the way the membrane device works in order to separate the gases from the feed current. As already mentioned, our study has as an objective the possibility of working without the explicit quantitative knowledge about the physics of the membranes. In order to replace this information, history data from the previous usage of membrane systems alike should be used in some way in order to provide this information. Below it will be commented how this procedure was performed in the industry case studied in this work.

3.2.1.1 Usage of history data

The usage of history data, as said before, aims to replace the unknown information about the physics that regulates the membranes and their interaction with the different streams. For one separation stage, two relations were needed in order to model the problem consistently. Considering that our study modeled a 3-stage system, to be discussed later, the first relation, which was obtained considering the validity of Fick's Law of Diffusion in our study, was used for every stage modeled, while one additional relation was researched for each of the stages separately.

As our first relation, it can be considered that the molar flow of CO₂ through a membrane unit, that is, the CO₂ content in the permeate stream divided by the number of membranes in the stage, is proportional to the difference between the mean of the gas partial pressure in the feed and non-permeate and the gas partial pressure in the permeate stream. In terms of the variables already defined previously, we can write:

$$\frac{C_P Q_P}{N} = f\left(\frac{C_F P_F + C_{NP} P_{NP}}{2} - C_P P_P\right) \quad \text{Equation 3.3}$$

In the above expression, f is the unknown function that relates the difference in partial pressures and the CO_2 molar flow through the membrane. The term $C_P Q_P$ is the expression of this molar flow in terms of the primary variables defined before and the terms $C_F P_F$, $C_{NP} P_{NP}$ and $C_P P_P$ are the partial pressures in each of the considered streams, defined as the product of the concentration of a gas in a mixture by the total pressure measured in this mixture.

The graph below shows the resulting curve when a parabolic function was adjusted, using data-fitting techniques, to the set of data corresponding to our industry case production history.

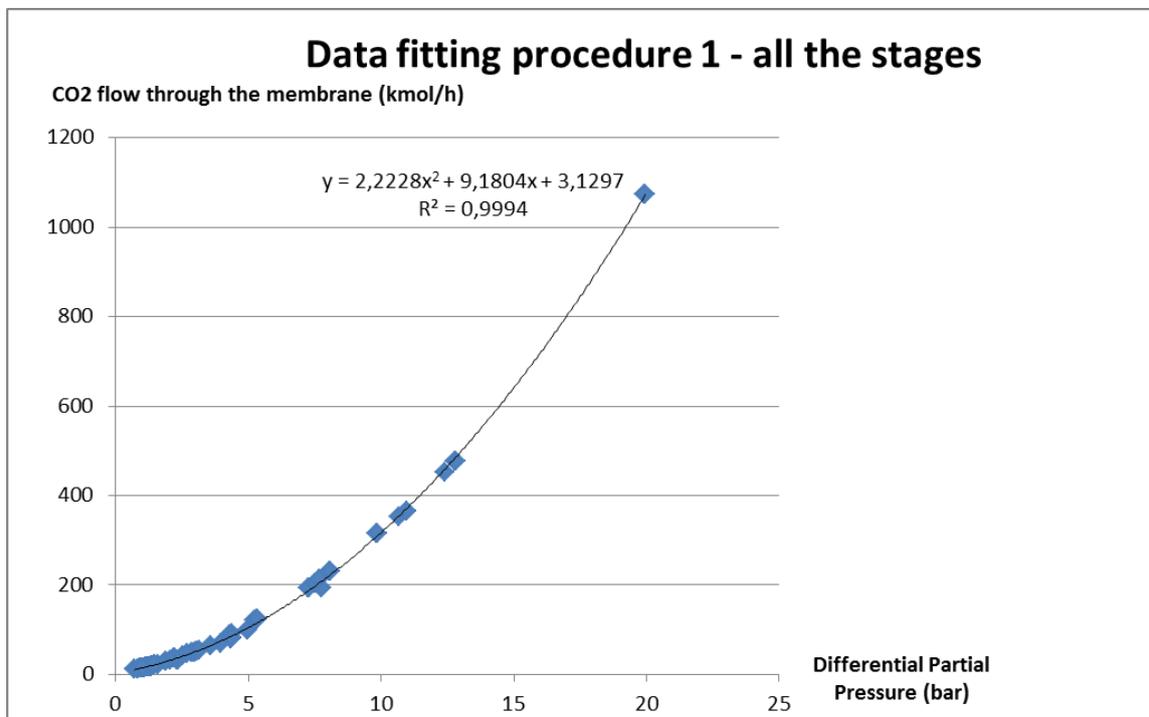


Figure 19: Data fitting procedure for differential partial pressure and CO_2 flow in the permeate for all the stages (Authors)

In fact, this procedure is one part of the modeling technique proposed in this work: to a given time, history data from the usage of the membrane systems until this time shall be collected and a membrane function shall be obtained by means of data fitting. The shape of the function is one of the decision parameters, to be decided by observation of the data dispersion, comparisons of the correlation coefficient for different adjustments or even some automatic procedure. In the present case, it was

observed that the quadratic model should present a good fitting, and it is indeed the case.

The second relation to be obtained was stage-dependent in our case. That is, for each of the three stages considered in our model, one specific function was obtained. In this way, for stage 3, it was obtained a function with the form:

$$Q_{NP} = f(Q_F) \quad \text{Equation 3.4}$$

That is, f relates the total molar flow in the feed stream with the total molar flow in the non-permeate stream. The shape of f can be observed in Figure 20.

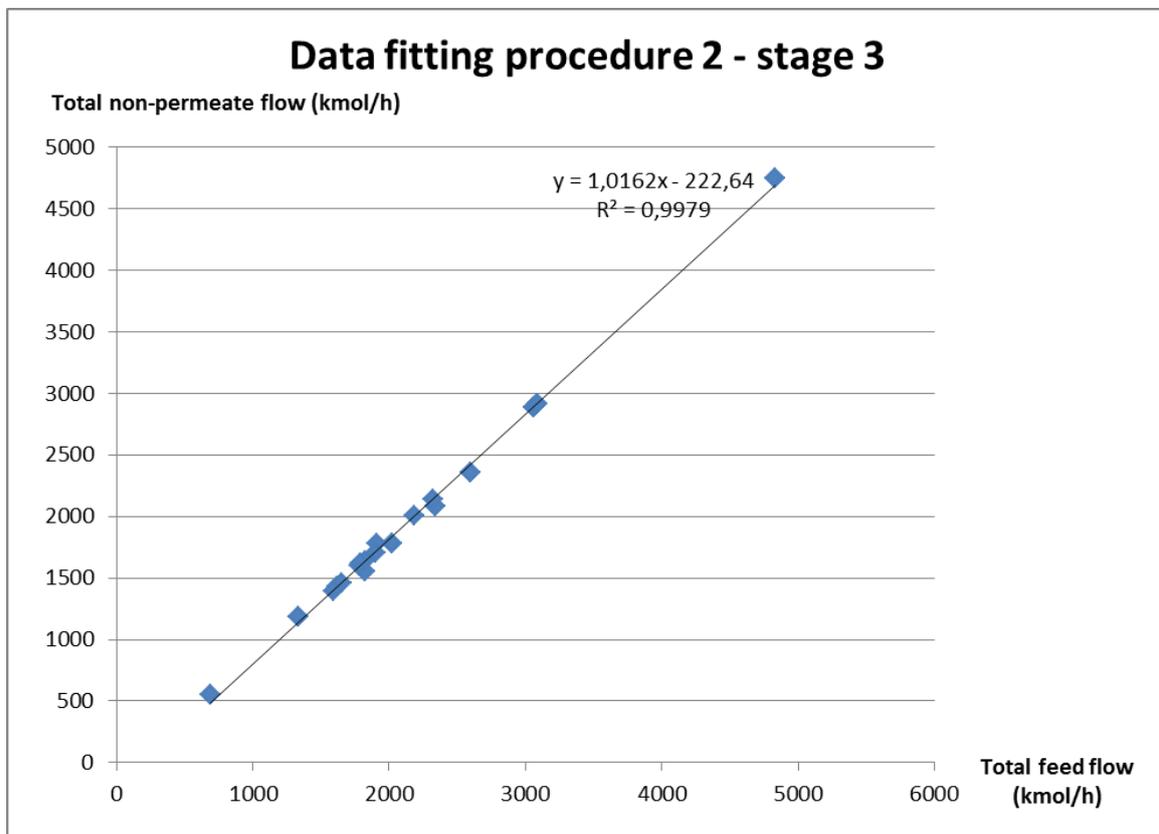


Figure 20: Data fitting procedure for non-permeate total flow and feed total flow for stage 3 (Authors)

For stage 2, the same approach was considered, that is, the total molar flow in the feed stream as a function of the total molar flow in the non-permeate stream. The result can be seen in Figure 21.

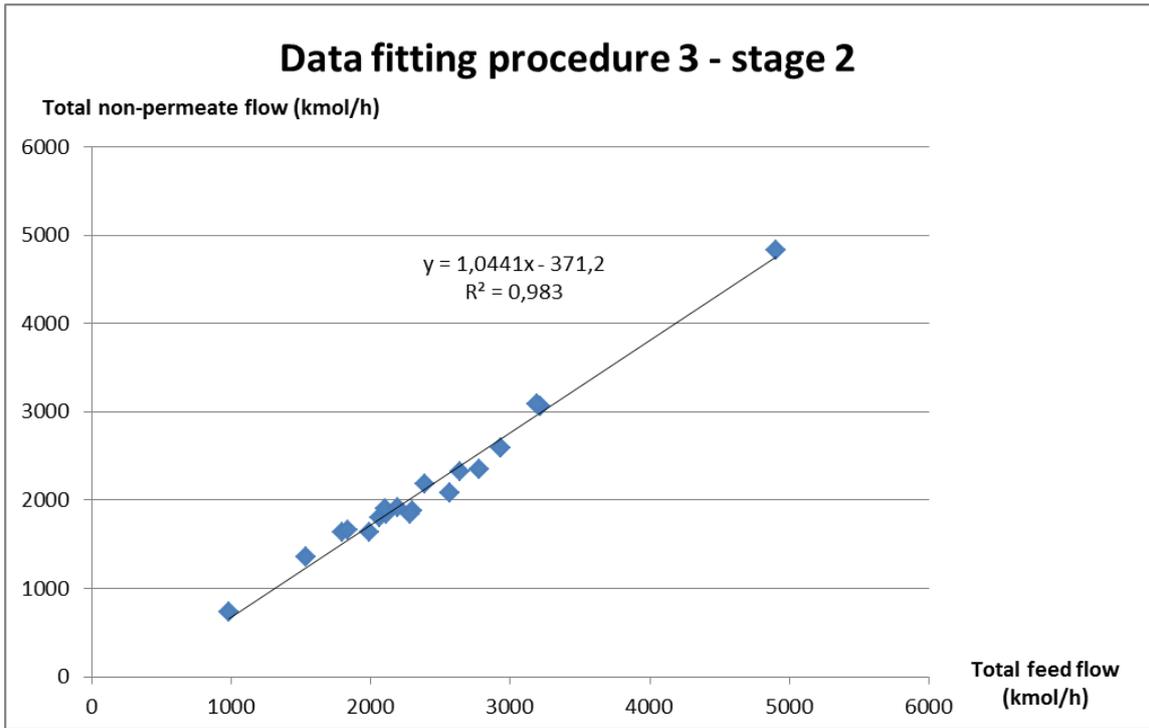


Figure 21: Data fitting procedure for non-permeate total flow and feed total flow for stage 2 (Authors)

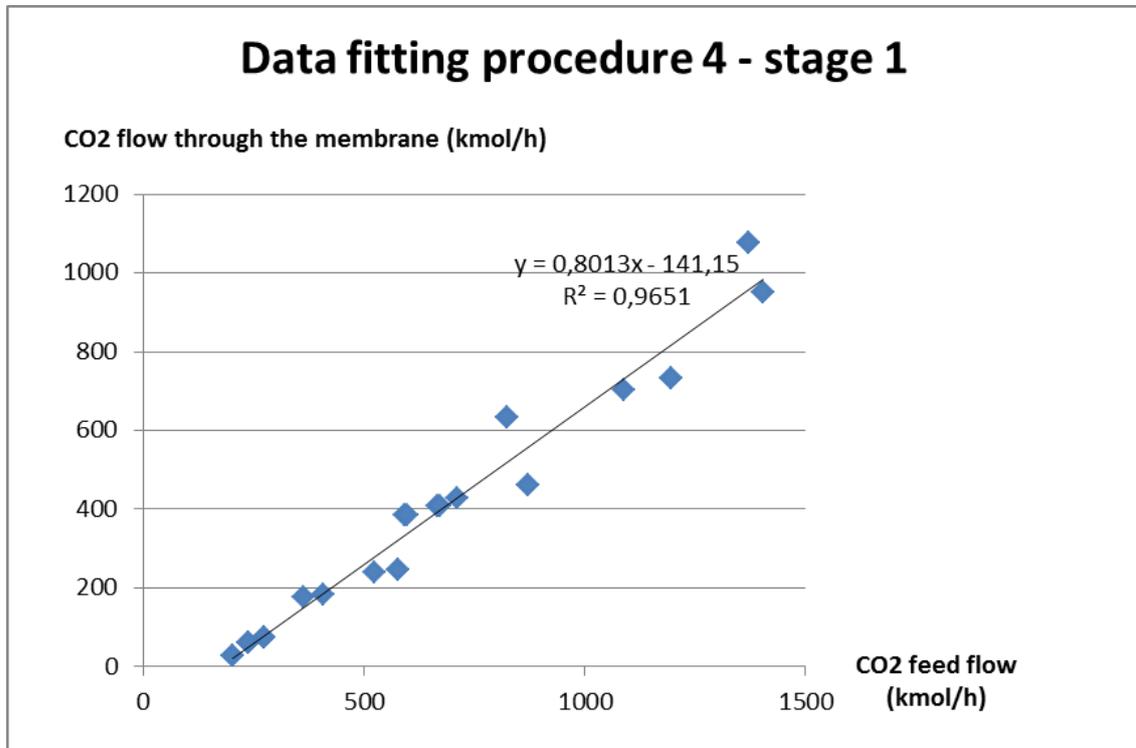


Figure 22: Data fitting procedure for permeate CO₂ flow and feed CO₂ flow for stage 1 (Authors)

Observing the behavior of data related to first-stage streams present in the industrial data used in this study, it seemed more accurate to use a relation between the CO₂ flows in the feed and permeate streams to its description. That is, for the first stage, it rules:

$$C_P Q_P = f(C_F Q_F) \quad \text{Equation 3.5}$$

This relation gets the shape shown in Figure 22 when adjusted to first-stage data.

With the above adjusted functions obtained by data fitting procedures, we have the complete set of equations necessary to model a tree-stage separation system, whose structure and background will be commented in the next section.

3.2.2 Composite separation systems

Membrane separation systems can be formed by specifically arranging a number of membrane separation units and stages. Different arrangements can enhance different profitable properties of the system. Some explanatory examples are presented and commented below.

When considering a parallel formation, the main objective with this type of positioning is dividing the flow and maintaining the driving force. In fact, when dealing with a very high flow rate, it is interesting to separate it in smaller streams in order to increase the area exposed to flux, prevent attending “membrane saturation” and delay the harmful effects of physical ageing.

When analyzing a series formation (or multi-step formation), the main intent is to maintain an efficient differential partial pressure throughout the membrane surface. As CO₂ flows faster than any other component through the membrane, its concentration will rapidly grow on the permeate side (C_P); even though this is a desirable side effect (as it prevents HC losses) it also contributes to a decrease on the driving force (ΔC), affecting process' efficiency. In order to reduce this problem, a series formation is applied.

Nevertheless, the later resource is only effective when non-permeate CO_2 concentration is still high. When dealing with low feed concentrations, the initial partial pressure on the non-permeate side is considerably low, which diminishes the driving force and reduces molecular flow through the membrane. In order to solve this problem an attempt is made to compensate the loss on driving force with an increase on the exposed area.

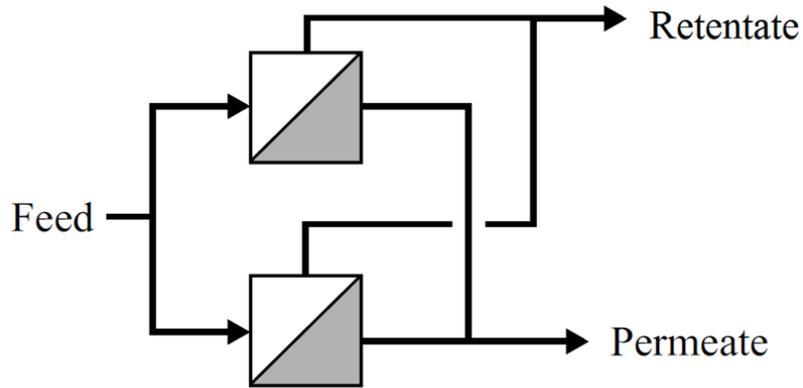


Figure 23: Parallel formation representation (adapted from[4])

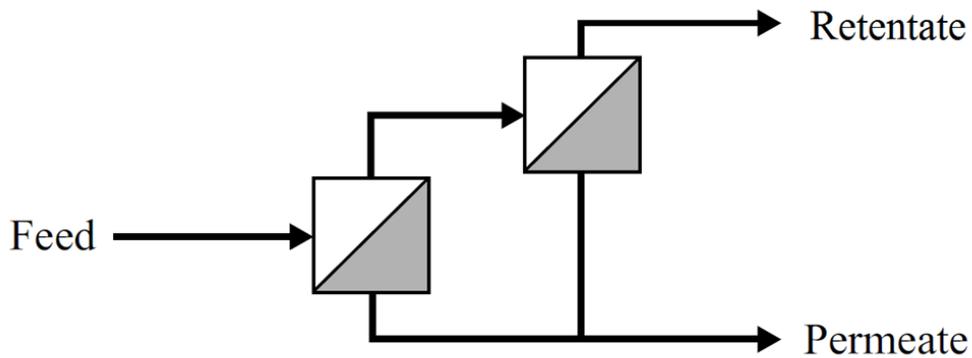


Figure 24: Two-step system representation (adapted from[4])

These concepts can be put together in order to have the best performance within a given scenario. A simplified scheme of a membrane's plant can be seen in Figure 25, where the mentioned concepts are taken into account.

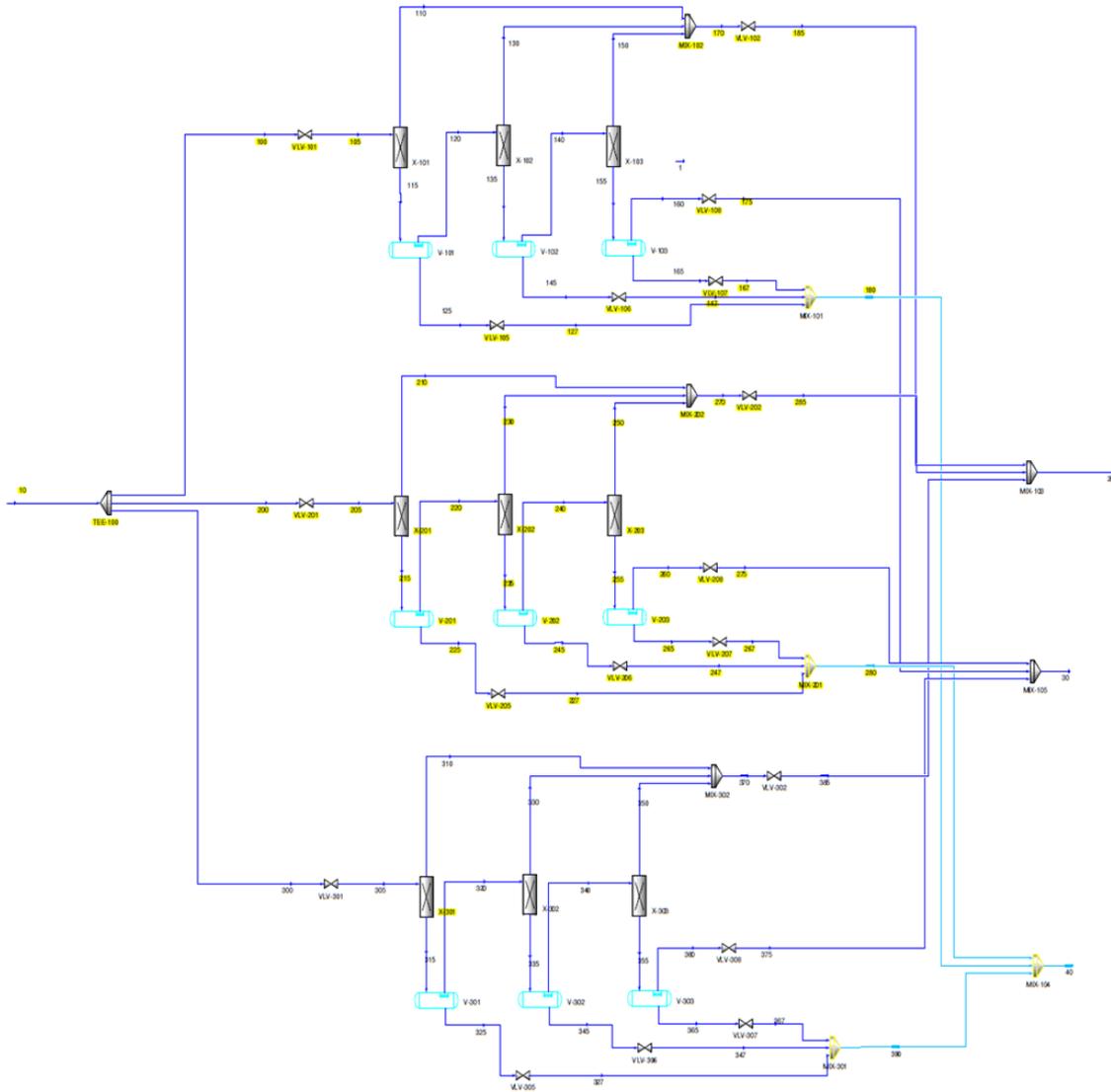


Figure 25: Membrane's simplified plant

Our case of study will be modeled as a three-stage system, where the non-permeate stream from a stage is the feed stream for the next stage, and the permeate streams meet in the end. We can represent this system as follows:

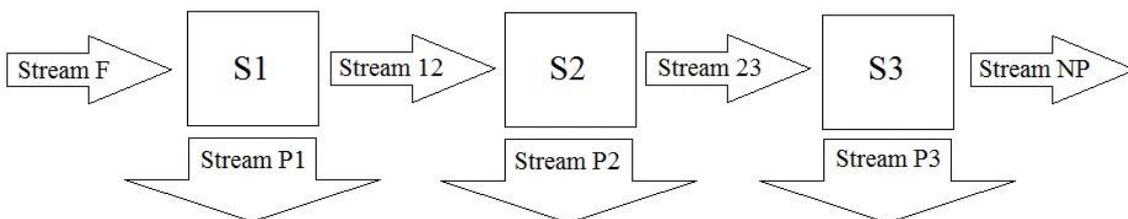


Figure 26: Three-stage membrane separation system scheme (Authors)

Following the subscript organization, the properties molar flow Q_{sub} , pressure P_{sub} and CO_2 concentration C_{sub} for each current will be referred with the subscript “sub” assuming the respective labels. In this way, the non-permeate current leaving the module 1 and serving as feed current for module 2 will present the properties Q_{12} , P_{12} and C_{12} , following the convention.

3.3 Algorithm and implementation

Using the mass balances and functions obtained by data fitting as shown above, it is possible to implement a simulator aiming to reproduce the behavior of the membrane separation system. The simulations will resemble the real observed results as much as the model is accurate enough, and in our case this means both choosing the right equations to model the system and having accurate data fitting. Another important point is that the simulator will always be more trustable close to the points which participated on the data fitting procedure. That is, simulating cases that are close to one of the real cases used in the data fitting procedures will always lead to more reliable results. It is though expected that the simulator becomes more robust as more data is incorporated to the history data.

Following the reality, it is considered that all the pressures and all the data related to the feed stream are known, together with the number and distribution of membrane modules among the stages. That is, it is known from the beginning the values of Q_F , C_F , P_F , P_{P1} , P_{P2} , P_{P3} , P_{12} , P_{23} , P_{NP} , N_1 , N_2 and N_3 . Since the stages are solved in order, that is, stage 1 is completely solved before stage 2, which is completely solved before stage 3, each stage can be solved with full information about the feed stream related to it. That is, stage 2 can use all the information with subscript 12 and stage 3 can use all the information with subscript 23.

Each of the stages is modeled using two mass balances and two adjusted functions. Since the nature of stages 2 and 3 is slightly different from stage 1, we will describe both situations separately.

3.3.1 Stage 1

Stage 1 is modeled using the following equations:

$$Q_F = Q_{P1} + Q_{12} \quad \text{Equation 3.6}$$

$$C_F Q_F = C_{P1} Q_{P1} + C_{12} Q_{12} \quad \text{Equation 3.7}$$

$$\frac{C_{P1} Q_{P1}}{N1} = f\left(\frac{C_F P_F + C_{12} P_{12}}{2} - C_{P1} P_{P1}\right) \quad \text{Equation 3.8}$$

$$C_{P1} Q_{P1} = g(C_F Q_F) \quad \text{Equation 3.9}$$

Being:

$$f(x) = 2.2228 x^2 + 9.1804 x + 3.1297 \quad \text{Equation 3.10}$$

$$g(x) = 0.8013 x - 141.15 \quad \text{Equation 3.11}$$

In order to find the value of the unknown variables, the following algorithm is used:

0) $Q_F, C_F, P_F, P_{P1}, P_{12}$ and $N1$ are known from the beginning.

1) From equation 4, $C_{P1} Q_{P1} = g(C_F Q_F)$ and we obtain the product $C_{P1} Q_{P1}$.

2) From equation 2, $C_{12} Q_{12} = C_F Q_F - C_{P1} Q_{P1}$ and we obtain the product $C_{12} Q_{12}$.

3) We can write $C_{P1} = \frac{C_{P1} Q_{P1}}{Q_{P1}} = \frac{C_{P1} Q_{P1}}{Q_F - Q_{12}}$ (using equation 1 for the denominator), where Q_{12} is unknown.

4) We can write $C_{12} = \frac{C_{12} Q_{12}}{Q_{12}}$, where Q_{12} is unknown, as above.

5) Steps 3 and 4 and equation 3 can be used to write:

$$\frac{C_{P1} Q_{P1}}{N1} = f\left(\frac{C_F P_F}{2} + \frac{Q_{12} C_{12} P_{12}}{2 Q_{12}} - \frac{C_{P1} Q_{P1} P_{P1}}{Q_F - Q_{12}}\right) \quad \text{Equation 3.12}$$

Using the bisection method, we can obtain the only unknown value in the above equation, Q_{12} .

6) Substituting the value of Q_{12} in the equations from steps 3 and 4, we can obtain C_{P1} and C_{12} .

7) Finally, from equation 1, $Q_{P1} = Q_F - Q_{12}$, obtaining Q_{P1} .

In the end of this procedure, we obtained the values for all the unknown variables, leaving stage 1 completely described.

3.3.2 Stages 2 and 3

Stages 2 and 3 follow both the same algorithm, since they are modeled by the same kinds of relations. The only changes will be in the values of the properties in the feed and non-permeate streams and in one of the adjusted functions, although these functions relate the same variables in each stage.

Using subscripts according to stage 2, being stage 3 analogously described, we have the following equations:

$$Q_{12} = Q_{P2} + Q_{23} \quad \text{Equation 3.13}$$

$$C_{12}Q_{12} = C_{P2}Q_{P2} + C_{23}Q_{23} \quad \text{Equation 3.14}$$

$$\frac{C_{P2}Q_{P2}}{N2} = f\left(\frac{C_{12}P_{12} + C_{23}P_{23}}{2} - C_{P2}P_{P2}\right) \quad \text{Equation 3.15}$$

$$Q_{23} = h(Q_{12}) \quad \text{Equation 3.16}$$

Being:

$$f(x) = 2.2228 x^2 + 9.1804 x + 3.1297 \quad \text{Equation 3.10}$$

$$h(x) = 1.0441 x - 371.2 \quad \text{Equation 3.17}$$

In order to find the value of the unknown variables, the following algorithm is used:

0) Q_{12} , C_{12} , P_{12} , P_{P2} , P_{23} and $N1$ are known from the beginning.

1) From equation 4, $Q_{23} = h(Q_{12})$ and we obtain Q_{23} .

2) From equation 1, $Q_{P2} = Q_{12} - Q_{23}$ and we obtain Q_{P2} .

3) Using equation 2, we can write $C_{P2} = \frac{C_{12}Q_{12} - C_{23}Q_{23}}{Q_{P2}}$, where C_{23} remains unknown.

4) Using the step 3 and equation 3, we can write:

$$\frac{C_{12}Q_{12}-C_{23}Q_{23}}{N2} = f\left(\frac{C_{12}P_{12}+C_{23}P_{23}}{2} - \frac{P_{P2}(C_{12}Q_{12}-C_{23}Q_{23})}{Q_{P2}}\right) \quad \text{Equation 3.18}$$

Using the bisection method, we can obtain the only unknown value in the above equation, C_{23} .

5) Using the relation in step 3, we obtain C_{P2} .

After this procedure, we could find the values for all the previously unknown variables. The solution for stage 3 follows the same algorithm, replacing subscripts P2 by P3, 12 by 23 and 23 by NP. Additionally, it must be used the appropriate function $h(x)$, already described in the section 3.2.1.1.

3.3.3 The 3-stage simulator

Considering the algorithms described above, it is straightforward to build the 3-stage simulator. Non-permeate streams in stages 1 and 2 have their values assigned to feed streams in stages 2 and 3, respectively. In this way, the 3-stage simulator can be viewed as a function S with the following structure:

$$\begin{aligned} & [Q_{12}, C_{12}, Q_{P1}, C_{P1}, Q_{23}, C_{23}, Q_{P2}, C_{P2}, Q_{NP}, C_{NP}, Q_{P3}, C_{P3}] \\ & = S(Q_F, C_F, P_F, P_{12}, P_{P1}, P_{23}, P_{P2}, P_{NP}, P_{P3}, N1, N2, N3) \end{aligned}$$

Thus, we built a function that receives as entries values from all the variables we have as a priori information and calculates all the other considered variables. This function simulates how a 3-stage membrane separator behaves given the entry variables. Its concordance with real data from the field depends both on the quality of our assumptions, given by the equations we chose to model the problem, and on the quality of the adjusted functions obtained from data-fitting.

3.4 Validation of the model

In order to check how accurate the model is when simulating the reality, its results will be compared to real cases from the industry, namely the ones we had access to make this study. Since this data is classified by Cameron, an overall of the results will be showed here, instead of the whole comparison.

Data from 30 streams were available to our work, so the comparison procedure consisted of simulating all these 30 streams using its respective initial values as inputs for the simulator and then comparing the simulated values of each output property with the values from the real cases. Instead of showing the results of every simulation, which, as mentioned above, was prohibited by Cameron, we are going to show the mean value, standard deviation, the two greatest values and the two smallest values of the relative errors between each property of each stream. The relative errors, given in percentages, were calculated as below:

$$Error(\%) = 100 * \frac{abs(Simulated\ value - Real\ value)}{Real\ value}$$

The notation abs(x) stands for the absolute value of x. Below are the tables with the results.

	C12	C23	Cnp	Cp1	Cp2	Cp3
Mean	4,76	8,44	19,98	30,38	20,46	13,57
Std Deviation	6,01	8,45	24,81	19,72	14,37	11,84
Maximum	23,99	28,23	104,36	77,61	41,99	39,11
2° Maximum	23,94	28,00	97,45	77,21	41,92	38,94
2° Minimum	0,18	0,32	0,86	6,58	0,34	1,05
Minimum	0,08	0,32	0,73	2,09	0,16	0,16

Table 5: Relative errors with respect to concentrations (Authors)

	Q12	Q23	Qnp	Qp1	Qp2	Qp3
Mean	12,15	13,46	15,37	51,74	48,83	19,17
Std Deviation	13,25	17,40	20,30	52,59	35,99	20,55
Maximum	47,43	69,13	83,31	215,86	130,53	75,36
2° Maximum	47,25	68,84	82,93	214,77	130,53	75,36
2° Minimum	0,68	0,89	1,73	8,98	4,83	1,45
Minimum	0,68	0,70	1,14	4,21	0,79	1,39

Table 6: Relative errors with respect to total molar flows (Authors)

	Q12C12	Q23C23	QnpCnp	Qp1Cp1	Qp2Cp2	Qp3Cp3
Mean	15,87	23,24	40,83	12,63	22,18	19,00
Std Deviation	15,98	29,09	64,63	8,02	15,40	21,83
Maximum	58,73	113,85	273,85	29,70	58,72	84,16
2° Maximum	58,73	113,79	261,95	29,70	58,54	83,85
2° Minimum	0,69	1,90	2,45	0,89	1,95	0,50
Minimum	0,59	1,85	1,81	0,39	0,42	0,43

Table 7: Relative errors with respect to CO₂ molar flows (Source: Authors)

Some observations can be made. First, it is possible to notice that some very good results could be obtained, if one looks at the two smallest errors obtained for each quantity. Unfortunately, very big errors, prohibitive to an industrial use, were also encountered. However, only with a bigger quantity of data one could decide if these big errors are really product of a bad model or simply represent corrupted or untreated data.

Furthermore, it is interesting to notice that the quantities $C_P Q_P$, which stand for the CO₂ flow rate in each of the permeate streams, can be more accurately simulated than the concentrations C_P and total flow rate Q_P alone. Particularly, the mean error in stage one is 12.63 for $C_{P1} Q_{P1}$, while 30.38 for C_{P1} and 51.74 for Q_{P1} . This is perfectly understandable when analyzing the solution algorithm to solve stage 1: the value of $C_{P1} Q_{P1}$ is directly obtained from $C_{P1} Q_{P1} = g(C_F Q_F)$, where $g(x)$ is one of the adjusted functions obtained from data fitting and C_F and Q_F are known variables, thus their exact values are used. Consequently, the only error present in the calculation of the quantity $C_{P1} Q_{P1}$ is the error from the data fitting procedure used to obtain $g(x)$. The quantities C_F and Q_F are calculated after the usage of both adjusted functions, thus errors arising from two data fitting procedures contribute to the final result.

One high point of the model that is not presented in the tables is the respect to the physics of the problem. There is nothing in the equations and algorithms constituting the model that could avoid concentrations and molar flows from being negative. Furthermore, nothing constrains concentrations to be between 0 and 1. Yet, these quantities not only remain positive and appropriately bounded, but also keep the same order of magnitude verified in the real data. This is a good sign that the model is adequate, even though adjustments and improvements are clearly necessary.

4 APPLICATIONS

As mentioned in the introduction, it can be important for an enterprise to be able to make good decisions about the usage of a membrane separation system even without the knowledge about the membranes inner behavior, being this information probably classified by the enterprise which sells the membrane systems' projects. For this purpose, the usage of a simulator, like the one developed in the previous chapter, is very important and, in most of the cases, essential.

Considering that a decision maker has a simulator to use, possibly one following the strategy explored in the last chapter, there are some ways in which information can be produced in order to improve the quality of the decision. We can name optimization and sensitivity analysis as two of these procedures.

4.1 Optimization using the 3-stage membrane simulator

Optimization is the procedure of finding the optimal - maximal or minimal - value of a specific function, called objective function, searching through a space of variables, the optimization variables, on which the objective function depends, and keeping these variables subjected to certain constraints. Optimization problems are inverse problems, in the sense that we know the value of the objective function associated to each combination of optimization variables, but we do not know which combination of variables will lead to the maximal or minimal - depending on the problem - value of the objective function.

The most straightforward method to solve optimization problems is the brute force. It consists basically of a trial-and-error procedure, where one chooses randomly a set of optimization variables and looks at the value of the objective function. Of course, this method is not only extremely inefficient but also do not guarantee that the optimal value will be found. In order to solve optimization problems with some hope of efficiency, a great variety of types and variations of optimization methods was developed and exists now in the literature. The choice of the method is considerably dependent on the type of optimization problem to be treated.

One example of optimization problem related to the subject of separation of CO_2/CH_4 using membrane systems is the following: one wants to minimize the total number of membrane modules used in all the three stages of a 3-stage system, subject to the fact that the CO_2 concentration at the non-permeate stream must be smaller than a given value, in order to avoid the formation of hydrates and a corrosive environment in the piping. Using the notation applied in the previous chapter, this problem is written mathematically in the following way:

$$\begin{aligned} \min \quad & N1 + N2 + N3 \\ \text{s.t.} \quad & C_{NP} < C_{lim} \end{aligned}$$

In this problem, being given all the other input variables to the membrane simulator than the numbers of membrane modules, a choice of $N1$, $N2$ and $N3$ gives a value for all the output variables, being C_{NP} one of them. It is simple to notice that a decrease in the number of membrane modules will generally worsen the efficiency of the separation of gases, thus leading to a greater value for C_{NP} . Consequently, the above optimization problem has not a trivial solution.

If considering the strategy of obtaining relations among variables through data fitting as described in the previous chapter, optimizing the usage of the membrane system and improving the quality of the simulator can be seen as a feedback procedure.

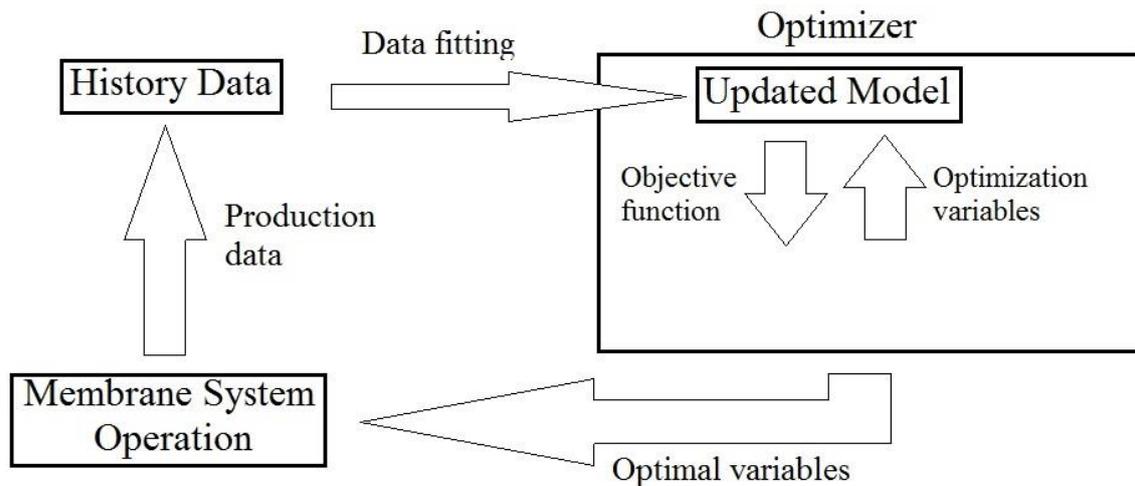


Figure 27: Optimization Methodology Scheme

The operation of a membrane system is always producing data, which can be used to obtain better adjustments for the functions from data fitting used in the membrane simulator. The simulator is then used in the optimization procedure, in order to obtain new optimal values for the optimization variables. These new values can be the same as the ones already used in the operation of the system, but if they are different, changes in the operational variables should be made. The continuous operation of the system will produce new data, probably different from previous ones because of the changes in operation, and new different data will be produced. If adequately used, this methodology can help the optimal decision in the operation of the membrane separation system.

4.2 Sensitivity analysis using the 3-stage membrane simulator

Sometimes, instead of developing a whole optimization methodology in order to find optimal operational variables, it can be of enough and easy help to perform a sensitivity analysis around the operation point. That is, one could investigate how a specific variable changes with small or unitary changes in other variables, possibly operational variables. It is profitable to know if small changes in the operation can lead to considerable improvements in some efficiency parameter.

For example, let's consider the same situation observed in the previous section: one wants to minimize the number of membrane modules subjected to a maximum value for the CO₂ concentration at the non-permeate stream. But let's ask less, in the way that, given an operational situation, described by its operational variables, one wants to check if, with less membrane modules, the operational constraint is still fulfilled. This can lead to a saving of 1 membrane module that was being used without necessity.

With numbers, let's consider the following case (synthetic):

Qf	Cf	Pf	P12	P23	Pnp	Pp	Cnp limit
3400 kmol/h	0.1	51 bar	50.5 bar	50 bar	49.5 bar	3 bar	0.0285

Table 8: Synthetic study case properties (Authors)

Furthermore, let's consider that the equipment producer sold a project using N1, N2 and N3 equals to 2, 3 and 4 membrane modules respectively, in order to meet the requirements a maximum CO₂ concentration of 0.0285 in the non-permeate stream. After installing the equipment and using it for a while, some history data is produced, and it is possible to adjust and use a membrane simulator. If we use the simulator developed in the previous chapter, we can perform a sensitivity analysis around the configuration 2-3-4 for the membrane modules, and decide if this something better can be done.

N1	N2	N3	Cnp
2	3	4	0.0275
1	3	4	0.0282
2	2	4	0.0312
2	3	3	0.0301

Table 9: Sensitivity analysis in the synthetic case (Authors)

As can be observed above, taking out one membrane module from stage 1 still leads to a CO₂ concentration in the non-permeate stream smaller than the maximum limit, thus respecting the constraint of the problem. Consequently, it is profitable for the enterprise to spare one membrane module from the first stage instead of keep using it. It happened thus that the sensitivity analysis performed using the simulator helped the enterprise to save one membrane module, leading to a more profitable situation than following strictly the project sold by the membrane company.

5 CONCLUSIONS

In this work, two main objectives were pursued. The first one was to give an introduction to the technology of gas separation, with special attention to the usage of polymeric membranes in this process. The second objective, being dependent on the knowledge presented by the first one, was to develop a simulation tool aiming to help the decision taking when using membrane separation systems. An industrial case was used as a background for information and data.

In order to justify the interest for membranes technology, it was first presented the necessity for gases separation in the petroleum industry. Using the Brazilian pre-salt reservoirs as an example, it was observed that big amounts of CO₂ are expected to be produced associated to the natural gas streams. Since not only CO₂ has no heat power associated to it but also it helps in the formation of dry ice and corrosive environments, CO₂ removal is of crucial importance when dealing with reservoirs with high concentration of this gas. The usage of carbon dioxide in enhanced oil recovery methods, namely WAG, and the possibility of its reinjection in the subsurface in order to decrease atmospheric emissions were also presented as reasons that can point to the benefits of CO₂ separation.

With the conclusion that gases separation is necessary and/or beneficial in some sense, different techniques for this procedure were presented. Alternative techniques such as absorption, adsorption and cryogenic processes were discussed in comparison with membranes technology. Since amines technology is well-established in the market nowadays, it was important to compare polymeric membranes and amines in a separated section.

The whole analysis of the state of the art related to the membrane technology, following the reasoning about its necessity and its prevalence over other technologies, allowed the conclusion that membranes separation systems are competitive and can be an important option when dealing with separation of gases, particularly in offshore environments.

The first part of this work provided informative background to the development of the second objective, which was the elaboration of a membranes system simulator. The need for this tool was justified: enterprises which produce membrane modules do not have in general the interest of transmitting the technology associated to the equipment, since keeping the know-how as a secret can aggregate value to the product *membrane modules*. Thus, the enterprise which wants to buy these modules depends on this secret knowledge, which is a very uncomfortable situation.

In order to solve this problem, it was proposed in this work the development of a model partially based on data fitting using history data from the streams present in the operation of the separation system, this procedure consisting of a reverse engineering method. Combining basic material balance equations and functions obtained by assisted data fitting, it was possible to develop a simulator in order to mimic in the best way the reality, represented by a real case study.

When analyzing the comparison between real data and data generated by the simulator, it was possible to notice that very good results could be obtained, but also very bad ones were present. The mean values of the errors and its standard deviations showed that the simulator cannot be used in industrial procedures yet, since a much better accuracy is desired in this usage. However, we believe that the lack of an enough amount of data led to such imprecision in the data fitting procedures. Since big amounts of data are produced in an industrial membrane plant, it is likely that this problem will not exist when the procedure described in this work is applied to an industrial routine. Also, as it was commented in the sections above, the results are qualitatively acceptable, in the sense that the basic physics of the problem - constrained values of concentrations, positive values of flows - are respected in all the simulations, without a priori constraints.

In the end, examples of direct applications of the developed tool were explored, indicating ways that an enterprise, after buying some membrane modules, can produce valuable information to help and guide the decision taking related to the separation system, without depending completely on the membrane seller.

The next steps in this research should be concentrated on two ways. First, the technique proposed in this work should be applied to longer time situations, where not only more data would be available, but also changes in the membranes due to plasticization would test if the optimization strategy proposed in the above sections would converge and improve the quality of information. Only with bigger amounts of data, covering a longer time and wider domains of variables, it will be possible to conclude if the approach proposed in this work is really efficient for industrial usage.

Second, it is important that theoretical knowledge of flow through polymeric membranes is gradually added to the modeling of the membrane system. Even though the procedure described has as an objective the production of information with low levels of technical knowledge about the membrane system, it is still possible to improve the model presented here in terms of technical knowledge with low investments in know-how applied to polymeric membranes.

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