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DEVELOPMENT OF A NOVEL CONCEPT OF HELIUM RECOVERY TECHNOLOGY

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Abstract

In this dissertation various hypothesis for a novel design for helium recovery technology are elaborated. As DMT currently makes use of membrane technology for biogas upgrading, it was found to be a suitable technology for the design in this project, with a possible combination with pressure swing adsorption (PSA).

This project provides an introduction to the current helium market, mentioning the current state of the technologies used for helium recovery, and which industries make use of them. This was made as an attempt to properly analyze with accurate information if a new design would be a viable and profitable concept, and in which market would such idea be able to insert itself in. After extensive research and some feedback from different companies, it was decided that the focus of this project should be on Cold Spray applications.

Chemcad, a software to design and simulate different chemical processes, was used to test the helium recovery system using membranes. Since this software lacks a feature that permits the use of cyclical modelling, simulations using PSA were not performed. In the tests using membranes, it was possible to see how the helium purity and recovery were affected by the different pressure ranges, membranes structures, and positioning of recycling units.

For an economical comparison of the different systems, a business case was built. Helium consumption values, and gas waste streams composition given from a Cold Spray manufacturer were utilized. For the technical part, the results from the Chemcad studies were used, and for the PSA, a theoretical approach was done to obtain proper dimensioning of the system. Afterwards, a house of quality was made for a broader comparison.

It was possible to conclude that for Cold Spray applications that require helium in their process, all the concepts that were designed in this project are profitable, and in less than 2 years a return of the investment is guaranteed. As for the best concept, if the size of the system is irrelevant, then a technology based only on PSA is the cheapest and most effective one. However, for a significant reduction of the footprint, a combination using a single membrane stage and a PSA system is the most viable choice, for a small additional investment and operational costs.

Keywords: Helium recovery, Gas separation, Membranes, Pressure Swing Adsorption (PSA)

Resumo

Nesta dissertação foram elaboradas várias hipóteses para um novo formato de tecnologia de recuperação de hélio. Como a DMT está a utilizar atualmente tecnologia com membranas para melhoramento de biogás, achou-se que esta tecnologia seria adequada para o desenvolvimento deste projeto, com uma possível combinação com adsorção com modulação de pressão (PSA, em inglês).

Este projeto providencia uma introdução para o atual mercado de hélio, mencionando o estado atual das tecnologias utilizadas para a recuperação de hélio, e que industrias as utilizam. Isto foi feito como uma tentativa para analisar adequadamente, com informação precisa, se um novo formato seria viável e lucrativo, bem como em que mercado é que tal ideia se poderia inserir. Após pesquisa extensa, e de algumas respostas por parte de diversas empresas, foi decidido que o foco deste projeto seria em aplicações de Spray Frio.

O Chemcad, um software para o desenho e simulação de diferentes processos químicos, foi usado para testar o sistema de recuperação de hélio, à base de membranas. Este software não permite o modelamento ciclico, então simulações com PSA não foram possíveis. Nos testes com membranas foi possível ver como a pureza e recuperação do hélio é afetada pelas diferentes gamas de pressão, estruturas de membranas, e posicionamentos das unidades de reciclagem.

Para uma comparação económica dos diferentes sistemas, um caso de negócios foi construido. Valores de consumo de hélio e a composição de correntes de resíduo de gás, dados por uma empresa de manufatura de Spray Frio, foram utilizados. Para a parte técnica, os resultados obtidos dos estudos com o Chemcad foram usados, e para o PSA, uma aproximação teórica foi feita para um dimensionamento apropriado do sistema. Um enquadramento de qualidade foi feito após, para uma comparação mais geral.

Foi possível concluir que para aplicações de Spray Frio, que requerem o uso de hélio no seu processo, todos os conceitos desenvolvidos neste projeto são lucrativos, em que menos de dois anos, um retorno do investimento é garantido. Em termos do melhor conceito, caso o tamanho do sistema seja irrelevante, a tecnologia baseada no PSA é a mais barata e efetiva. No entanto, para uma redução significante do tamanho, uma combinação usando um sistema de membranas de uma etapa, com PSA, é a escolha mais viável, com apenas um custo adicional no investimento e nos custos operacionais.

Palavras-chave: **Recuperação de hélio, Separação de gases, Membranas, Adsorção com modulação de pressão (PSA)**

Declaration

I hereby declare, under word of honour, that this work is original and that all non-original contributions is indicated, and due reference is given to the author and source

Gonçalo Martins 08/02/2021

Sign and date

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Notation and Glossary

A	area	m^{2}
d_p	diameter particle	m
D	diffusivity	m^{3}.s^{-1}
g	gravitational acceleration	m.s^{-2}
J	diffusion flux	mol.(m^{-3}.s)$^{-1}$
ℓ	membrane thickness	m
P	permeability	H/m
P	pressure	Pa
Q	flowrate	m^{3}.s^{-1}
S	solubility	mg.L^{-1}
t	time	S
u_i	velocity interstitial	m.s^{-1}
u_{mf}	velocity minimum fluidization	m.s^{-1}
V_g	permeation volume	m^{3}
x	position length	m

Greek Letters

ε_p	porosity particle	
ε_b	porosity bed	
ε_b	porosity total	
ϕ_s	sphericity adsorbent	
μ_f	viscosity fluid	Pa.s
ρ_f	density fluid	Kg.m^{-3}
ρ_p	density particle	Kg.m^{-3}
ρ_d	pressure driving force	

List of Acronyms

CERN	European Council for Nuclear Research
DMT	Dirkse Milieu Technologie
MRI	Magnetic Resonance Imaging
NMR	Nuclear Magnetic Ressonance
PSA	Pressure Swing Adsorption

1. Introduction

1.1 Presentation of the project

Helium is a very scarce element on Earth, and since it is also non-renewable, and due to its increased usage in the past decades, it means that its available quantity keeps decreasing. Therefore, the price has been skyrocketing, and unless new natural gas fields with relevant quantities of helium are found, the price will keep increasing. Because of this, companies that depend on helium are in a race to either replace it with a cheaper option, or a recovery system is built in.

DMT is a company that specializes in the usage of membranes in their biogas upgrading system, and due to the recent development of novel membranes that can be applied in helium gas separation, an opportunity to possibly built a helium recovery system emerged. This project was designed to investigate different product markets where such a system would be desired.

After extensive research and talks with several different companies in different sectors of the market, it was decided to develop the recovery system for Cold Spray applications, in which they use gases such as air, nitrogen and helium to accelerate particles to perform coatings on different subtracts. Even though they use a lot of nitrogen and air, which is a lot cheaper, the use of helium is preferred since they can obtain higher speeds at lower temperatures, which results in higher quality of coating, and for some industries, it makes helium essential. The main contaminants to helium in the cold spray applications is air, so other companies in different industries that possibly have the same contaminants, may also profit from such a recovery system.

Following this decision, as well as in parallel to this decision, literature was reviewed to understand current existing technologies focusing on the recovery of helium, which are currently focused on cryogenic, PSA and membrane recovery systems. Since the cryogenic system would elevate the costs immensely, it was decided to focus on a gas phase-based recovery system for the helium. The main goal of this dissertation was to design and validate different possibilities and select the best viable solution for DMT and for the cold spray industry.

As mentioned before, DMT already has extensive experience with designing membrane systems. DMT uses Chemcad for modeling, which they provided to test and design the membrane parts of the different possible scenarios. Since the PSA requires a cyclical modelling mode (which is not supported by the Chemcad version used by DMT), Chemcad would be ineffective. Therefore, the PSA part of the system in this thesis was focused on calculations regarding dimensioning and costing.

1.2 DMT Presentation

DMT is a Dutch company based in the province of Friesland in the Netherlands, in Joure. The company exists since 1987 and has currently over 125 operational sites worldwide. It is a company that specializes in engineering and delivering turn-key installations that help companies turn their waste into products (such as example biomethane, a green gas) in such a way that they provide profitable solutions for everyone involved, while creating reliable ways to improve our environmental conditions.

The main product line is related to biogas upgrading, where CO2 is removed, and raw biogas is turned into green gas. DMT is currently number one worldwide in this type of technology. Moreover, DMT provides other gas cleaning technologies such as desulphurization, and keeps striving to improve and increase their market in order to create a cleaner world, through the efforts of the research and development team, where I had the pleasure to work at.

1.3 Project contribution

This project provides an insight on the usage of helium and its market. It can introduce the existing helium recovery technologies, their benefits, as well as disadvantages and some of the companies that currently work in this kind of systems, and companies that needs further research in this kind of technologies.

This dissertation delves deeper into the study of different structures of membrane arrangements through the software Chemcad, which can be proven useful for the specific scenario of the helium recovery system that is being designed, but for other potential uses of membrane separation as well. It also provides a simple design for a PSA system which can be useful as an introduction to PSA systems, as well as for overall pricing estimations, as it was the goal of this work.

1.4 Thesis structure

The current dissertation is divided in six chapters, the first one being the introduction of this project and its goals, as well as the company where it was developed.

The second chapter discusses the current state of the art of helium usage and recovery. It gives a short description of helium and its usefulness, the existing relevant recovery technologies for this element, as well as a short explanation to membrane and PSA technology, since they are the ones who are explored further in this work.

The third chapter gives an introduction into the materials and tools vital to the development of the different systems that are compared. It shows not only which are used and why, but also the main characteristics and the calculations involved in their design.

The fourth chapter presents a deep study on the design of the membrane part of the system. It describes different arrangements, focusing on recycling structures, different operational pressures and different numbers of membranes and its effect on the composition of the permeate and recovery rates of helium.

The fifth chapter was reserved to discuss the best results obtained with the different system designs. A business case was drafted as part of the technical economic analyses. Moreover, a house of quality was used to highlight the main differences and advantages or disadvantages of each scenario.

A final assessment with the main conclusions and suggestions to be taken from this project are highlighted in the sixth chapter.

2. State of the art

2.1 Helium and its market

Helium is the chemical element number 2, and the first one on the noble gas group, it was first detected during a solar eclipse by Georges Rayet in 1868, due to its signature yellow spectral line in the emitted sunlight but was only proven to exist in 1895, because it was found to be emanating from a uranium ore. Helium is the second most abundant element in the universe, but due to its low density, it tends to escape our atmosphere which makes it very scarce on Earth, with an approximate concentration 5,2 ppm by volume in the atmosphere. The only reason it exists on Earth is because it is a by-product of radioactive materials, which accumulates in natural gas fields, where we can extract it from.

The production of helium is through Nitrogen Rejection Units or Liquid Natural Gas plants, the biggest industrial companies that perform this type of production are: Air Liquide, Air Products, Linde, Matheson, Messer and Praxair. Conventional helium plants use a combination of a cryogenic distillation system to produce crude helium which is then purified by a PSA unit, however, there are other plants who have combined a membrane design with the PSA units to perform helium production.

It is estimated that there are currently 8 million tons of geological helium reserves, which are mainly from the U.S., Qatar, Algeria, and Russia, with some new gas fields with high concentrations being recently discovered in Africa. The annual production of helium from natural gas is estimated to be around 30.000 tons. In the following figure 1, it is possible to see helium production worldwide of 2019.

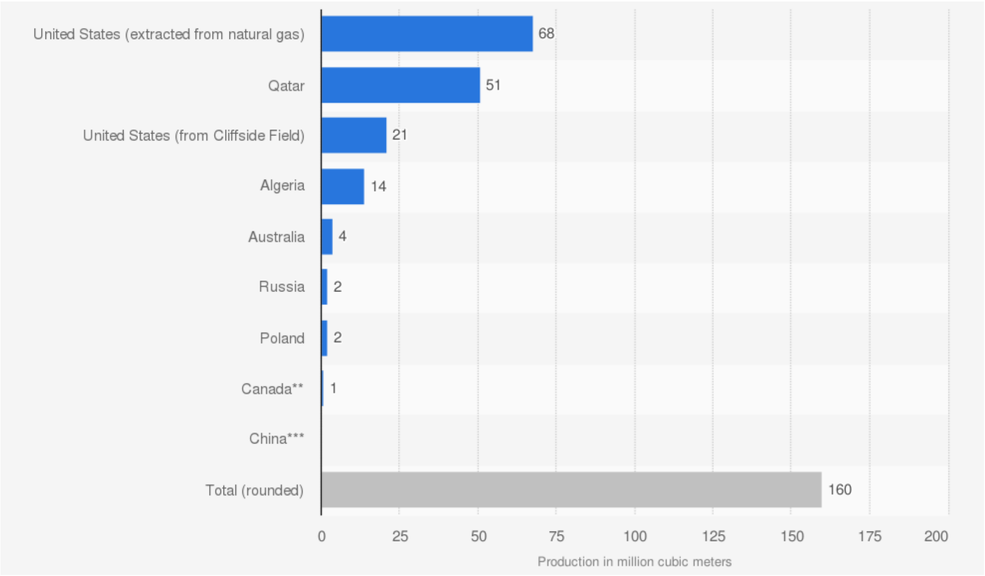


Figure 1 - Production of helium worldwide, by country in 2019 [1]

This element has many appealing properties, it is inert, it is not toxic nor flammable, it is the second smallest particle and the second lightest, and it has the lowest boiling point amongst all the elements. Due to its incredible variety of unique properties, it is highly valued in a wide range of different fields, with an estimated global consumption of around 150 million m^3 per year. In the following chart of the figure 2, we can see the approximate percentages of each industry on the consumption of helium from 2017.

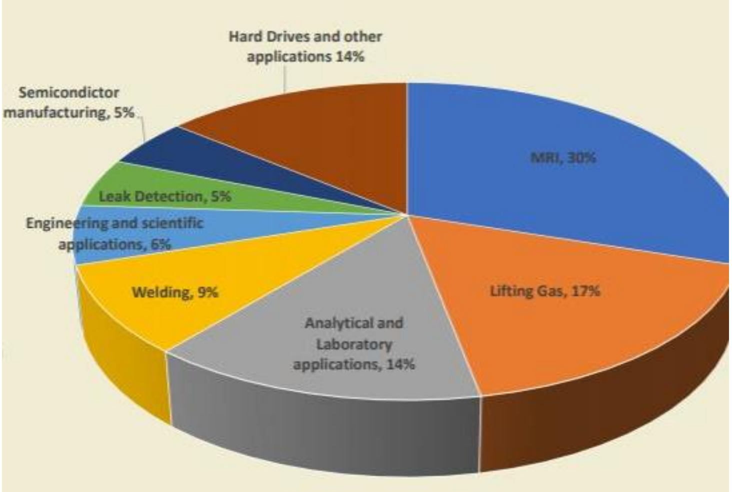


Figure 2 - Helium Consumption in different Markets in 2017 [2]

Since the demand for helium keeps increasing, and since helium is a non-renewable gas, its price keeps increasing, with the only foreseen way of it lowering, is if more natural gas fields, with relevant concentrations of helium are discovered, or if innovative helium recovery systems are provided in a way that majorly affects the demand for helium. In the following graph of the figure 3, obtained in the year 2015, we can have an idea how the helium reserves and price have been fluctuating.

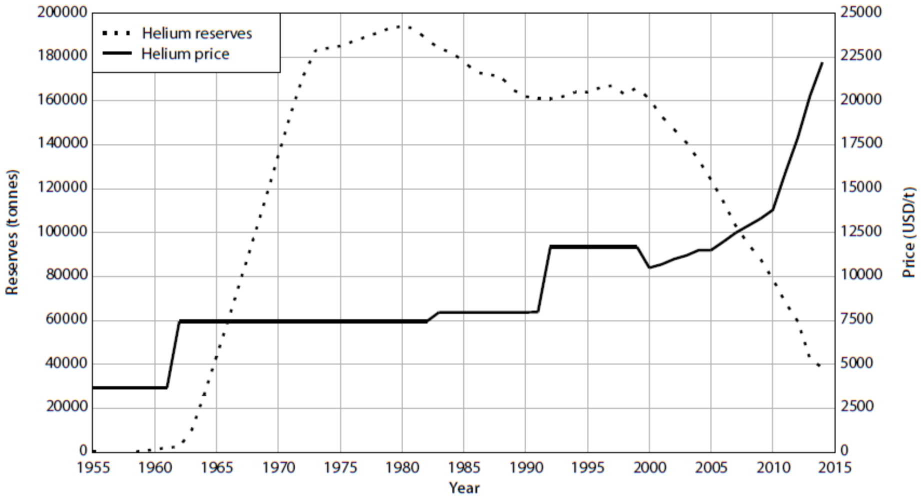


Figure 3 - Helium reserves and prices [3]

Helium most known as a lifting gas, either for party balloons or airships, however, this is a very small part of the market. The industry that uses it the most is the cryogenics industry. This is because helium is the element with the lowest boiling point, and together with its very high specific heat and thermal conductivity. This makes it the ideal cooling agent for superconductive magnets, for example for MRI and NMR machines, or particle accelerators like the ones used in CERN, even nuclear reactors use helium as a cooling medium. In this industry, since they use high quantities of helium with high levels of purity, in cryogenic temperatures, there are already a lot of recovery systems in the market, from companies like, Linde, Quantum Design, Cryo Technologies, Demaco Holland BV, and others. There are also several universities who, due to the amount of helium consumption for their cryogenic cooling systems, developed their own systems.

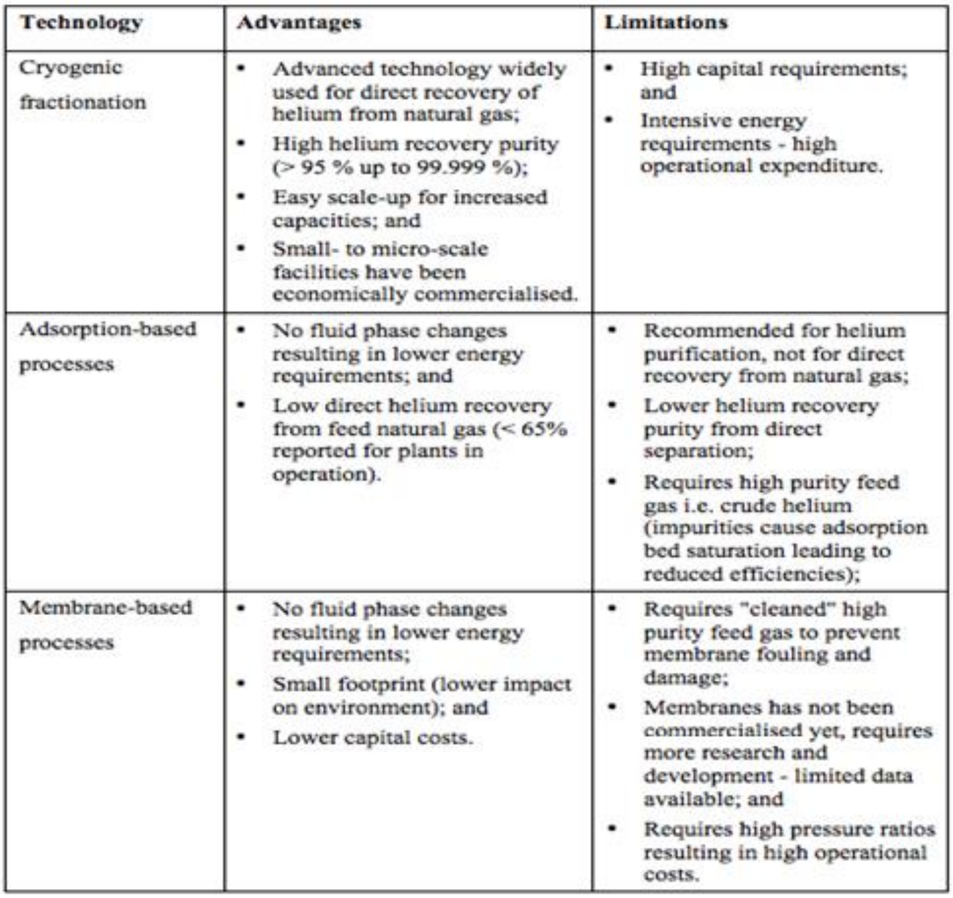
It is also widely used in the semiconductor industry due to its inertness. It is used as a protective gas, or to control the atmosphere during the growth of silicon and germanium crystals. Its conductivity properties make it very useful for cooling in this sector. The welding industry also requires helium because it is chemically inert and it also has the highest ionization potential of any atom, so it can be used as a shielding gas, in arc welding, which prevents the metal from oxidizing in the molten state. Both these industries use a lot of helium gas, and they require high levels of purity, usually of grade 4.0 (99,99%) but can be as high as 6.0 (99,9999%), which tend to produce gas waste streams with a lot of contaminants, making the recovery systems very hard to build, and very expensive. Some examples have been found, like Linde's helium recovery system for semi-conductor manufacturing, and ReiCat's for the plasma arc welding industry.

There are other industries that may not use as much helium gas but don’t produce many contaminants, which make them a bit more attractive for helium recovery systems. such as the fiber optic manufacture, where helium is important as a cooling agent for high speed production of fiber optics and cold spray applications, where they can use helium to throw small particles into a substrate for high quality coating. Individual recovery systems have been developed, such as Nextrom’s recovery system of helium in fiber optics manufacture, and Polycontrol’s recovery system for cold spray applications.

There are many other smaller uses for helium, from breathing gas mixtures for deep drivers, helium-neon lasers for eye surgery, laser pointers to supersonic wind tunnels. It is even important for the advancement of our understanding of the quantum realm, because after being cooled down to below a certain temperature, it stops behaving like an ordinary liquid, and becomes a superfluid, with practically no viscosity. At even lower temperatures it is theorized to behave like a superglass, an amorphous solid with superfluid properties, however that has yet to be proven. However, due to the low helium usage in these fields, a recovery system simply would not be economically feasible.

2.2 Helium recovery technologies

There are a high variety of systems that recover helium, whether in its production from natural gas, or from industries that use it in quantities that make its recovery vital. Figure 4 sums up the three main technologies where the recovery systems are based.



Technology	Advantages	Limitations
Cryogenic fractionation	• Advanced technology widely used for direct recovery of helium from natural gas; • High helium recovery purity (> 95 % up to 99.999 %); • Easy scale-up for increased capacities; and • Small- to micro-scale facilities have been economically commercialised.	• High capital requirements; and • Intensive energy requirements - high operational expenditure.
Adsorption-based processes	• No fluid phase changes resulting in lower energy requirements; and • Low direct helium recovery from feed natural gas (< 65% reported for plants in operation).	• Recommended for helium purification, not for direct recovery from natural gas; • Lower helium recovery purity from direct separation; • Requires high purity feed gas i.e. crude helium (impurities cause adsorption bed saturation leading to reduced efficiencies);
Membrane-based processes	• No fluid phase changes resulting in lower energy requirements; • Small footprint (lower impact on environment); and • Lower capital costs.	• Requires "cleaned" high purity feed gas to prevent membrane fouling and damage; • Membranes has not been commercialised yet, requires more research and development - limited data available; and • Requires high pressure ratios resulting in high operational costs.

Figure 4 - Helium recovery technologies [4]

In technologies based in cryogenic fractioning, separation is usually achieved at temperatures below -65ºC, and can achieve high levels of purity and recovery alike. These are usually divided in two groups, multi-flash cycles and high-pressure distillation column processes. Multi-flash separators have higher energy requirements compared to high-pressure distillation ones but have lower capital costs and have lower helium concentrations in overhead vapor streams. Either way, both these groups have a high capital cost, and high energy requirements, so even though they are both very efficient, their cost is also very high.

For the adsorption-based ones, the most known most researched and most widely used is PSA technology for helium recovery, or for purification part of the process. This technology involves the diffusion of a component in a bulk fluid into the pores of a solid surface and its corresponding binding. The driving force for the adsorption is the concentration difference, which means that the pore area will have a low concentration of the component which the bulk phase is rich of. The desorption, however, cannot be done the same way. To release the adsorbed component and regenerate the surface material there is a need to use specific technology. When that technology changes the pressure to obtain that result, that is called the Pressure Swing Adsorption (PSA), if vacuum is used for that pressure change, then it is called a Vacuum Pressure Swing Adsorption (VPSA). This can also be achieved by a temperature difference, through a Temperature Swing Adsorption. Other less known processes include fluidized and moving bed operations, but in industrial levels they are still undesirable at the moment.

Even though membrane technologies for helium recovery have not received the same amount of research and effort as cryogenics or adsorption systems, it still is a technology that is quickly emerging, and getting a lot of interest, because membranes usually have higher uptime and overall reliability. It is also a purely physical process, where a gas, or liquid flow, will encounter a membrane, that will block certain unwanted particles from passing through, while allowing the desired particles to pass, creating two different fractions, the permeate, and the retentate. However, it still has some issues, to achieved high purities it required multi-stage, which quickly raises its operational and capital costs, which defeats its purpose. It may also require pre-treatment, to prevent fouling in the membranes.

2.3 Membrane Separation

Membrane technology is relatively new to commercial applications, with the first installation surging in the 1960s, however, the science behind it has a long historical development in laboratory study. It is currently one of the fastest emerging technologies and has been for the past decades.

Gas separation by membrane technology is mainly dependent on each component's permeation rates. This depends on each component's specifications, partial pressure difference on the components on both sides of the membrane, the membranes specifications and the interactions of both membranes and components. In a system completely based on membranes, complete recovery is extremely difficult, because the partial pressure difference is the main driving force, which means there is always some remnants of the desired product in the residue stream.

Usually, natural gas comprises mostly of nitrogen and methane, almost up to 90%, so for the separation and recovery of helium using membranes, research focuses on the He/CH_4 and He/N_2 separation. In the recovery projects for companies that use helium with few contaminants, or even just air as a contaminant, the focus should also be on He/N_2, and He/O_2. In the following figure 5 we can have an idea how the permeability dependence of difference particles is to their corresponding gas kinetic diameter in microporous silica membranes.

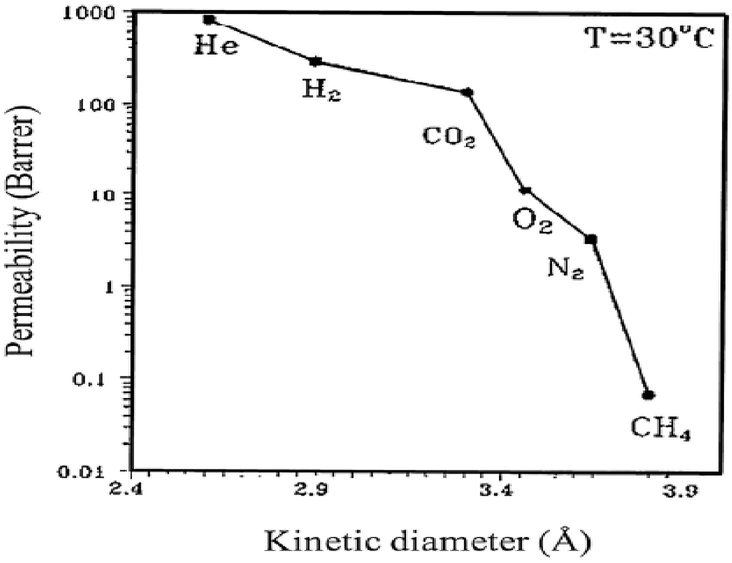
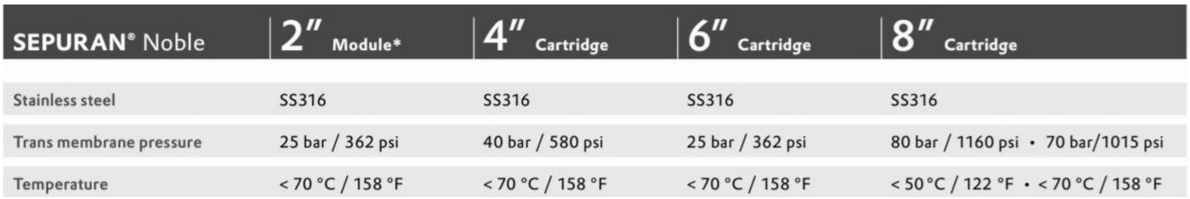


Figure 5 - Permeability vs kinetic diameter in silica membranes [5]

There is a huge variety of membranes in the current market, the most known is the dead-end membrane, where the feed is passed through a membrane and the retentate is blocked there, while the filtrate is released at the other end. The most used industrially is the crossflow membrane, in which most of the feed flows tangentially across the surface of the membrane, these can be in spiral wounds, where the feed enters from the outer layers, and the permeate exits from the inner layers, and the retentate or concentrate, leaves in the outer layers, or in hollow fibers, which are usually packed into cartridges which can then be used.

There are already some natural gas fields that extract helium using membranes, even if just a part of the process. Like in the village of Mankota, Canada, in a recovery process designed by Linde, using Evonik's Sepuran Noble membranes, whose features we can see in figure 6. Generon's recovery system is also adapted to helium membrane separation from natural gas fields, but data on where this system is in place was not found.



SEPURAN® Noble	2″ Module*	4″ Cartridge	6″ Cartridge	8″ Cartridge
Stainless steel	SS316	SS316	SS316	SS316
Trans membrane pressure	25 bar / 362 psi	40 bar / 580 psi	25 bar / 362 psi	80 bar / 1160 psi • 70 bar/1015 psi
Temperature	< 70 °C / 158 °F	< 70 °C / 158 °F	< 70 °C / 158 °F	< 50 °C / 122 °F • < 70 °C / 158 °F

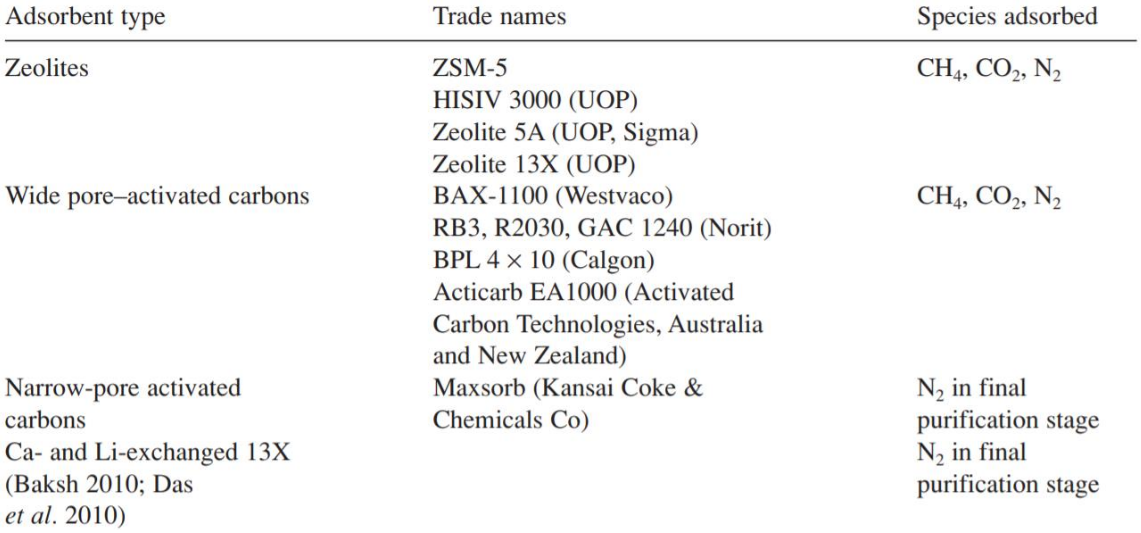
Figure 6 - Standard operation values for various sizes of the Sepuran Noble membrane [6]

2.4 Pressure Swing Adsorption

Adsorption is the phenomenon of certain particles that, through its characteristics, adhere to a surface. This is a consequence of surface energy, which depend on the details of the species involved in the adsorption process, this can happen through a physical property, chemical one, or even through electrostatic.

The PSA works by letting a feed stream, containing a mixture of gases, run through fixed beds, filled with adsorbents, that have the characteristics to adsorb the necessary components, which will be the retentate. The rest, that is not adsorbed, will be the permeate, which are usually the lighter components, and will travel through the column faster than the other components. The process must be stopped before the adsorbent is fully saturated, and the heavy components pass through the beds. That is why these technologies usually have at least two beds, so that while one is in its desorption phase, the other can keep working, and the process can be done in a continuous mode.

In the figure 7 it is possible to see the types of adsorbents, already commercially available for helium recovery, with their corresponding trade names and the species that are adsorbed.



Adsorbent type	Trade names	Species adsorbed
Zeolites	ZSM-5 HISIV 3000 (UOP) Zeolite 5A (UOP, Sigma) Zeolite 13X (UOP)	CH_4, CO_2, N_2
Wide pore–activated carbons	BAX-1100 (Westvaco) RB3, R2030, GAC 1240 (Norit) BPL 4 × 10 (Calgon) Acticarb EA1000 (Activated Carbon Technologies, Australia and New Zealand)	CH_4, CO_2, N_2
Narrow-pore activated carbons	Maxsorb (Kansai Coke & Chemicals Co)	N_2 in final purification stage
Ca- and Li-exchanged 13X (Baksh 2010; Das *et al*. 2010)		N_2 in final purification stage

Figure 7 - List of commercial adsorbents for selective adsorption from helium[7]

3. Gas Separation Technologies

3.1 Membranes

In this project, Chemcad, a chemical process simulation software used to design and simulate a variety of process flowsheets, was utilized for the modelling of the different membrane setups. For the simulations, hollow fiber membranes were designed, in a counter-flow pattern where the feed would enter through the bore side.

Hollow-fiber membrane consists of a large number of membrane fibers, packed in parallel in a bundle, and sealed at one end, while the other end is encased in an epoxy plug, where the fibers are left open. The bundle is placed in a metal shell, or several bundles through several shells, both ends of these shells have opening to permit the gas to flow. In this design, the feed gas enters through the bore side, where the more permeable components pass from the inside of the fibers, through openings on the fiber tube sheet. A counter-current flow configuration was adopted in the scenarios since this tends to alleviate concentration polarization and minimizes stagnant regions. It is expected that the helium permeates more through the fibers and leaves through the shell side, while the contaminants, argon, nitrogen, and oxygen, will mainly flow through the bore side.

For the simulation conditions, the membranes were based on previous data obtained by DMT for polyimide membranes made from BDPA, which were selected for biogas upgrading, due to their high thermal, chemical, and mechanical durability. These membranes are classified as dense polymeric membranes, where the gas molecules transport follows the solution-diffusion model, proposed by Graham, as shown in (1). The permeability, P, of the gas molecules is determined by diffusivity, D, and solubility, S.

$$\boldsymbol{P = D * S} \tag{1}$$

Permeability of membrane materials can also be defined through the following formula:

$$\boldsymbol{P = \frac{V_g . l}{A . t . \rho_d}} \tag{2}$$

With $\boldsymbol{V_g}$ as the permeation volume of gases and vapors present, l as the membrane thickness, A as membrane area, t as the unit of time, and $\boldsymbol{\rho_d}$ as the driving force of pressure.

With Fick’s law of diffusion, applied for gas systems, the diffusion flux, J, can be defined as:

$$J = P_{c}\cdot\frac{\partial \mathrm{p}}{\partial \mathrm{x}} \tag{3}$$

With P_c as permeability coefficient and $\frac{\partial \mathrm{p}}{\partial \mathrm{x}}$ describing the rate of the pressure driving force throughout the length of the membrane. Permeation properties of some relevant gases can be seen in fig. 8.

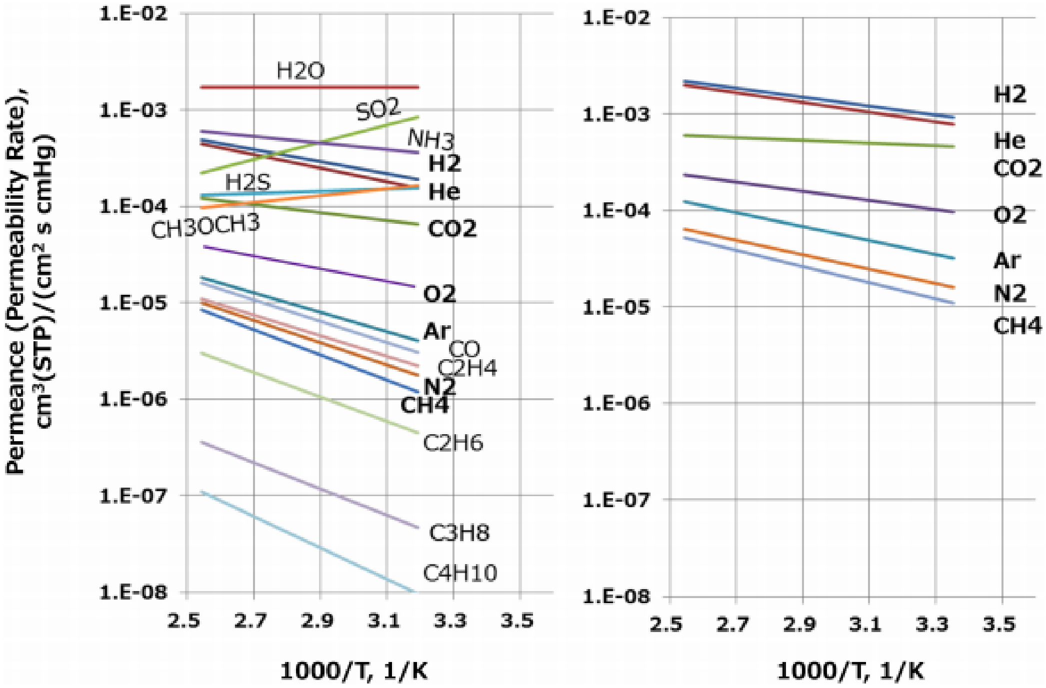


Figure 8 - Examples of gas and vapor permeation properties of polyimide hollow fiber membranes [10]

The simulations, revealed further in this paper, were run at a fiber length of 1m, with internal diameter of 200 μm and the external one of 300 μm, with a total number of fibers equaling 50 thousand, which gave an approximately total surface area of 47,124 m^2. The permeance, which is expressed as a thickness normalized permeability, P/l, is input in gas permeation units, GPU. For the components present in the feed, the values input were 300 GPU for helium, 5 GPU for nitrogen, 3 GPU for oxygen and 2 GPU for Argon.

3.2 PSA

The dimensions of the bed were calculated regarding the flowrate as a main concern, because for the PSA to function properly the process cannot reach fluidization, and to avoid that, the interstitial speed should be lower than 80% of the minimum fluidization velocity, u_{mf}, which was calculated using the Ergun equation stated in equation (4):

$$\boldsymbol{g}.(\boldsymbol{\rho_p}-\boldsymbol{\rho_f}).(\mathbf{1}-\boldsymbol{\varepsilon_{mf}}) = \mathbf{150}.\,\mu_{\boldsymbol{f}}.\boldsymbol{u_{mf}}.\frac{\mathbf{1}-\boldsymbol{\varepsilon_{mf}}}{\boldsymbol{\phi_s}.\boldsymbol{\varepsilon_{mf}}^{\mathbf{3}}.\boldsymbol{d_p}^{\mathbf{2}}}+\frac{\mathbf{1,75}.\boldsymbol{\rho_f}.\boldsymbol{u_{mf}}^{\mathbf{2}}}{\boldsymbol{\phi_s}.\boldsymbol{d_p}.\boldsymbol{\varepsilon_{mf}}^{\mathbf{3}}} \tag{4}$$

With g representing gravitational acceleration with 9.81 m.s^{-2}, $\boldsymbol{\rho_p}$the density of the adsorbent particle, $\boldsymbol{\rho_f}$ the density of the fluid, both densities in kg.m^{-3}, μ_f the fluid viscosity in Pa.s, $\boldsymbol{\phi_s}$ as the sphericity of the adsorbent, $\boldsymbol{\varepsilon_{mf}}$ the minimum fluidization porosity of 0,4 with no units and $\boldsymbol{d_p}$ as the adsorbent particle diameter, in meters. Using, $\boldsymbol{u_i}$**,** the interstitial velocity in m/s, as 80% of u_{mf}, the area, and subsequently, the dimensions of the PSA are calculated, using equation (5):

$$\boldsymbol{u_i} = \frac{\boldsymbol{Q}}{\boldsymbol{\varepsilon_t}.\boldsymbol{A}} \tag{5}$$

With Q as the flowrate in m^3.s^{-1}, the area, in m^2, and $\boldsymbol{\varepsilon_t}$ the total porosity of the system, which is calculated using the bed porosity, $\boldsymbol{\varepsilon_b}$, and posority of the adsorbent particle, $\boldsymbol{\varepsilon_p}$, as the following formula (6) shows:

$$\boldsymbol{\varepsilon_t} = \boldsymbol{\varepsilon_p} + \boldsymbol{\varepsilon_b}.(\mathbf{1}-\boldsymbol{\varepsilon_p}) \tag{6}$$

With the minimum fluidization velocity calculated, the maximum interstitial velocity could be obtained from it, and from that, the area of passage in the PSA bed could be obtained, and its diameter. As for the length, it was derived from the L/d ratio, which from literature research on helium recovery with PSA, was thought to be of 4.

As for the adsorbent, after literature research, it was decided that for helium recovery with air as a contaminant, as is this case, the Lithium-Exchanged Low-Silica X zeolite, or in short, LiLSX zeolite, is the most appropriate. This adsorbent has as spheric shape with a diameter of 1mm, so for the calculations a sphericity of 1 was used, it also has a density of 1200 kg.m^{-3}, and a porosity of 0,58, with the PSA bed a porosity of 0,36, meaning that the total porosity would be equal to 0,731.

By making use of the results obtained by the study on LiLSX zeolite performed by the Department of Chemical Engineering, Lehigh University, represented in the reference [15] and [16], and using the software Scanit, a few points were obtained from their graphs, and with those points, the graphs of the figs. 9, 10 and 11, were constructed, and using the Langmuir model approach stated in (7), in Excel, it was possible to obtain key characteristics of this adsorbent on the contaminants Argon, Nitrogen and Oxygen.

$$\boldsymbol{Q = Q_{max}\frac{bP}{1+bP}} \tag{7}$$

$$\boldsymbol{b = b_0 exp\left(\frac{-\Delta H}{RT}\right)} \tag{8}$$

With $\boldsymbol{Q}$ being the total amount adsorbed, and $\boldsymbol{Q_{max}}$ refers to the adsorption capacity, b_0 is in the units of atm^{-1}, ΔH the heat of adsorption in J.mol^{-1}, R being the ideal gas constant of 8,314 J.(mol.k)$^{-1}$, and T the temperature in K.

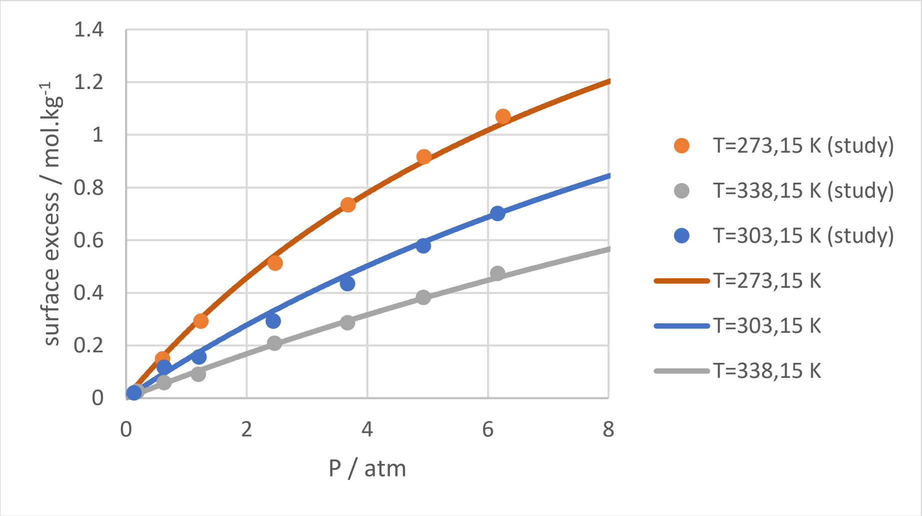


Figure 9 - Adsorption Isotherms of pure contaminants Argon on LiLSX zeolite.

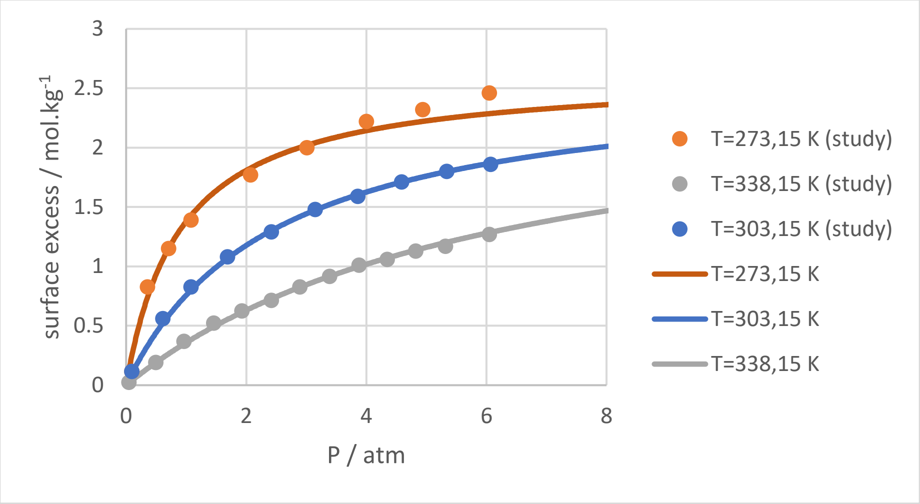


Figure 10 - Adsorption Isotherms of pure contaminants Nitrogen on LiLSX zeolite.

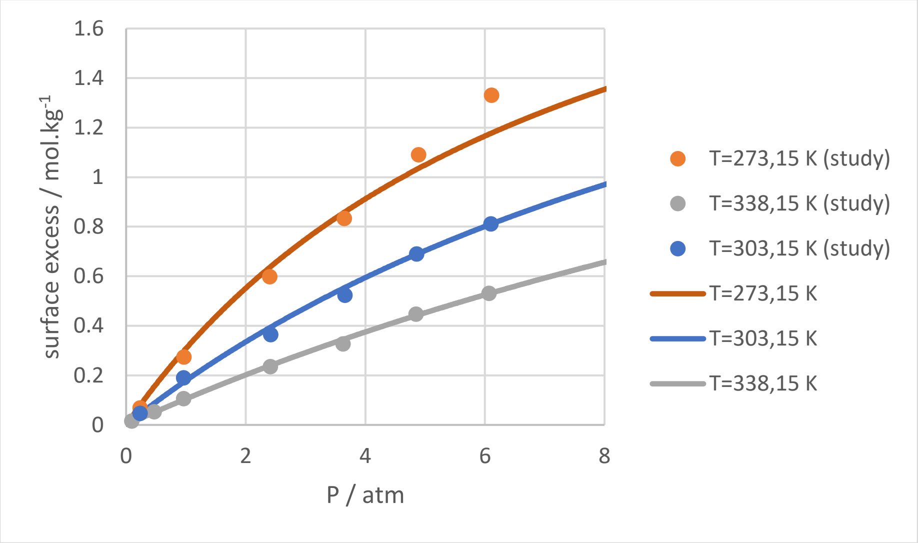


Figure 11 - Adsorption Isotherms of pure contaminants Oxygen on LiLSX zeolite.

As displayed in the graphs, the points obtained in the study start to distance themselves a bit at the low temperature of 273 K, and at pressures higher than 5 atm, but since in this project the PSA is designed to work at temperatures of 303,15 K, it was assumed that this lack of proximity is irrelevant, and the results obtained are still valid.

From the graphs and the Langmuir model displayed in (2) it was possible to obtain the properties displayed in table 1. Initially, from the pure adsorption isotherms the adsorption capacity saturation was slightly higher than that of Nitrogen which was 2,63 mol.kg^{-1}, however, since the PSA is to work with the three contaminants together, the maximum capacity of adsorption is equal to the one with the lowest value. The other two were adjusted to obtain the same values of 2,63 mol.kg^{-1}, while changing the other two parameters, b_0 and ΔH, to still have an approximate curve to the points obtained in the study and have more realistic values.

Table 1 - Thermodynamic properties obtained through the adsorption isotherms with the Langmuir model.

	Q_{max} (mol.kg^{-1})	b_0 (atm^{-1})	$-\Delta H$ (kJ.mol^{-1})
Argon	2,63	$3{,}04.10^{-1}$	13,278
Nitrogen	2,63	$4{,}52.10^{-2}$	22,940
Oxygen	2,63	$3{,}16.10^{-1}$	13,717

Even though the PSA was not modeled, it was still hypothesized as a Skarstrom cycle, with two beds working in parallel, at pressures of 5 bar. The following image represents the pfd that would represent this system.

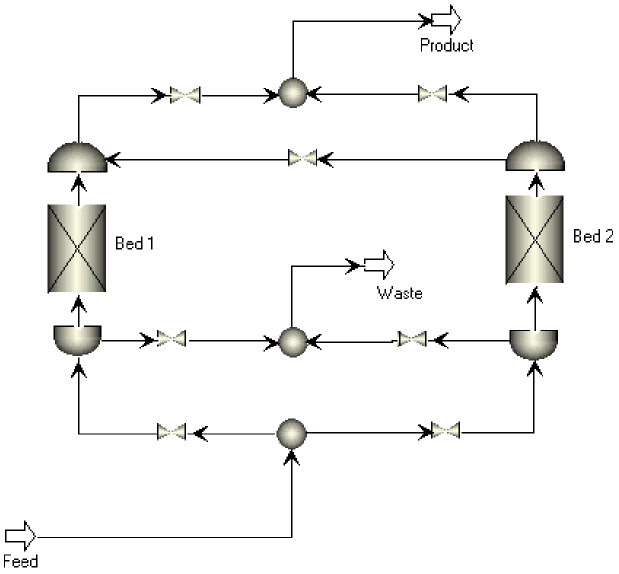


Figure 12 - Flowsheet for the PSA system assuming a Skarstrom cycle

4. Membrane Modelling

4.1 Membrane with 1 stage

At the start of the simulation, a simple design was tested, with one compressor and one membrane, as displayed in figure 13. The composition of the feed, F, that was input in the design of each scenario, was based on the usage of helium of a high- pressure cold spray equipment and is displayed on table 2. This information was provided by a manufacturer of said technology. Even though it is not mentioned, water is also present in the composition, but it was calculated through the software, assuming a relative humidity of 85%, as it is the yearly average in the Netherlands.

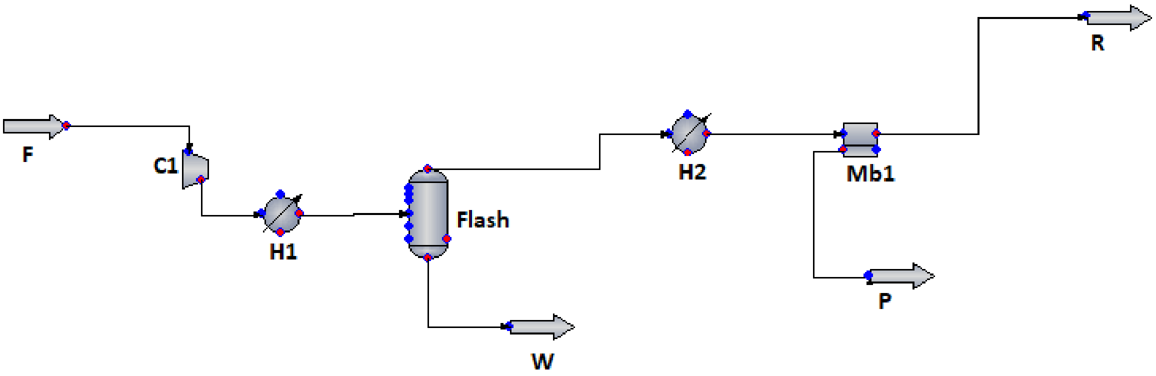


Figure 13 - Flowsheet for 1 stage membrane system – Setup A

Table 2- Feed composition

Composition	%mol	$Nm^3.h^{-1}$
He	2,75	165,00
N2	75,97	4558,30
O2	20,37	1222,20
Ar	0,91	54,50

The feed is first compressed, and then has the temperature lowered before entering the flash unit, in order to remove sufficient humidity to make sure that no water in its liquid form enters the membrane. Afterwards, it is heated up again for optimum conditions of the membrane, which should be between 20-45˚C, so a standard of 30˚C was chosen for all the simulations. The conditions of the membranes, that remain constant for all scenarios are describe in table 3. Per simulation only the number of shells were changed, together with the driving force that is the pressure difference between the permeate and the retentate, these two are the main variables that influence the outcome of the simulations.

Table 3 - Membrane Characteristics

Membrane type	Hollow fibers
Feed entrance	Bore side
Flow type	Counter-current
Fiber length	1 m
Fiber internal diameter	0,2 mm
Fiber external diameter	0,3 mm
Surface area	47,124 m^2
Feed pressure drop	0,1838 bar

Using the software's sensitivity analysis, it was possible to see how these variables influence, in terms of purity, by analyzing the helium mole fraction in the permeate's composition, and in terms of recovery, by analyzing the amount of helium moles that leave through the Retentate. Both of these are graphed against the pressure that was input in the compressor C1. Figs. 14 and 15 display graphs that show them both, respectively:

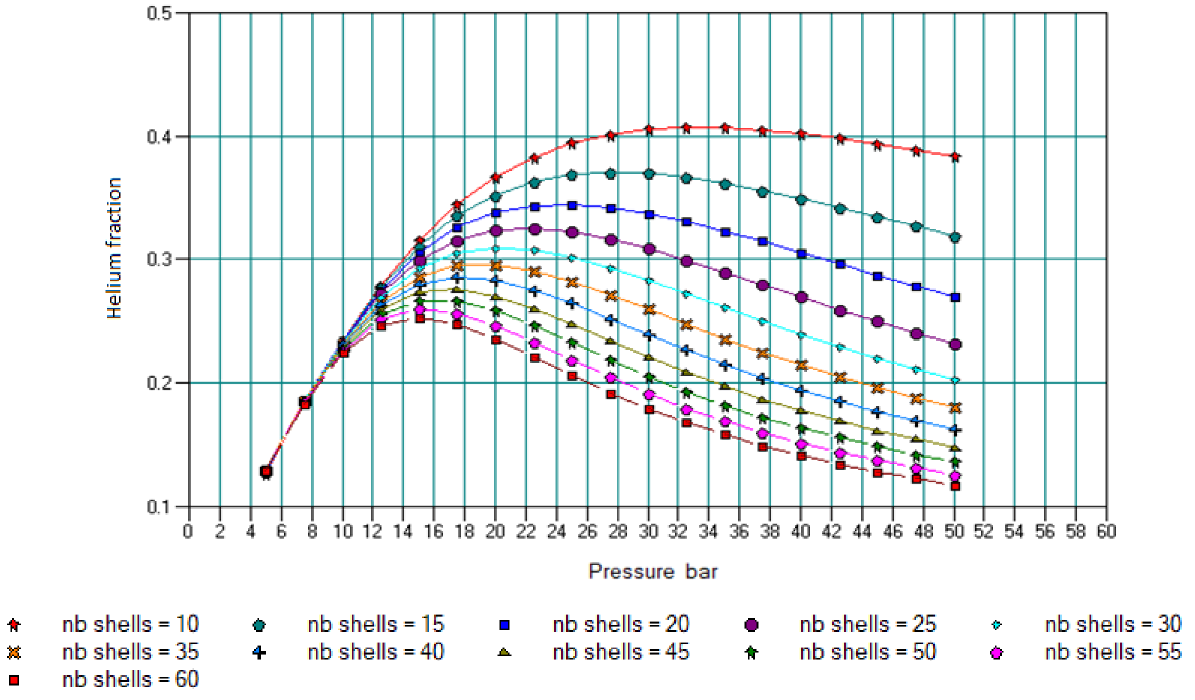


Figure 14 - Helium mole fraction in the Permeate vs Pressure in bars

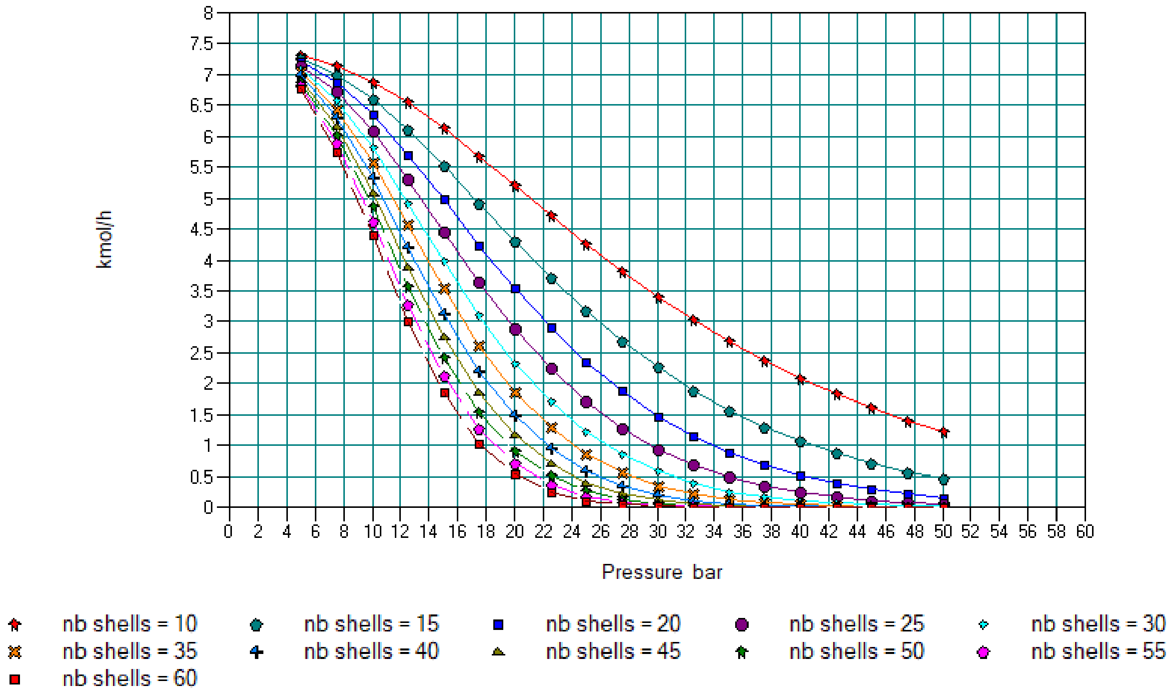


Figure 15 - Quantity of helium moles that leave through the Retentate vs the pressure used in the system, in bars

As one would expect, increasing the pressure on the feed side, it forces more gas particles to go through the permeate side, of course, after a certain point, too much gas contaminants also pass through, decreasing the purity of the permeate. To obtain appropriate results, there is a need to focus on high recovery, otherwise there would be no point in building a recovery system. With this thought in mind, it was decided to try a realistic, yet, still high value, of 95% recovery. Seeing as 7,37 kilomoles of helium were fed in the system, per hour, for a value that is required, the amount of helium that leaves through the retentate, had to be lower than 0,37 kmol.h^{-1}.

From this last graph it seems a bit hard to see the actual differences between the different curves of the different number of shells. Luckily, the software permits a zoom-in function without having to rearrange the terms of the run, or the graph. Using the following graph of the fig. 16, it was possible to decide on an appropriate number of shells and the pressure to be fed to the membrane system:

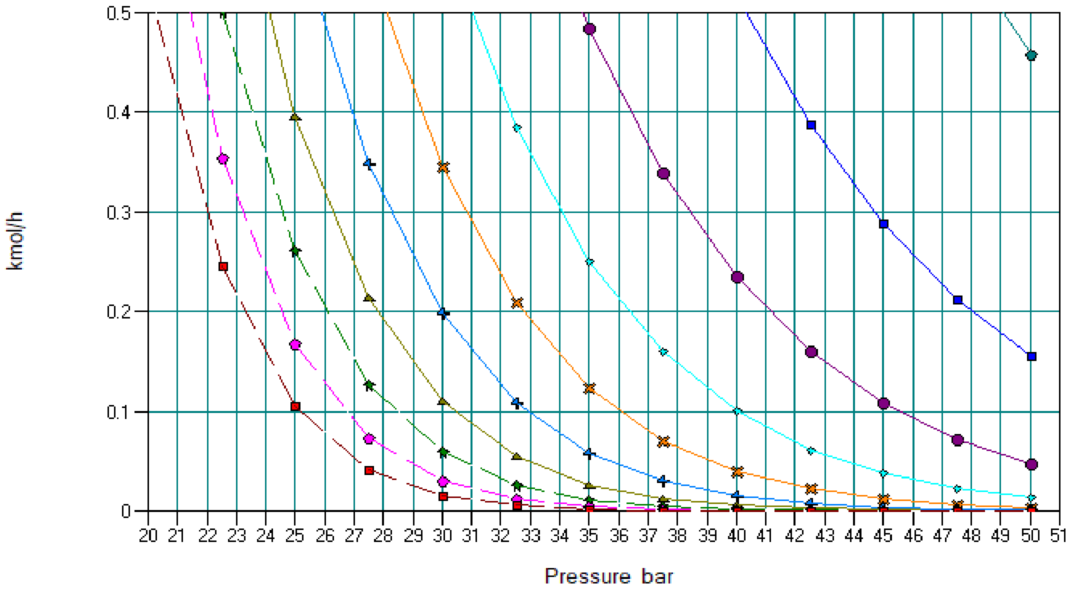


Figure 16 – Zoomed version of figure 14, focusing on x axis [20:51] bar and y axis [0:0,5] kmol.h^{-1}

Since the goal in this project was to find an appropriate system of helium recovery, finding the right number of shells and amount of pressure is vital. A huge quantity of pressure would mean a huge energy consumption, especially since the feed has such a high flowrate. Adding more shells, which is the same as having more membranes working in parallel, obviously increases the pricing, since more membranes are bought, but it also increases the energy consumption since more pressure is lost for each membrane.

Seeing how the pressure and number of shells alters the purity of the permeate and the amount of recovery, it was then possible to select a value to both, optimizing the purity, while keeping a high recovery.

Regarding the design of the flowsheet, not much else could be changed, seeing as this was standard for a 1 stage membrane system. However, a recycle for half the retentate was set in a scenario B, to see if there was any benefit to it. Figure 17 shows the pfd of the mentioned setting, and table 4 the optimized results, of both scenarios, with their respective characteristics.

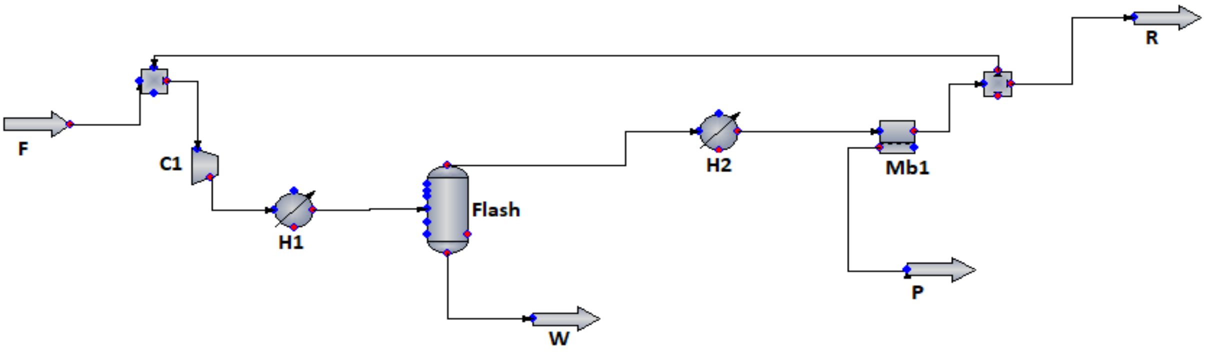


Figure 17 - Flowsheet for 1 stage membrane system, with recycling unit – Setup B

Table 4 - Optimized results according for each setup of the 1-stage membrane systems

Setup	P (bar)	Nb shells	Purity (%)	Recovery (%)
A	35	27	27,78	94,86
B	60	20	23,30	95,07

From the results obtained, it is possible to check what has already expected. While having a recycle unit, permits the lowering of the number of shells, since the focus is not on all the helium, or most of it, going through the permeate. However, since there is no actual step to clean the recycle, all it is doing is sending all the contaminants that were removed, back into the flow. Increasing the flowrate, which results in a need to increase the pressure, and decreases further the already little helium fraction that entered with the feed.

Even with the optimized scenario A, with a purity of almost 28%, it was still a far reach from the requested purity of 99,9%, vital for the gas to be usable in the cold spray application. To do that, further purification was mandatory, forcing the creation of a variety of scenarios, with multiple membrane stages.

4.2 Membranes with 2 stages

In hollow fiber membranes, where the feed is on the bore side, the retentate leaves with most pressure, and it is assumed that the permeate side leaves at ambient pressures. So, for a two-stage membrane system, if the second membrane is built on the permeate of the first one, a recompression step is mandatory. Knowing this, three different scenarios were generated and tested. Figures 18, 19 and 20, show the layout of these scenarios.

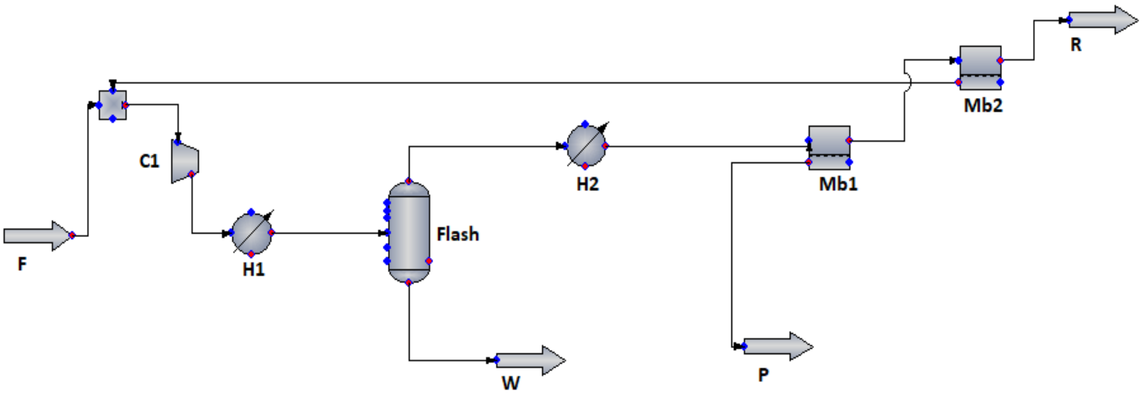


Figure 18 - Flowsheet for 2 stage membrane system, with one compressor – Setup A

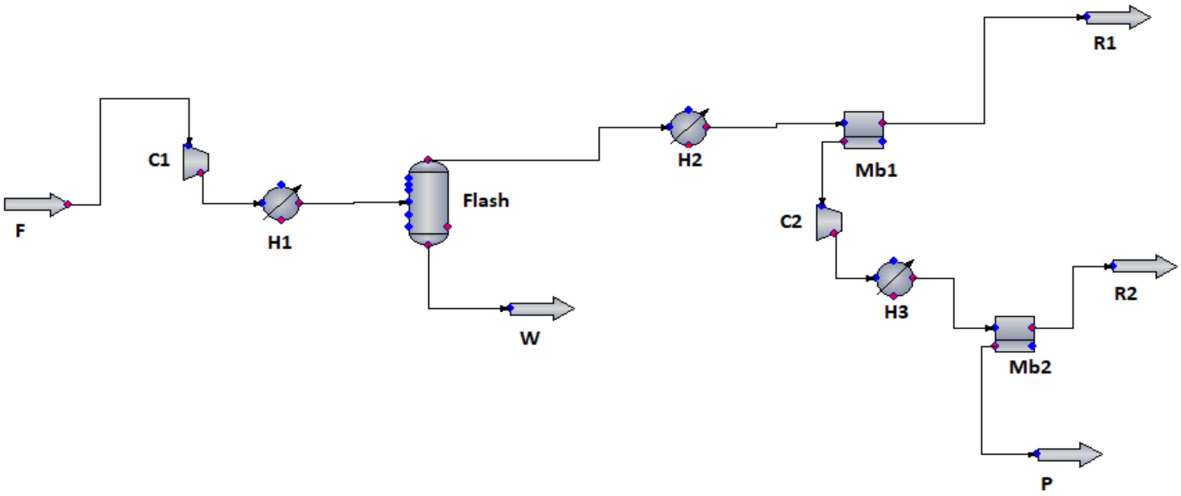


Figure 19 - Flowsheet for 2 stage membrane system, with two compressors, and no recycling unit – Setup B

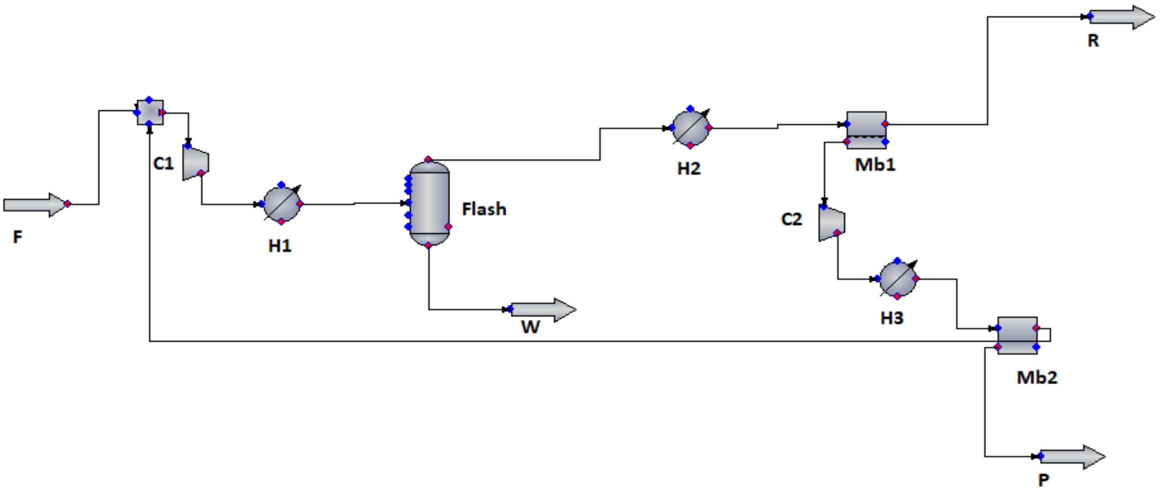


Figure 20 - Flowsheet for 2 stage membrane system – Setup C

Setup A was designed to utilize the remaining high-pressure flow from the retentate, in an attempt at maximizing the purity while minimizing the energy consumption. Setup B is a straight-forward system, with 2 stages in series. Scenario C is similar to B, but with a recycling unit in the second membrane, which permits the second membrane to focus on high purity, without adding too many contaminants to the initial flow, corrupting the system. Table 5 presents the obtained results for each optimization scenario, as well as the values needed for each of them.

Table 5 - Optimized results according for each setup of the 2-stage membrane systems

Setup	P C1 (bar)	P C2 (bar)	Nb shells Mb1	Nb shells Mb2	Purity (%)	Recovery (%)
A	28	-	10	40	55,21	94,84
B	30	15	50	8	66,31	95,50
C	35	9	65	2	96,32	99,23

From the observation of the table, we can see the expected lower result of setup A. However, the main attribute here is how high the helium fraction went in setup C. Even though it is still not the ideal result, it already decreases the flowrate tremendously for a potential PSA system follow-up, hopefully, reducing a flowrate of slightly over 6000 Nm^3/h to one close to 170 Nm^3/h.

In terms of energy, since the configuration A only has one compressor, it would spend around around 1500 kWh, while configuration B would spend around 1900 kWh, and configuration C would go up to 2400 KWh due to its high pressure and its recycling flowrate of 1866 Nm^3/h.

4.3 Membranes with 3 stages

For the 3-stage membrane system, the scenarios tried were based on the best obtained results of the 2-stage membrane. The goal of the different scenarios was to test the different positioning of the recycle unit. As one can see from the following images, setup A recycles the retentate of the second membrane stage into the feed. Setup B recycles the retentate of the third stage, also to the feed. Setup C recycles the retentate of the third membrane to the permeate of the first stage, for it to be fed to the second stage. And the setup D takes the recycle from both the second and the third stage and merges them with the feed. The described scenarios are displayed in the following pfds of figures 21, 22, 23 and 24, with table 6 highlighting their respective results:

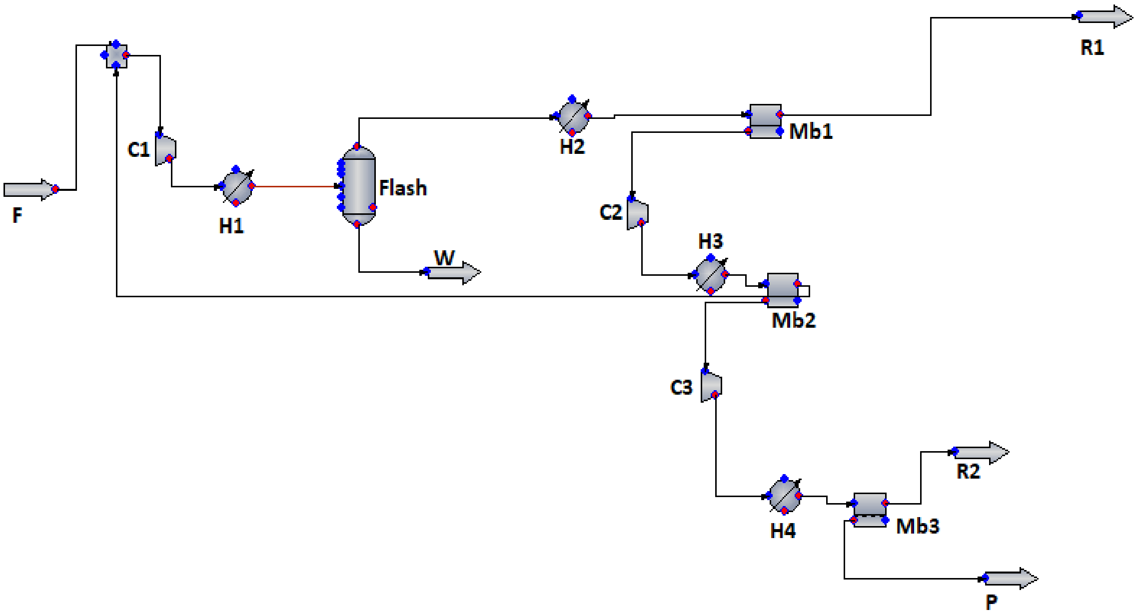


Figure 21 - Flowsheet for 3 stage membrane system – Setup A

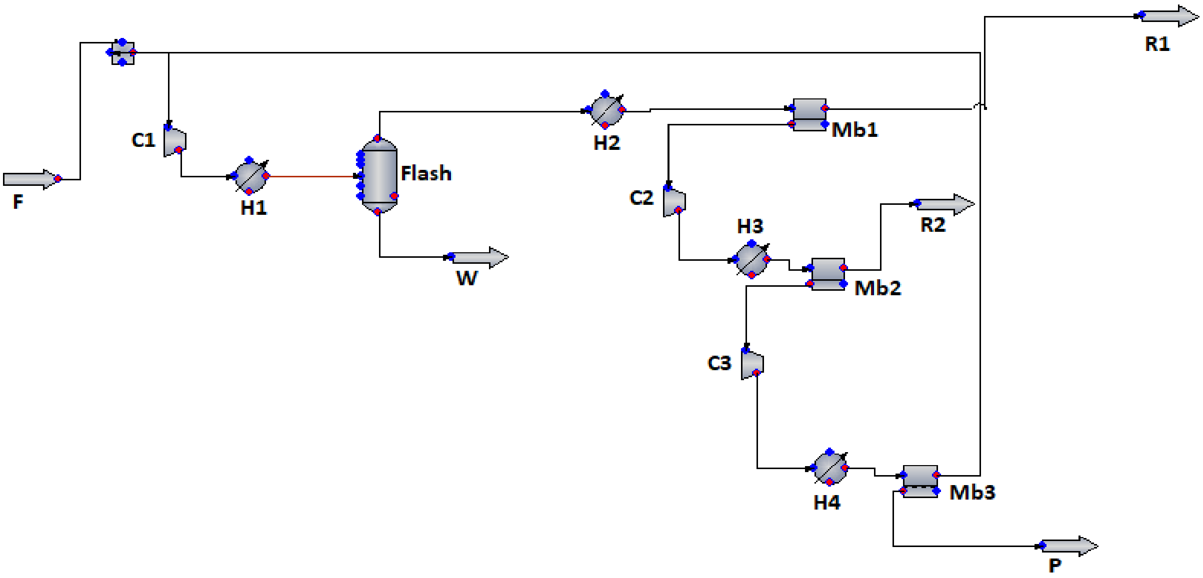


Figure 22 - Flowsheet for 3 stage membrane system – Setup B

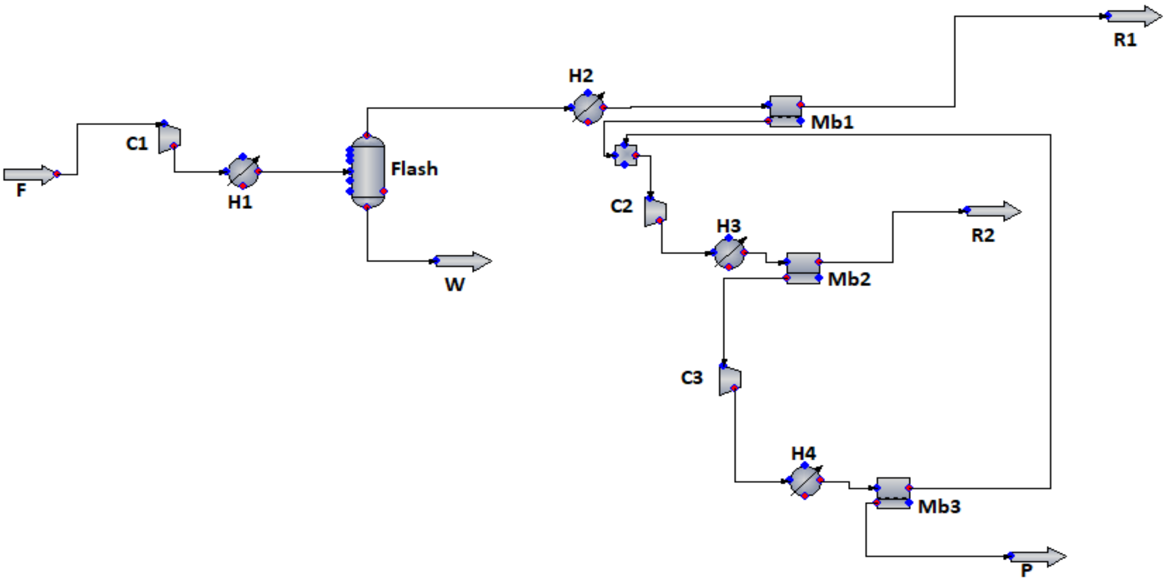


Figure 23 - Flowsheet for 3 stage membrane system – Setup C

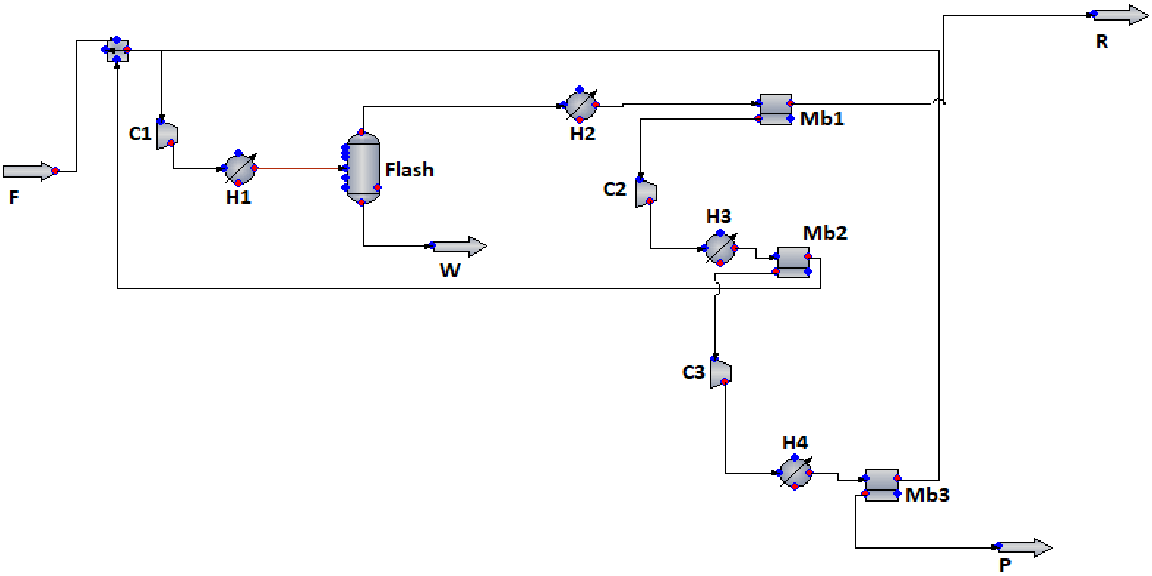


Figure 24 - Flowsheet for 3 stage membrane system – Setup D

Table 6 - Optimized results according for each setup of the 3-stage membrane systems

Setup	P C1 (bar)	P C2 (bar)	P C3 (bar)	Nb shells Mb1	Nb shells Mb2	Nb shells Mb3	Purity (%)	Recovery (%)
A	30	15	12	60	5	1	95,58	96,67
B	30	20	9	60	10	1	98,10	98,75
C	25	16	9	70	18	1	98,55	98,72
D	30	8	8	60	3	1	98,39	99,43

To maximize the purity and recovery, in each stage there is a need to try to minimize the amount of helium that is lost through the retentate. In the first stage, the values of pressure and shells was settled at 30 bar and 60 membranes, respectively. However, by increasing/decreasing the pressure slightly and respectively, decreasing/increasing the number of shells working in parallel, the result will remain unaffected. In setup C that is the case, even though the variables are slightly different, when entering in the first membrane stage, the flow composition in its permeate is practically the same as the other setups.

In the second stage, the influence of the recycle setup starts to show. If there is a recycle in the retentate of this unit, the focus on this stage can be on increasing the purification, so the number of shells can be lower. If there is no recycle, the opposite occurs, the number of shells must increase, to make sure helium is not lost through the retentate.

In the final stage, the difference in the helium purity becomes relevant. Since there is no recycle in setup A, the pressure has to be high in order to not lose much helium, which in turn, decreases its purity. Having a recycle on this unit, has the advantage of not having to worry about the recovery, so the focus can be on lowering the pressure, further increasing the purity, while at the same time, keeping the recovery.

While the difference of where the recycle merges, whether in the feed, or in the permeate of the first membrane stage, looks at first like a minor difference, looking at the results it is clear that it is not the case. The mole rate that leaves through the retentate of the third stage is not large, so when merging with the feed, it makes a very small difference, since the composition barely changes. However, by merging it with the permeate of the first membrane, the helium fraction in the flow increases a lot, decreasing the toll on the other membrane stages.

As for the setups C and D, the question is whether there should be a recycle unit in the third stage or if in both the second and third stage. The results are not that different, it can be argued that since there is a recycle unit in membrane three, then the recycling the in the second membrane stage is unnecessary, since there is no need to worry about the purity. But since the pressure and number of shells are lower in scenario D, then it may be slightly more economical to have a recycle unit in both stages, through a very small sacrifice of the helium purity.

4.4 Membranes with 4 stages

In the previous stage the helium purity obtained was quite high, however, the results are still lacking. The objective in this project is to design a viable system that achieves a 99,9% helium purity for the cold spray application, with a recovery rate around 95%. To have a basis for comparison, the goal is to achieve a technology that achieves such purity with just membranes, and for that, another stage was added for testing. As such and based on the results and ideas from the previous testing, the setups in figures 25, 26, 27 and 28 were designed.

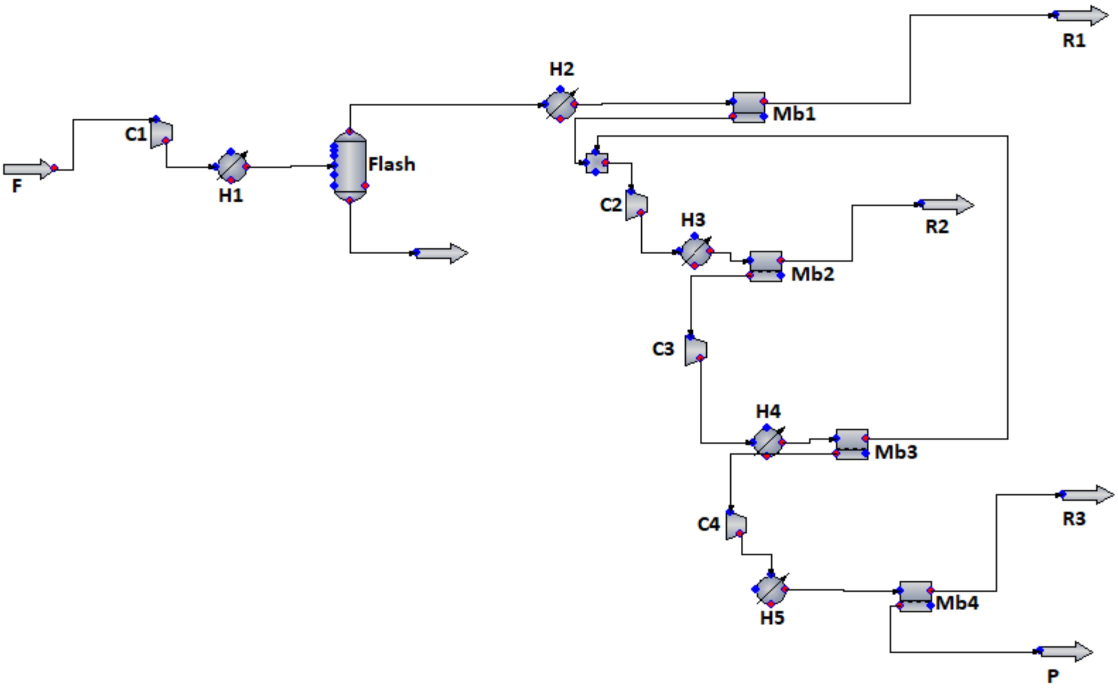


Figure 25 - Flowsheet for 4 stage membrane system – Setup A

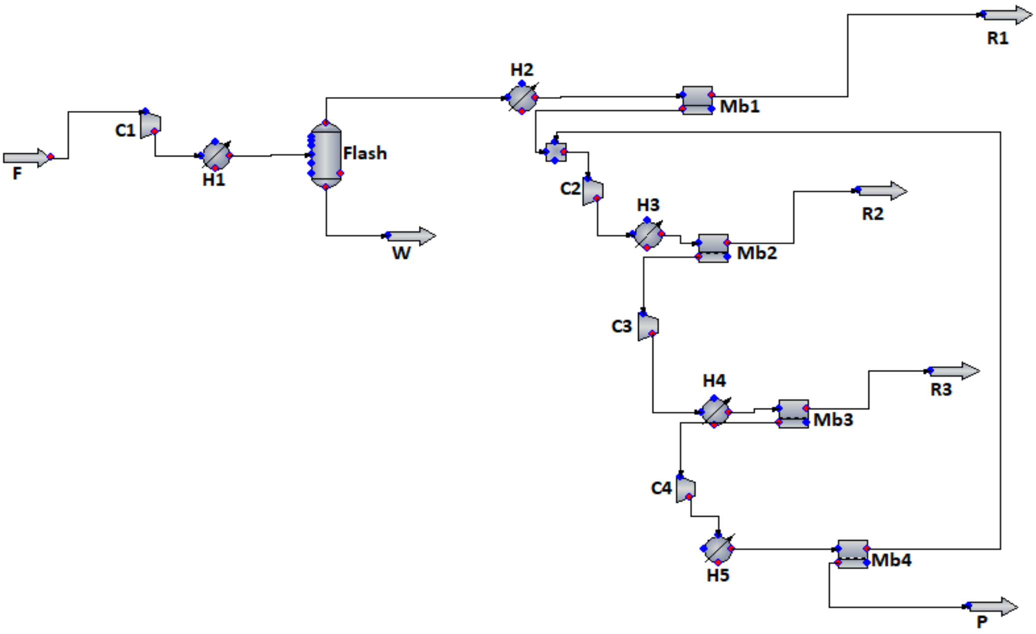


Figure 26 - Flowsheet for 4 stage membrane system – Setup B

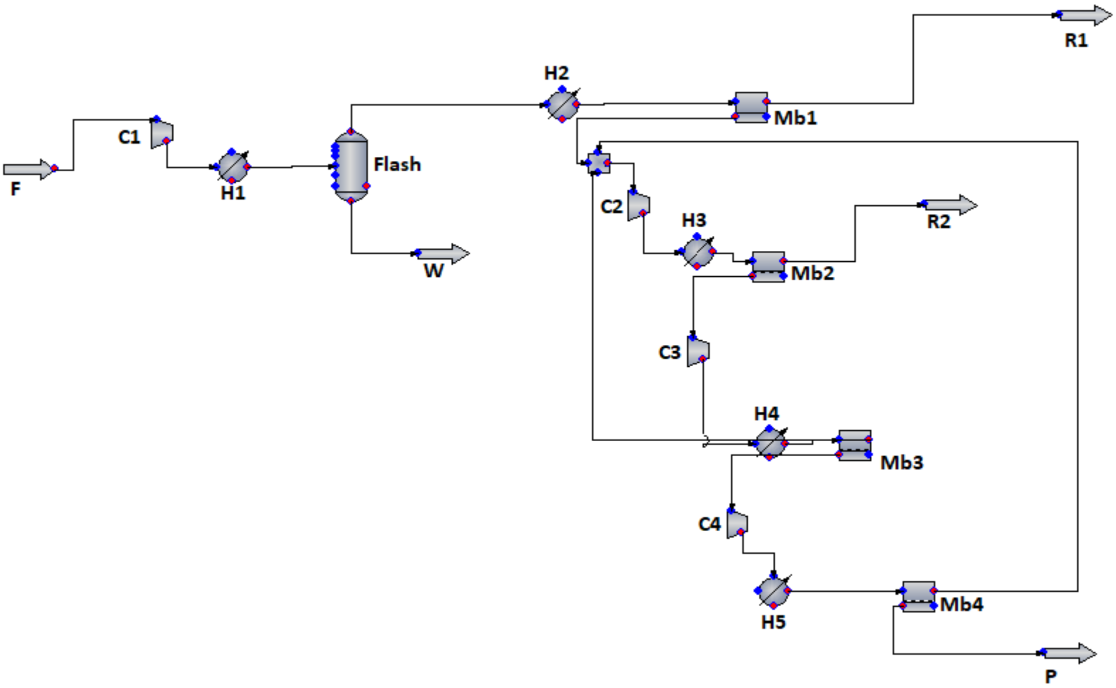


Figure 27 - Flowsheet for 4 stage membrane system – Setup C

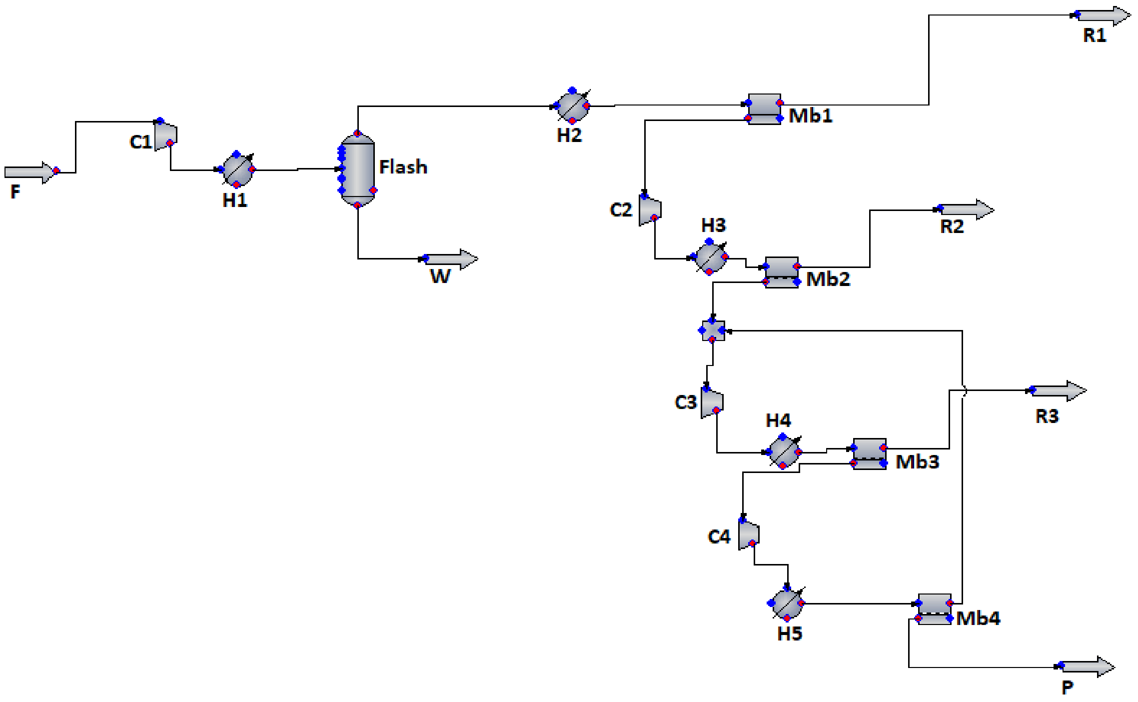


Figure 28 - Flowsheet for 4 stage membrane system – Setup D

Since with the three-stage membrane tests, the recycle units directed to the feed already showed it was not the best options, the designs in this four-stage system that included a similar, were removed from the showed scenarios, as they posed no benefits to the outcome, and provided no new information. In table 7, the optimized results are presented

Table 7 - Optimized results according for each setup of the 4-stage membrane systems

Setup	P C1 (bar)	P C2 (bar)	P C3 (bar)	P C4 (bar)	Nb shells Mb1	Nb shells Mb2	Nb shells Mb3	Nb shells Mb4	Purity (%)	Recovery (%)
A	30	15	9	5,75	55	20	1	1	99,81	96,54
B	30	15	12	7	55	15	3	1	99,03	97,73
C	30	15	9	6,5	55	15	2	1	99,37	99,15
D	30	15	10	7	55	15	5	1	99,19	97,60

During testing, and analyzing the results, it was clear that the scenarios where the helium purity were higher was when the pressure input in the last stage, was lower. The lowest possible values were inserted in the final compressor. If the values input were lower, the calculations just would not converge through the software, or it would turn out corrupted. As to why some designs can go lower, from observation it can be theorized that the low number of shells in the third membrane stage influences this outcome. Since scenario B and D have the highest amount of shells in this third stage, the pressure that the fourth stage can intake is lower, subsequently, the purity achieved is also lower. In the setup C, the number of shells in the third stage could not be lower than two, possibly because having two recycle units increases the flowrate, demanding more pressure.

With all the different designs tested, setup A in the 4-stage membrane system had the best results obtained in a membrane only system. It achieves a helium purity as high as 99,81%, with a recovery higher than 96%, with an energy consumption close to 2100 kW. This result can be enough, but it should be noted that the other 0,19% consists of oxygen, which may be detrimental, depending on the usage.

Other designs involving a 5-stage membrane system were also designed and tested thoroughly, but none of the results obtained increased purity than the ones in the 4-stage membrane system. Since the results were unsatisfactory and brought nothing notable to refer, they were omitted from this dissertation.

5. Economical Overview

5.1 Case Studies

With the objective to properly evaluate difference scenarios, the best setups, from the most varied range were chosen. The goal is to compare, for a helium recovery technology, whether it would be better to use a PSA only system, a membrane only system, or a hybrid version of both.

As membrane-only technology a 4-stage membrane system was chosen, due to the high purity of helium produced in this setup. A simplified PSA-only system was designed, with the parameters discussed in chapter 3.2, with the feed composition shown in table 2.

For the hybrid systems, three setups were chosen. Using the best scenario in a single stage membrane system, as well as the 2-stage and 3-stage, since their high purity lowers the burden for the PSA, so evaluating should also be worthwhile. These last three were combined with PSA technology to obtain the desired purity, and this part was designed in the same way the PSA only system was. The following table 8 describes the mentioned cases to be studied.

Table 8 - Case studies

Characteristics	MS only	Hybrid MS 1 stage	Hybrid MS 2 stage	Hybrid MS 3 stage	PSA only
Membrane stages	4	1	2	3	0
Membrane setup	A	A	A	A	A
PSA diameter (m)	-	1,1	0,6	0,6	1,1
PSA Length (m)	-	4,4	2,4	2,4	4,4
Adsorbent mass (kg)	-	4110,5	667,1	667,1	12331,6
Nb of PSA columns	0	2	2	2	6

In the table, the number of columns is shown, but it is important to note, that for each PSA systems, two columns are used. Which means that for the hybrid scenarios, one set of two columns are used, and for the PSA only system, 3 sets were used, this to avoid having two huge PSA columns, which would have an enormous footprint.

5.2 Business case

The best way to compare a system for an industry, is to evaluate it economically. As such, a business case was produced. Taking in consideration values that were provided by a cold spray technology manufacturer, it was possible to have an idea how much helium is spent if used as the only gas, as well as the actual cost of the helium. In table 9, it is possible to see, side by side, the different scenarios, the membrane only system, the PSA only system, as well as the three hybrid versions, a scenario in which no helium recovery exists was also added for proper comparison. The consumption of the gas, if helium is the only gas used, together with the production of said gas, assuming a 95% recovery is displayed in the table, as well as the inlet and outlet gas compositions in the systems.

Table 9- Business case parameters by scenario

Main parameters	Bottled Helium (no re-use)	MS only	Hybrid MS 1 stage	Hybrid MS 2 stage	Hybrid MS 3 stage	PSA only
Helium consumption per year (Nm^3)	540.000	540.000	540.000	540.000	540.000	540.000
Helium yearly production (Nm^3)	0	513.000	513.000	513.000	513.000	513.000
Gas flow (Nm^3/h)	270	6000	6000	6000	6000	6000
Pressure (barg)	300	45	45	45	45	45
Gas inlet composition (v%):						
He	99,99	2,75	2,75	2,75	2,75	2,75
O_2	0,00	20,37	20,37	20,37	20,37	20,37
Argon	0,00	0,91	0,91	0,91	0,91	0,91
N_2	0,01	75,97	75,97	75,97	75,97	75,97
Recovered helium composition (v%):						
He	-	99,81	99,99	99,99	99,99	99,99
O_2	-	0.19	0,00	0,00	0,00	0,00
Argon	-	0,00	0,00	0,00	0,00	0,00
N_2	-	0,00	0,01	0,01	0,01	0,01

In tables 10 and 11, the capital costs (CAPEX) and operation costs (OPEX) are provided. In the CAPEX, the total investment accounts to the cost of each system to a possible client, with a depreciation assumption of 10 years, and an interest rate of 7%.

Table 10 - Capital costs (CAPEX) summarization

CAPEX (Investment)	Bottled Helium (no re-use)	MS only	Hybrid MS 1 stage	Hybrid MS 2 stage	Hybrid MS 3 stage	PSA only
Total investment	€ 0	€ 4.672.300	€ 3.648.200	€ 4.397.000	€ 4.948.300	€ 3.564.700
Recovery Plant Cost	€ 0	€ 4.522.300	€ 3.498.200	€ 4.247.000	€ 4.798.300	€ 3.414.700
Other costs	€ 0	€ 150.000	€ 150.000	€ 150.000	€ 150.000	€ 150.000
Depreciation (€/year)	€ 0	€ 467.230	€ 364.820	€ 439.700	€ 494.830	€ 356.470
Interest (€/year)	€ 0	€ 163.531	€ 127.687	€ 153.895	€ 173.191	€ 124.765

In the OPEX, we can see that around 4.4 million euros are spent on cold spray applications using only helium. The other scenarios spend 5% of that value each year, which is based on the recovery of 95%, however, with a helium recovery system, there does not exist a need to buy so much helium, so the price of replacement should be less. The utilities refer to the power consumption of each system throughout the year, with the assumed cost of electricity of 0,09€/kWh. All the prices in the CAPEX and OPEX are shown in more detail in the Appendix A.

Table 11 - Operational costs (OPEX) summarization

OPEX (Investment)	Bottled Helium (no re-use)	MS only	Hybrid MS 1 stage	Hybrid MS 2 stage	Hybrid MS 3 stage	PSA only
Helium bought	€ 4.400.000	€ 220.000	€ 220.000	€ 220.000	€ 220.000	€ 220.000
Total Utilities (€/year)	€ 0	€ 374.580	€ 296.111	€ 433.446	€ 369.264	€ 105.286
Maintenance (€/year)	€ 0	€ 116.808	€ 91.205	€ 109.925	€ 123.708	€ 89.118
Operating labor (€/year)	€ 936	€ 23.400	€ 23.400	€ 23.400	€ 23.400	€ 23.400

In table 12, a summarization of the expenses can be seen. In here the total costs per year are displayed, and for an easier understanding of the benefits of the recovery systems, the total helium consumption per year, is divided by the total cost, giving the price of helium per normalized cubic meter. The cost of helium for the no re-use scenario is done with the same calculation, but since the operating labor is a fractional cost of the helium bottles, the value obtained was equal to the actual helium price per Nm3, which corresponds to the 8,15€.

Table 12 - Total costs summarization

Scenario name	Bottled Helium (no re-use)	MS only	Hybrid MS 1 stage	Hybrid MS 2 stage	Hybrid MS 3 stage	PSA only
TCO (€/year)	€ 4.400.936	€ 1.209.805	€ 1.001.616	€ 1.233.799	€ 1.239.448	€ 800.215
Total Capital costs (€/year)	€ 0	€ 630.761	€ 492.507	€ 593.595	€ 668.021	€ 481.235
Total Operational costs (€/year)	€ 4.400.936	€ 734.788	€ 630.716	€ 786.771	€ 736.371	€ 437.804
euro/Nm^3 Helium	€ 8,15	€ 2,53	€ 2,08	€ 2,56	€ 2,60	€ 1,70
Annual saving	-	€ 3.191.131	€ 3.399.319	€ 3.167.136	€ 3.161.487	€ 3.600.720
ROI (Years)	-	1,46	1,07	1,39	1,57	0,99

In the table 12, it is also possible to see the annual savings, which is a relative value, since it is calculated considering how much helium is spent. For systems who use a fraction of that helium, that value may be lessened, so it is important to take that into consideration when analyzing the table.

Based on the total investment that the company must take, and the yearly savings, the return of investment was calculated. For each scenario, and for industries that use this amount of helium, a return of that investment, in whichever recovery system is chosen, is hastily returned.

5.3 House of quality

Knowing the overall costs of each case study is a good way of comparison. However, when investing on a system, especially a new technology, there are many factors that should be considered. To simplify that, a house of quality was made, considering the general expenses, the purity and recovery, the long-term reliability, the complexity of the equipment, and the footprint that the machinery will take.

Table 13 allows for a general overview of this process, the relative weight of each case study, and their overall positioning when compared between each other.

Table 13- House of Quality summarization

Technology **Requirement (Explicit and Implicit)**	**Bottled Helium (no re-use)**	**Membrane only**	**Hybrid (MS-1 stage)**	**Hybrid (MS-2 stage)**	**Hybrid (MS-3 stage)**	**PSA only**
Product Purity	5	4	5	5	5	5
CAPEX	5	3	4	3	3	4
OPEX	1	3	3	3	3	4
High up-time/reliability	5	4	3	3	3	4
Yield/Recovery	1	5	5	5	5	5
Ease of operation (Complexity of technology and operation)	5	3	2	2	2	3
Footprint	5	2	3	3	1	1
Target (1-5)	3,5	3,5	3,5	3,5	3,5	3,5
Rating	3,48	3,52	3,67	3,48	3,38	4,05
Relative Weight	16,1%	16,3%	17,0%	16,1%	15,7%	18,8%
Position	4	3	2	5	6	1

The product purity is self-explanatory, it was a rating based on the purity of the outlet composition, which for all scenarios, is of 99,99%, except the membrane only system, which is of 99,81%. For the CAPEX and OPEX, it was based on the costs which were presented in the previous subchapter.

All scenarios are assumed to have a long-term reliability, however, for a fair rating, the max grade of 5 was given to helium bottles, which cannot fail. The grade 4 was given to the scenarios where there is only one type of technology used, while the 3 was given to the hybrids where there is more probability of problems arising. A similar thought was taken into the ease of operation, where the difference between the no-system and the recovery systems is larger since it is the difference between having technology, and not having it.

For the yield, all the systems had an approximate 95% recovery, and obviously not having a recovery system has the worst grading. The footprint of the helium bottles is the opposite, since it occupies practically no space, while the other systems had the grading based on the size of their machinery.

In the appendix B, it is possible to see how each requirement affects the rating. In the figure 29, we can see a visualization of the ratings obtained by each scenario, with a red line to highlight the targeted 3,5, symbolizing a positive scenario.

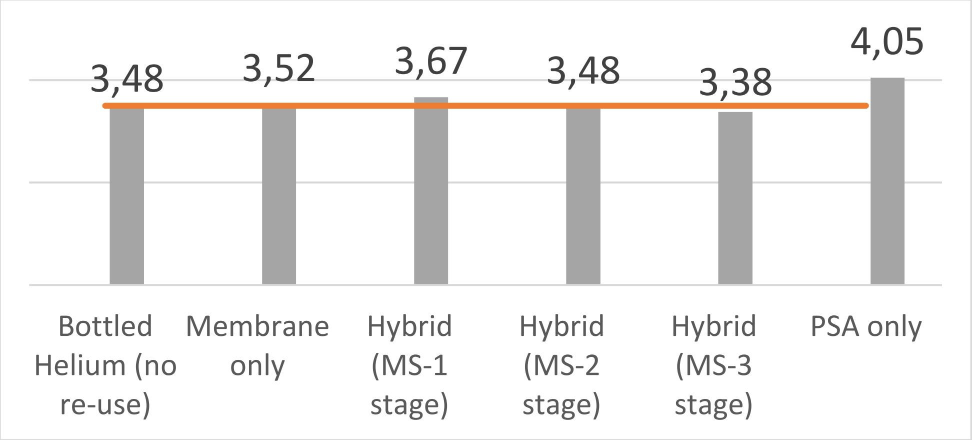


Figure 29- House of Quality ratings

As it is clear, the PSA only system seems to be the best choice, as it is the cheapest option, with a high reliability, high purity, and high recovery with the only problem being its huge footprint, due to having 6 columns of 1,1 m of diameter and 4,4 meters tall. The second best rated scenario, the hybrid system with only 1 membrane stage, has a worst mark due to the complexity of having multiple technologies, and the seemingly lower reliability at long term, however, it has a much smaller footprint, at a just slightly higher price. The hybrid system with the membrane counterpart with 3 stages has the worst rating, as it is the most expensive, complex mix of technologies and having a huge footprint.

6. Final Assessment

6.1 Conclusions

The goal of this project was to create a case study and evaluate the worth of the possible construction of a helium recovery system. By the end of this dissertation, it was proven that, for Cold Spray applications, this kind of technology is not only feasible, but necessary.

With the Cold Spray Industry in mind, a feed composition for the recovery systems was formulated, based on the gas waste streams of Cold Spray applications. Since no other gases or volatile materials are used, the contaminants for the helium are air, which accounts for most of its composition, of around 97,25%, with the other 2,75% consisting of helium. Some solid materials may accompany it, but solid-gas separators are already built-in for the gas waste streams of typical cold spray applications, making them neglectable.

Using the provided software, Chemcad, a deeper analysis on a variety of different configurations of a membrane system for helium recovery was done. The simulations were done with several stages of membranes, achieving the best result with a 4-stage membrane, achieving a helium purity of 99,81%. The stages that obtained lower purity were combined with a PSA, in order to achieve the necessary purities.

Using different structures, which include the recovery technology based only on membranes, or on PSA, as well the hybrid systems of 1, 2 and 3 stages of membranes, a business case and the house of quality were built for comparison, adding a no re-use scenario for a better description of the situation. Analyzing them, it was possible to conclude that the PSA has the best positive points, with its only downfall being the big footprint that it would take to build it. Using a hybrid system, with a single membrane stage, proves to reduce this footprint significantly, without increasing the costs by much. In both these scenarios a high purity of at least 99,99% is guaranteed, and a recovery of 95%.

6.2 Accomplished objectives

In the initial phase of this project, a huge variety of markets were researched, to discover how useful it would be to build a gas helium recovery system, and which industry should it be focused on. Which after a lot of reviews, and some feedbacks from actual companies, it was possible to conclude that the Cold Spray Industry would value this kind of technology the most.

With Chemcad, it was possible to analyze different membrane structures. From this study it was possible to see how the helium purity and recovery is affected by pressure, by using membranes in parallel or in series, and how their number varies respectively, and it was even possible to study how different settings of the recycling stage affects the overall productivity of the system.

In the end, an economical overview, based on different price estimations was built accordingly. With that, a realistic comparison of the different chosen scenarios was possible, which proves the worth of this kind of system, in a world where helium is being depleted.

6.3 Future work

This project was built as the ground floor, as a means to see if this system can be useful for DMT. This project proves that for companies that use Cold Spray technology and need to use helium, for their high-quality coating, a helium recovery system is viable, and highly beneficial. However, a business case validation should be performed, for other companies that could benefit from using helium, but do not demand high-quality materials, and as such, use a mix of helium and nitrogen. And could extend the helium usage when applying a recovery system.

The characteristics of the membranes, which were used in the simulation, were based on experimental membrane designed for biogas upgrading. Obtaining a membrane material specifically designed for helium recovery would possibly not only improve the systems, but quite possibly lower their cost.

The design of the PSA systems was mainly focused on the dimensioning and pricing, for the economical comparison. A further study on this technology, which includes not only the design, but also the simulation and possible testing of said system, should be done.

Moreover, the current concept design needs to be presented to a potential client for feedback. The potential footprint and obtained gas purity, especially the impact of the small residues of O2 need to be discussed with potential end clients.

7. References

[1] Oil and Gas Industry Produces Helium Needed in MRI Equipment. (2020). Retrieved 8 February 2021, from https://www.instituteforenergyresearch.org/fossil-fuels/gas-and-oil/oil-and-gas-industry-produces-helium-needed-in-mri-equipment/

[2] Prospect, D. (2021). Desert Mountain acquires another helium prospect – Resource World Magazine. Retrieved 8 February 2021, from https://resourceworld.com/desert-mountain-acquires-another-helium-prospect/

[3] Grynia, E.,Griffin, P.J. Helium in Natural Gas- Occurrence and Production. Gas Liquids Engineering Ltd, Canada, 2016

[4] *Process Technologies for Helium Recovery from Natural Gas: A Review - EPCM Holdings. (2017).*

[5] Soleimany, A., Hosseini, S.S., Galluci, F. Recent Progress in Developments of Membrane Materials and Modification Techniques for High Performance Helium Separation and Recovery.(2017). *Chemical Engineering and Processing: Process Intensification*,122, 296-318

[6] Sepuran Noble's Brochure. Evonik, Germany.

[7] Rufford, T.E., Chan, I., Huang, S.H., May, E.F. A Review of Conventional and Emerging Process Technologies for the Recovery of Helium from Natural Gas. Volume 32 Issue 1, 49-72, January 2014

[8] Average monthly humidity in Joure (Friesland), Netherlands. (2021). Retrieved 22 January 2021, from https://weather-and-climate.com/average-monthly-Humidity-perc,joure-friesland-nl,Netherlands

[9] Ahmad, F., Lau, K., Lock, S., Rafiq, S., Khan, A., & Lee, M. (2015). Hollow fiber membrane model for gas separation: Process simulation, experimental validation and module characteristics study. *Journal Of Industrial And Engineering Chemistry*, *21*, 1246-1257

[10] Tanihara, N., Nakanishi, S. & Yoshinaga, T. (2016). Gas and vapor separation through polyimide membranes. Journal of the Japan Petroleum Institute, 59, 276-282

[11] Ko, D. (2018). Optimization of hollow fiber membrane modules to sequester carbon dioxide from coalbed methane. Journal of Membrane Science, 546, 270-283

[12] Krol, J., Boerrigter, M. & Koops, G. (2001). Polyimide hollow fiber gas separation membranes: preparation and the suppression of plasticization in propane/propylene environments. Membrane Science & Technology. 184, 275-286

[13] Ma, X. & Yang, S. (2018). Synthesis, Characterization and applications: Polyimide gas separation membranes. *Advanced Polyimide Materials*. 257-322

[14] Soroko, I. (2011). Polyimide organic solvent nanofiltration membranes-formation and function. *Imperial College London.*

[15] Wu, C., Kothare, M. & Sircar, S. (2014). Equilibrium adsorption isotherms of pure N2 and O2 and their binary mixtures on LiLSX zeolite: experimental data and thermodynamic analysis. *American Chemical Society*, 53, 7195-7201

[16] Wu, C., Kothare, M. & Sircar S. (2015). Correction to “Equilibrium isotherm and mass transfer coefficient for adsorption of pure argon on small particles of pelletized LiLSX zeolite”. *American Chemical Society,* 54, 5196

[17] Das, N., Kumar, P., Mallik, C., Bhandari, R. (2012). Development of a helium purification system using pressure swing adsorption. *Current Science,* 103, 631-634

[18] Das, N., Kumar, P., Mallik, C., Bhandari, R. (2010). Multi-component adsorption studies on LiLSX and CMS for helium separation

[19] Verdade, A. (2020). The potential of Aspen Adsorption software package to simulate pressure swing adsorption units

[20] Moran, A. (2014). A PSA process for an oxygen concentrator

[21] Wan, C., Yang, T., Lipscomb, G., Stookey, D., Chung, T. (2017) Design and fabrication of hollow fiber membrane modules. Journal of Membrane Science, 538, 96-107

Appendices

Appendix A

Table A.1 – Equipment Pricing

	MS only	Hybrid MS 1 stage	Hybrid MS 2 stage	Hybrid MS 3 stage	PSA only
Main equipment cost (sum)	**€ 2.613.875**	**€ 2.012.438**	**€ 2.452.188**	**€ 2.776.000**	**€ 1.963.438**
C1	€ 200.000	€ 200.000	€ 200.000	€ 200.000	€ 200.000
C2	€ 115.000	€ 50.000	€ 115.000	€ 115.000	-
C3	€ 60.000	-	€ 35.000	€ 60.000	-
C4	€ 35.000	-	-	€ 35.000	-
Flash	€ 25.000	€ 25.000	€ 30.000	€ 25.000	-
H1	€ 120.000	€ 120.000	€ 120.000	€ 120.000	€ 120.000
H2	€ 28.000	€ 28.000	€ 28.000	€ 28.000	-
H3	€ 28.000	-	€ 8.000	€ 28.000	-
H4	€ 28.000	-	-	€ 8.000	-
H5	€ 8.000	-	-	-	-
Mb1	€ 349.250	€ 171.450	€ 412.750	€ 444.500	-
Mb2	€ 127.000	-	€ 25.000	€ 114.300	-
Mb3	€ 12.500	-	-	€ 12.500	-
Mb4	€ 6.350	-	-	-	-
PSA Bed	-	€ 120.000	€ 50.000	€ 50.000	€ 360.000
Dehumidifier	-	-	-	-	€ 25.000
Valves	€ 280.000	€ 280.000	€ 280.000	€ 280.000	€ 280.000
Piping, skids, connections	€ 196.000	€ 154.000	€ 168.000	€ 182.000	€ 175.000
Eletrical cabinet, software, PLC, VFDs, wiring	€ 217.000	€ 170.500	€ 186.000	€ 201.500	€ 193.750
Utilities	€ 98.000	€ 77.000	€ 84.000	€ 91.000	€ 77.000
Cooling agent + pump	€ 84.000	€ 66.000	€ 72.000	€ 78.000	€ 66.000
Gas measurement	€ 35.000	€ 70.000	€ 70.000	€ 70.000	€ 35.000
Insulation	€ 30.000	€ 60.000	€ 60.000	€ 60.000	€ 30.000
Transmittors	€ 9.000	€ 18.000	€ 18.000	€ 18.000	€ 9.000
Other (25%)	€ 522.775	€ 402.488	€ 490.438	€ 555.200	€ 392.688

Table A.2 - Contractual Pricing

	MS only	Hybrid MS 1 stage	Hybrid MS 2 stage	Hybrid MS 3 stage	PSA only
Sub-contracted Labor	€ 40.000	€ 40.000	€ 40.000	€ 40.000	€ 40.000
Certification	€ 2.000	€ 2.000	€ 2.000	€ 2.000	€ 2.000
Project Execution Risk (8%)	€ 212.470	€ 164.355	€ 199.535	€ 225.440	€ 160.435
Unexpected Purchase Cost (10%)	€ 265.588	€ 205.444	€ 249.419	€ 281.800	€ 200.544
Labor	€ 129.688	€ 129.688	€ 129.688	€ 129.688	€ 129.688
Holding Fee (5%)	€ 226.115	€ 174.910	€ 212.350	€ 239.915	€ 170.735
Overhead (18%)	€ 564.108	€ 436.363	€ 529.765	€ 598.543	€ 425.955
COGS	€ 3.133.933	€ 2.424.236	€ 2.943.141	€ 3.325.240	€ 2.366.416
Total Costs	€ 4.053.843	€ 3.165.196	€ 3.814.944	€ 4.293.386	€ 3.092.794
Warranty (1%)	€ 45.223	€ 34.982	€ 42.470	€ 47.983	€ 34.147
Operating Profit	€ 423.234	€ 298.022	€ 389.586	€ 456.931	€ 287.759
Project sales value	€ 4.477.077	€ 3.463.218	€ 4.204.530	€ 4.750.317	€ 3.380.553
Gross Profit	€ 1.343.145	€ 1.038.982	€ 1.261.389	€ 1.425.077	€ 1.014.137
Contract Price	€ 4.522.300	€ 3.498.200	€ 4.247.000	€ 4.798.300	€ 3.414.700

Table A.3 - Business case assumptions

Depreciation	10	year
Interest	7	%
Maintenance estimation	2,5	% of investment
Production hours per year	2000	hours per year
Labour (operator) cost in West/North Europe	46800	€/(FTE) year
Insurance cost	1,5	% of fixed capital
Local taks	1	% of fixed capital
Outsourced labor	40000	euro
Operator hourly wage	62,5	euro/h
LiLSX zeolite	1,971	euro/kg
Helium	8,15	euro/Nm3
Electricity	0,09	euro/kwh

Appendix B

Table B.1 – Relative weight of requirements of the house of quality

<table>
<tr><th>Row</th><th>Weight Chart</th><th>Relative Weight</th><th>Importance (1-10)</th><th>Requirement (Explicit and Implicit)</th></tr>
<tr><td>1</td><td>||||||||||||||</td><td>14%</td><td>3</td><td>Product purity/composition</td></tr>
<tr><td>2</td><td>|||||||||||||||||||</td><td>19%</td><td>4</td><td>Capital expenses (CAPEX)</td></tr>
<tr><td>3</td><td>|||||||||||||||||||||||</td><td>24%</td><td>5</td><td>Operational expenses (OPEX)</td></tr>
<tr><td>4</td><td>||||||||||||||</td><td>14%</td><td>3</td><td>High up-time/reliability</td></tr>
<tr><td>5</td><td>||||||||||||||</td><td>14%</td><td>3</td><td>Yield/Recovery</td></tr>
<tr><td>6</td><td>|||||||||</td><td>10%</td><td>2</td><td>Ease of operation (Complexity of technology and operation)</td></tr>
<tr><td>7</td><td>||||</td><td>5%</td><td>1</td><td>Footprint</td></tr>
</table>