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Techno-economic study of multi-stage membrane configurations for biogas upgrading with 0.2 % methane slip

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Techno-economic study of multi-stage membrane configurations for biogas upgrading with 0.2 % methane slip

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Abstract

Methane is one of the strongest greenhouse gases and major component of natural gas and bio-methane. Through the Global Methane Pledge, the effort goes towards reducing global methane emissions by 30 % by 2030, which could mitigate global warming. Several countries in Europe have already implemented restrictions regarding methane slip (below 0.2 %) from commercial membrane biogas upgrading plants. DMT is interested in optimizing the *Carborex® MS system (Standard MS 0.5 % slip)*, with 29.3 % recycling, through the development of low slip options. Previously, a *0.2 % slip MS system by recycling increase* was developed due to the placement of a heat exchanger before the second stage. Besides that, it is also possible to add an off-gas treatment (thermal oxidizer unit) to eliminate the methane slip.

Hence, the work aims to develop several low slip configurations, based on first and third stage cooling temperatures with performance optimization, to obtain H-gas product quality with lower recycling. The business case economically evaluated the different low slip cases, benchmarking with the Standard MS case (0.5 % slip) and the option of having an RTO placed after the *Carborex®* to treat the off-gas stream.

Initially, a parametric study was performed to understand the system's behavior regarding cooling temperatures. It was acquired that the cooling temperature should not operate below 5.0 °C. Configurations were modeled with minus 10 % degradation in the polishing step (second stage) to understand aging/ fouling effects. Remediations steps were carried out, i.e., re-heating temperature and membrane number regulation. The selected method for developing H-gas product quality (2.5 % of CO₂) was the regulation of the intermediate heat exchanger.

Moreover, after performing the sensitivity study of different configurations, the systems with lower recycling were chosen for the business case. Thus, the selected first-stage cooling system (Case 1) exhibits 34.3 % of recycling. The cooling temperature was set at 10.0 °C, and the intermediate heat exchanger operated at 25.4 °C. The selected third-stage cooling system (Case 3) shows 40.4 % of recycling, operating at 6.0 °C cooling temperature. The re-heating temperature was set at 30.9 °C.

Regarding the business case, results have shown that Case 1 is the cheapest system among the low slip systems, presenting a total cost of ownership (TCO) of 438.0 k€ yearly. Case 3 and the system of *0.2 % slip MS by recycling increase* (44.0 %) accounts for 444.7 k€ and 447.4 k€ yearly TCO, respectively. The OPEX is the parameter that majority impacts the TCO (60.0 % weight). The option of placing an RTO increases 66.1 k€ on the TCO of the Standard MS case, going from 427.1 up to 493.3 k€ yearly. Thus, the option of having an RTO (0 % slip) is the most expensive one. The biogas upgrading price varied between 0.0749 and 0.0873 €·Nm⁻³_{product}, from the standard to the option of placing a thermal oxidizer unit.

Keywords:

Biogas upgrading plant, membrane separation, methane slip, first and third stage cooling, H-gas product quality

Resumo

O metano é um dos mais fortes gases de efeito estufa libertado com a combustão de gás natural e bio-metano. Através do Global Methane Pledge, o esforço vai no sentido de reduzir as emissões globais em 30 % até 2030, o que poderá mitigar o aquecimento global. Vários países europeus já implementaram restrições para o *slip* (abaixo de 0,2 %) deste componente das instalações comerciais de tratamento de biogás por membranas. A DMT está interessada em otimizar o sistema *Carborex® MS* (sistema padrão com *slip* de 0,5 %) com 29,3 % de reciclo, através de opções com baixo *slip*. Previamente, foi desenvolvido o sistema *0.2 % slip MS by recycling increase*, utilizando um permutador de calor anterior ao estágio 2. Além disso, é também possível adicionar uma unidade de oxidação térmica para eliminar o *slip* do fluxo secundário de gás.

Assim, este trabalho centrou-se na simulação de várias configurações com baixo *slip* (0,2 %), através de temperaturas de arrefecimento aplicadas às correntes do primeiro e terceiro estágio do sistema, com otimização da performance, para se obter um produto de elevada qualidade de gas (*H-gas*) com menor taxa de reciclo. O caso de estudo avaliou economicamente os diferentes sistemas de baixo *slip*, comparando com o sistema *Standard MS* (0,5% *slip*) e a opção de ter um RTO colocado após o sistema *Carborex®*, para tratar o fluxo secundário de gás.

Inicialmente, foi realizado um estudo paramétrico para se poder compreender o comportamento do sistema, relativamente às temperaturas de arrefecimento. Foi compreendido que a temperatura de arrefecimento não deve ser estabelecida abaixo dos 5 °C. Além disso, as configurações foram modeladas com menos 10 % de degradação na etapa de polimento (segunda etapa) para compreender os efeitos de envelhecimento sobre o desempenho do sistema. Foram realizadas etapas de remediação, ou seja, através da regulação da temperatura de reaquecimento e do número de membranas. O método selecionado para a remediação do produto de elevada qualidade (com 2,5% de CO₂) foi através da regulação da temperatura de reaquecimento.

Posteriormente, tendo em conta os objetivos de qualidade do produto foi feito um estudo de sensibilidade de diferentes configurações onde foram selecionados os sistemas com menor reciclo para se proceder com a avaliação económica. Assim, o sistema de arrefecimento no primeiro estágio (Caso 1) exibiu 34,3 % de reciclagem. A temperatura de arrefecimento foi fixada em 10 °C, e foram estabelecidos 25,4 °C para a temperatura de operação do permutador intermediário. O sistema selecionado para o arrefecimento no terceiro estágio (Caso 3) apresenta 40,4 % de reciclagem, operando a 6 °C de temperatura de arrefecimento. A temperatura de reaquecimento foi fixada em 30,9 °C.

Relativamente ao caso de estudo, os resultados mostraram que o Caso 1 é o sistema mais económico entre os sistemas de baixo desliz, apresentando um custo total de compra de 438.0 k€ anuais. O caso 3

e o sistema "*0.2 % slip MS by recycle increase*" possuem 444,7 k€ e 447,4 k€ de TCO anuais associados, respetivamente.

O OPEX é o parâmetro que maioritariamente impacta o TCO (60,0 % de peso) neste caso de estudo. A opção de colocar um RTO aumenta 66,1 kWh ao TCO do sistema standard *Carborex*®, passando de 427,1 k€ para 493,3 k€ anuais. Assim, a opção de ter um RTO (acompanhado de 0 % de *slip*) é a mais dispendiosa. O preço de tratamento do biogás variou entre 0,0749 e 0,0873 € por volume de biometano, desde o sistema padrão (mais barato) até à opção de colocar uma unidade de oxidação térmica (mais dispendioso). O custo associado aos sistemas com 0,2 % *slip* estão compreendidos entre essa gama de valores.

Palavras-chave:

Instalação de *upgrade* de biogas, separação por membranas, *methane slip*, Arrefecimento do primeiro e terceiro estágio, produto de elevada qualidade (*H-gas*)

Declaration

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

Porto 4 July, 2022

A handwritten signature in black ink, reading "Miguel Rubio Cabral". The script is cursive and fluid, with the first letters of each word being capitalized and prominent.

(Miguel Fernando Rubio Pereira Gonçalves Cabral)

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Notation and Glossary

A	Surface area	m^2
D_i	Diffusivity of i	$\text{m}^2 \cdot \text{s}^{-1}$
E_a	Activation Energy	$\text{J} \cdot \text{mol}^{-1}$
F	Flow rate	$\text{Nm}^3 \cdot \text{h}^{-1}$
N	Flux through the membrane	$\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$
P_i	Permeability	$\text{mol} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$
Q_i	Permeance	$\text{mol} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$
R	Universal gas constant	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
S_i	Solubility of i	$\text{mol} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$
SC_i	Separation Capacity	$\text{Nm}^3 \cdot \text{h}^{-1} \cdot \text{bar}$
T	Temperature	$^{\circ}\text{C}$

Greek Letters

$\alpha_{i,j}$	selectivity	
δ	Membrane thickness	m
ΔH	Enthalpy	$\text{J} \cdot \text{mol}^{-1}$
Δp	Partial pressure difference	bar
ΔP	Driving force	bar

Indexes

0	Reference
f	Feed
i	Index
j	Index
p	Permeate
r	Retentate

List of Acronyms

CAPEX	Capital expenditures
CNG	Compressed natural gas
DTO	Direct Thermal Oxidizer
EOS	Equation of state
GMP	Global Methane Pledge
GPU	Gas permeation Unit
G-gas	Groningen product quality gas
HAP	Hazardous pollutants
HE	Heat Exchanger
H-gas	High product quality gas
LEL	Lower explosive limit
LNG	Liquified natural gas
L-gas	Low product quality gas
OPEX	Operational expenditures
RCO	Regenerative Catalytic Oxidizer
RecCO	Recuperative Catalytic Oxidizer
RTO	Regenerative Thermal Oxidizer
UEL	Upper explosive limit
S1	First stage of membrane separation
S2	Second stage of membrane separation
S3	Third stage of membrane separation

TCO Total cost of ownership
 VOCs Volatile organic compounds

Compounds

CH₄ Methane
 Co Cobalto
 Cr Cromium
 Cu Cooper
 CO₂ Carbon dioxide
 H₂O Water
 N₂ Nitrogen
 O₂ Oxygen
 Pt Platinum

1 Introduction

1.1 Framing and presentation of the work

Methane (CH_4) is the major component of natural gas and bio-methane. It is characterized as being one of the strongest greenhouse gases, having a more detrimental effect than carbon dioxide (CO_2), 86 times more, over a 20-year period, even though it remains in the atmosphere for less time (between 10 to 15 years)¹.

Through the Global Methane Pledge (GMP) the effort goes toward reducing global methane emissions by at least 30 % by 2030, which could eliminate over 0.2 °C global warming by 2050. Thus, the CH_4 emissions that go out to the atmosphere from the anthropogenic activity must be strongly regulated to improve the air quality and slow down climate change ².

The biogas upgrading industry has also been affected by this trend. Therefore, several countries in Europe have already implemented relevant legislation to reduce methane emissions. DMT as a market leader in membrane upgrading is particularly interested in optimizing its system operation to minimize the methane slip of the *Carborex® MS* (standard 0.5 % slip).

DMT has already developed a low slip system with an intermediate heat exchanger prior to stage 2, to meet the 0.2 % requirements. However, the problem is based on the recycle increase, which impacts mainly the power consumption of the compressor (before the first stage) and system's OPEX.

Hence, in this study, several multistage membrane configurations with first stage cooling and third stage cooling were modeled, and further analyzed to determine the optimal operating conditions if the target is the development of H-gas quality (2.5 % of CO_2) product with low slip (0.2 %). For the modeling part, it was used the computer application *Simulation of gas separation modules in real time*, provided by Evonik Industries. The recycle was an essential parameter throughout the analysis of the different configurations.

This project aims to build a business case calculation of which system would be the best economically through DMT's guideline strategies and compare the modeled low slip options with the current offers in the market, i.e., the *Carborex® MS* standard case, *0.2 % slip MS by recycling increase* or the option of using a thermal oxidation as an off-gas stream treatment. In other words, the project scope included an economic evaluation and comparison of the different options to achieve the desired targets, while benchmarking with DMT's standard system.

1.2 Presentation of the company

DMT Environmental Technology is a Dutch company, currently in the business of developing technical solutions in biogas conditioning and biogas upgrading plants, providing gas to grid, bio-CNG, and bio-LNG pipelines options. The company developed past activities in the treatment of groundwater, odor abatement, and provision of sequence batch reactors, as well as projects in water treatment and gas desulphurization. Among the different offers provided by DMT, the current commercialized products are *Carborex® MS*, a multistage membrane configuration that allows obtaining biomethane with high quality; and Sulfurex, which is a pre-treatment unit for desulphurization. DMT'S headquarter is located in Joure, Netherlands, where it was founded, but with a global presence, i.e., Europe, USA, and Canada. In 2021, DMT was acquired by Broadview Energy solutions BV continuing its market activity.

1.3 Contribution of the author to the work

Literature research was conducted to find techniques to reduce methane slip from biogas upgrading plants, mainly in the thermal oxidation field. Working with the Evonik Software, it was possible to perform a membrane separation system. Several proposal configurations with first and third stage cooling were modeled. A business case was built, providing useful information to the company about the feasibility of the tested systems.

1.4 Organization of the dissertation

This master thesis is divided into 6 chapters:

1. **Introduction:** Framework of the project, presentation of the company where the project was developed, and general information.
2. **Context and state of the art:** Overview of methane and different biogas upgrading technologies, with deepen knowledge about membrane separation process. Overview of DMT's standard system for 0.5 % slip, *Carborex® MS*. At last, technologies for off-gas treatment were presented.
3. **Computer application:** The software utilized by the author is explained in this chapter. The main considerations applied in the simulation, proposed configurations and modeling methodology are described.
4. **Results and discussion:** Discussion of the obtained results for the different low slip configurations through cooling first and third stage. The main part of the work is presented in this chapter.
5. **Conclusion:** The main conclusions acquired by the author are shown with critical analysis, regarding the feasibility of the different processes.
6. **Assessment of the Work:** Presentation of the main objectives and tasks developed in this work.

2 Context and State of the art

2.1 Methane emissions in biogas upgrading plants

A biogas upgrading plant aims to enhance the calorific value of the raw biogas, which is a mixture of mainly CH₄ (55-65 %) and CO₂ (35-45 %). Other gases are also typically present in lower concentrations, such as nitrogen (N₂), oxygen (O₂), water (H₂O), hydrocarbons, hydrogen sulfide (H₂S), and ammonia (NH₃), if it is biogas provided by anaerobic digestion ³.

The upgrading biogas process factors 90 % of total biomethane produced worldwide. Nevertheless, over 80 % of the 191 TW·h raw biogas generated today is directed for local energy and heat rather than being upgraded to biomethane and injected into the gas grid. Efforts are needed to transit this supply to grid biomethane enhancing its energy usage^{4,5}.

During the upgrading process, biogas is typically pre-treated to remove contaminants and ends up with a methane-rich product stream, as well as a CO₂-rich by-product. The latter is typically vented to the environment, releasing some of the methane into the atmosphere ⁶. Today's premise is using CO₂ in food-grade applications (CO₂ capture and storage technology) with a high purity while reducing the methane content in the off-gas stream.

A key performance parameter of the upgrading process is the methane slip. This parameter indicates the methane lost via the stack and it is close to the product loss. The product loss means the ratio between the quantity of methane lost via stack and the quantity of methane that is obtained in the product stream.

Furthermore, the methane slip in the biogas upgrading process is defined as being the proportion of methane lost via stack, i.e., to emissions, and methane in the biogas fed to the system, as expressed by equation (2.1), which represents the CH₄ leaked from the system ⁷.

$$\text{methane slip (\%)} = \frac{\% \text{CH}_{4,\text{stack}} \times \text{stack flow}}{\% \text{CH}_{4,\text{feed}} \times \text{feed flow}} \times 100 \quad (2.1)$$

In other words, the methane slip means a waste of a fraction of the available biofuel, which results in reduced revenue from unexploited renewable energy ⁸.

Currently, the offering value of methane slip in the market for membrane separation is below 1% and typically 0.5 %. However, some European countries, such as Germany and Sweden, already require methane slip at 0.2 % to meet the said targets, considering the strong greenhouse effect of methane.

Due to the pressure on the worldwide energy transition, Germany established that heat demand in the production process must be covered by renewable sources within a 0.5 kWh·Nm⁻³ power consumption limit for biogas upgrading plants. This step was taken to support only efficient biomethane production ⁹.

2.2 Biogas upgrading technologies with low slip methane

Several systems have been developed in the market to remove the CO₂ from the raw biogas, complying with the methane slip restrictions, i.e., processes using water scrubbing, amine chemical absorption, cryogenic upgrading, pressure swing adsorption as well as membrane separation¹⁰, which is the technology currently applied by DMT.

The following **Table 1** presents a comparison between the different technologies found in the market to treat biogas ⁶. As it is possible to see the two processes, amine chemical absorption and membrane separation exhibit lower values of methane slip, which is a guideline of this project.

Table 1 - Typical characteristics of biogas upgrading industrial plants⁶.

Biogas upgrading technologies	Water Scrubber	Amine Chemical Absorption	Pressure Swing Adsorption	Membrane Separation
Typical content in biomethane (v/v %)	95.0 – 99.0	> 99.0	95.0 – 99.0	95.0 – 99.0
Methane recovery (%)	98.0	99.96	98.0	90 – 99.5
Methane slip (%)	1 %	< 0.1 %	1-1.5 %	0.5 %
Electric energy demand [kWh·m ⁻³ biomethane]	0.46	0.27	0.46	0.25 – 0.43
Heating demand	-	high	-	-
Consumables	Drying agent	Amine solution	Adsorbents	Membranes

Regarding chemical absorption, amine solvents are effective at nearly atmospheric pressure and require little electrical energy. As seen in **Table 1**, amine chemical absorption presents a lower methane slip value in comparison with the physical absorption method (water scrubbing). Green Methane company (Italy) offers amine scrubbing for upgrading with 0.1 % slip. The electrical power consumption is between 0.15 – 0.2 kWh·Nm⁻³, considering a flow range higher than 500 Nm³·h⁻¹ ¹¹.

Despite the low methane slip value, the amine solvents require thermal energy to release the absorbed gas and amine regeneration inside the stripper, as well as amine solvent make-up to reduce process efficiency loss. In addition, its disadvantage remains in the use of a chemical such as a monoethanolamide or diethanolamine (due to the reported toxicity levels to the environment)^{12,8}.

Recently, hot potassium carbonate solvent (HPC), K₂CO₃, was investigated by Paolini et al., 2019 in a demonstrative plant funded by Green Methane (Italy), for CO₂/CH₄ pair-gas separation. In this case, due to the stated reduced solubility of methane in the K₂CO₃ solvent, a methane slip of 0.078 % was achieved

by HPC. Thus, this solvent could be an alternative to the amine ones, reducing the negative effects and increasing methane recovery.

On the other hand, membrane separation technology is particularly appealing for biogas upgrading since there is no heating demand as in the chemical absorption technique and does not require the use of hazardous compounds. Along with low energy consumption, and easily engineered modules, this technology is capable of reaching a CH₄ recovery efficiency higher than 99.5%, while pure CO₂ is obtained. Thus, the membrane separation stands out as a feasible and sustainable way to upgrade the biogas with low methane slip ⁶.

Typically, membrane separation needs multiple steps to achieve the required product purity. In the market, the dominant membrane material is polymers, such as polyethersulfone (PES), polyetherimide (Utem 1000), and Polyimide (Matrimide 5218). Polymeric materials, however, suffer from a trade-off between the selectivity and the permeability of the permeants (CO₂ and CH₄), which dictates the membrane performance for a gas pair separation ⁶.

Regarding this trade-off, it was shown through Robeson's upper bound report, that the diffusion coefficient governs the separating capabilities of polymers for the gas pair CO₂/CH₄. As the polymer molecular spacing becomes smaller, permeability is reduced due to decreasing diffusion coefficients, whereas the separation properties are enhanced ^{13,14}.

Despite the promising characteristics of membrane separation, there is no patent available in the market claiming a methane slip lower than 0.2 % using only membrane multi-stage modules. Therefore, off-gas post-treatment technologies must be considered, and the cost evaluated as well.

2.3 Membrane-based biogas upgrading

Membranes for gas separation are used to separate different molecule species (in this case, CO₂ and CH₄) according to their molecular interactions with the membrane material, which allows one to permeate more easily while hindering the permeation of the other. Thus, the membrane acts as a selective barrier to the different compounds. This leads to the selectivity separation of CO₂ due to its higher permeation over the CH₄ molecules ⁷. The driving force is given by the pressure drop between the downstream, permeate side at low pressure, and the upstream, feed side at higher pressure. A schematic representation of a CO₂ semi-selective polymeric membrane for CO₂/CH₄ separation based on crossflow transport is illustrated in (**Figure A.1, Annex A**) ¹⁵.

For biogas upgrade industrial-scale plant, due to the large surface area requirements, the commonly used structures of membrane modules are hollow fibers and spiral wounds.

The hollow fiber allows a higher surface area per unit volume leading to a great rate of separation capacity, as it provides mechanical support, and it is easier to handle. The typical values for hollow fiber modules

are $10\,000\text{ m}^2\cdot\text{m}^{-3}$, while the spiral wound provides a range between $[200\text{-}1000]\text{ m}^2\cdot\text{m}^{-3}$. Otherwise, it is also possible to have the flat sheet (envelop) structure, which is suitable for small industrial applications since it allows $[30\text{-}500]\text{ m}^2\cdot\text{m}^{-3}$ ¹⁶.

The following **Figure 2.1** shows a schematic representation of a membrane's module based on a shell and tube vessel. The polymeric membrane is supported on a hollow fiber structure separating the bulk CO_2 from the feed gas.

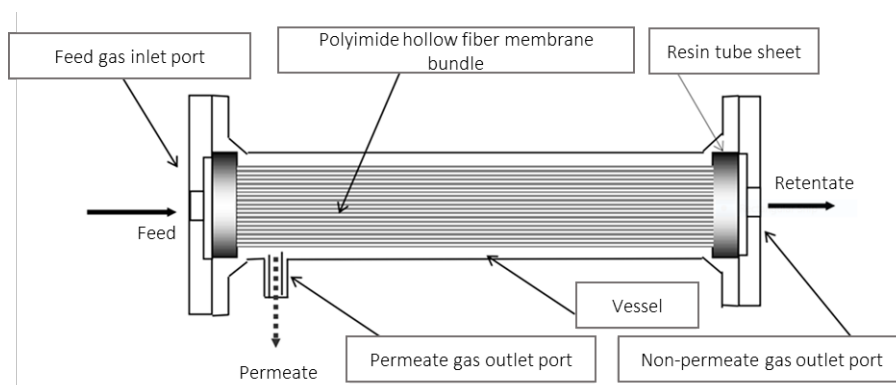


Figure 2.1 - Schematic representation of a shell and tube module with hollow fiber membranes ¹⁵.

The feed gas enters the bore side of the module and goes towards the retentate side. The carbon dioxide permeates through the polyimide membrane layers and is obtained at the permeate stream. The methane-rich stream is present on the retentate side. Due to the need of having a constant driving force along the membrane length, a counter-current configuration is set. Thus, as the methane is retained at the downside of the system, the pressure increases (backward) and forces the CO_2 to move to the bottom of the shell, where it is obtained (permeate).

Given the different types of membranes that allow the separation of CO_2/CH_4 gas pairs, diverse separation mechanisms are expected. Most polymeric (organic) membranes have a dense layer, in which the gas transport occurs due to the solution-diffusion mechanism. For a dense membrane supported on a porous matrix for structural integrity, the mechanism is composed of the following steps ⁷:

- Transport through the porous support
- Sorption on the active polymeric layer
- Diffusion through the membrane
- Desorption at the permeate side

Despite that, inorganic membranes as they have a porous structure, the transport is dependent on the pore size (molecular sieving for pore size $< 0.6\text{ nm}$, surface diffusion for pore size $< 2\text{ nm}$, and Knudsen diffusion when the pore size is in the range of $2\text{-}50\text{ nm}$) ¹⁷.

The scientific background of the permeance flux that passes through the membrane layer and the fundamentals of permeability, selectivity and separation capacity are described in **Appendix A**.

2.4 The Carborex® MS

2.4.1 Overview of the system

The following **Figure 2.2** represents the schematic system used by DMT to upgrade the raw biogas. The *Carborex® MS* consists of several steps, namely pretreatment, compression, membrane separation, and quality control step.

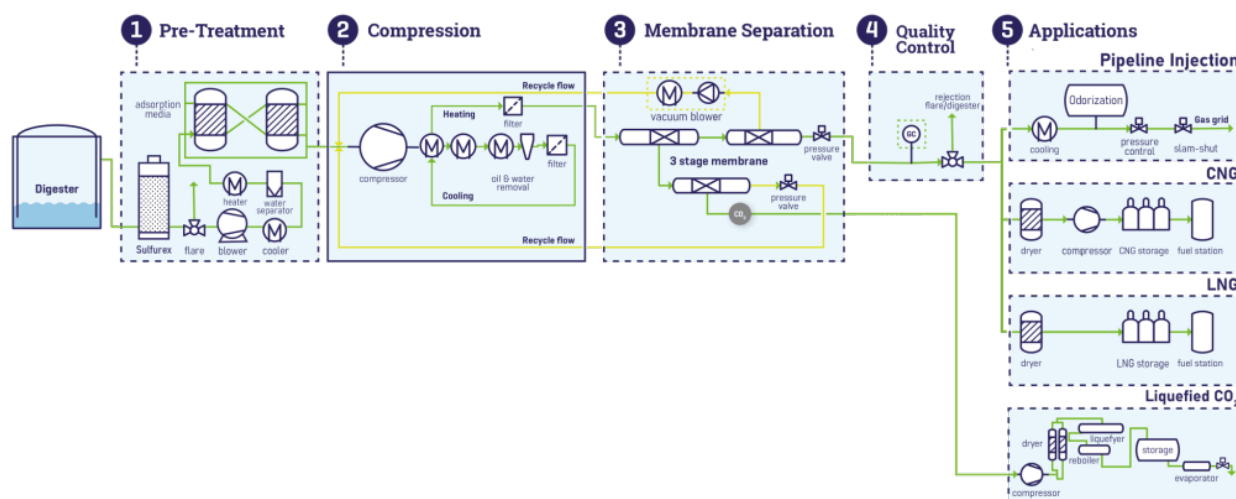


Figure 2.2 - Carborex-MS schematic representation, by DMT, 2020¹⁸

Pre-treatment is generally needed due to the presence of some pollutants such as VOCs, siloxanes, NH_3 , and H_2S which must be removed before the membrane separation of CO_2/CH_4 . Trace compounds can severely impact the system's performance. Pollutants such as H_2S and VOCs can cause membrane clogging, while NH_3 has the most damaging and non-reversible effect on membrane performance.

The pre-treatment step consists of a cooling step for dewatering purposes, while the contaminants are removed via activated carbon vessels. For feedstocks with high H_2S content, DMT offers a desulfurization step with either chemical or biological scrubbing.

Since it is needed enough driving force (ΔP) to push the raw biogas into the membrane surface, the stream passes by a compressor to enhance the feed pressure to a range of between 10-17 bara. The temperature is also regulated in this step and the typical operating range is 20-40 °C.

Since the temperature is elevated, some heat-exchangers follow for dewatering and temperature adjustment. Filters are installed to ensure the removal of any dust or oil particles prior to the membrane system (compressing step). As a result, the raw biogas is prepared to go to the multi-stage membrane separation system.

The typical MS configuration for the European market consists of 3-stages, modified according to the customer's needs, as it is shown in **Figure 2.3**. The first stage is used for bulk separation of CO₂, while stage 2 acts as a polishing step to achieve the desired product quality. Stage 3 is included to regulate the methane slip.

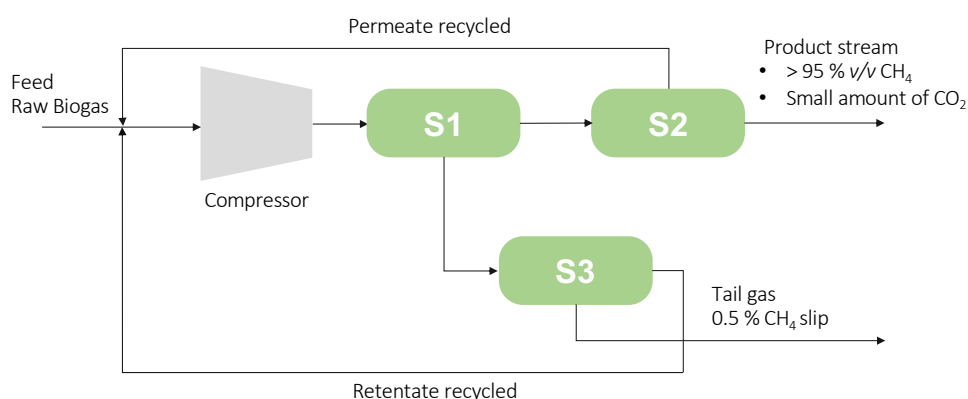


Figure 2.3 - Schematic representation of the 3-stage MS for biogas upgrading

In the first stage (S₁), it is obtained on the retentate side a CH₄ rich stream with mainly 60-80 % CH₄ and 40-20 % CO₂. On the permeate side, a stream with mainly CO₂ (60-80 %) and 40-20 % CH₄ is obtained at lower pressure.

The permeate of S₁ goes to a third stage (S₃) where two streams are obtained, i.e., a retentate stream with mainly CH₄ that is recycled to the gas compressor, and the permeate stream, tail gas, with mainly > 98 % of CO₂ and traces of methane. The retentate from S₁ goes to the second stage (S₂). There, a product stream with the required CH₄ purity is obtained at the retentate side (biomethane). The permeate, composed mainly of CO₂, is recycled back to the compressor, together with the retentate methane-rich stream of S₃.

Moreover, after the upgrading step, the stream passes into a quality control step, where the concentration of methane and CO₂ are measured, and part of the flow is recycled back to the digester or a flare to burn out the gas (if the composition is not the required one).

At the end of those steps, the upgraded biogas can be applied to different applications, such gas grid injection, for heating and cooking, compressed natural gas (CNG), or liquified natural gas (LNG), depending on the product quality requested. For gas grid injection, the requested upgraded biogas can follow different guidelines, i.e., it may be based on H-gas (≥ 95 % CH₄ in the biomethane), L-gas ($\cong 90$ % CH₄ content), or even G-gas (Groningen product quality gas), which is approximately 96 % of biomethane ¹⁹.

2.4.2 Joule-Thomson effect

When biogas is passing through the membranes, the permeate flow is accompanied by a decrease in the temperature. This is due to both heat exchange taking place within the module (molecules exchange heat

with membrane layer/ module), but also due to the pressure drop occurring and, therefore, expansion of the gas in the outlet ²⁰.

In addition, since CO₂ exhibits a higher Joule Thomson coefficient (see **Table 12, Annex A**) applications involving CO₂ at high feed pressure are prone to large temperature changes in the module. Therefore, decreasing the temperature might lead to the condensation of condensable gas components. Thus, the appearance of liquid form or droplets on the membrane surface would induce an additional mass transfer resistance, reducing the permeance flux. Thus, it would affect the separation capacity and damage the membrane and separation performance ²¹.

This effect is important, in the sense of establishing a maximum range of operating pressure for the *Carborex® MS* since it is known that the permeance and the selectivity of the membrane material are dependent on temperature. Also, the Joule-Thomson effect is taken into consideration in the modelling part, as it is embedded in the program software.

2.4.3 Arrhenius Relation Permeability

The Arrhenius law indicates that permeability (P_i) is a function of temperature (T), and reckons with activation energy (E_a), as given by equation (2.2)

$$P_i(T) = P_{i0} \cdot \exp \left[\frac{-E_a}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (2.2)$$

Where R is the molar gas constant, T_0 is a reference temperature and P_{i0} is the reference permeance. When the E_a is positive for a given species, its permeability across a specific membrane increases with temperature, as is the CO₂/CH₄ case. Nevertheless, since the activation energy for methane is significantly higher than for CO₂, the selectivity decreases with temperature ²⁰.

For polymeric membranes, any change in the membrane structure induced by heat treatment produces thermal fluctuations in the membrane matrix. Moreover, increasing the operating temperature allows higher mobility of the molecules as well as larger volumes of free space inside the membrane structure⁶.

In a previous project developed by DMT, the requested design was a unit for H₂-gas grid injection and low methane slip $\leq 0,20$ %. The membrane separation system was designed as a 3-stage system, with Evonik membranes (app. 20 membrane's modules) and intermediate re-heating step between stage 1 and stage 2 at 30 °C. This intermediate heater exchanger was used to gain better control of biomethane product quality, without raising the temperature in the third stage.

This is because increasing the temperature in the second stage leads to higher membrane's permeance and lower selectivity between the pair CO₂/CH₄, which will lead to better biomethane quality. In addition, since the permeance flux also increases, more recycling will go back to the first stage. For the same surface area in this stage, the permeance flux that goes to stage 3 decreases, and consequently, less methane

slip. If a heat exchanger was placed before stage 3 (temperature increase), it would result in a higher methane slip.

2.5 Thermal Oxidation for off-gas treatment

The elimination of CH₄ of the tail gas can be done through complete thermal oxidation, which will convert the remaining methane into carbon dioxide and water vapor when mixed with air, as given by equation (2.3). The transformation of methane into CO₂ may not seem to be the best option for reducing greenhouse gas emissions because it means a loss of product and formation of carbon dioxide, but indeed it is a satisfactory improvement in terms of net radiative forcing.



This reaction is extremely exothermic ($\Delta H_{298\text{ K}} = 890.61 \text{ kJ}\cdot\text{mol}^{-1}$), so it will release a considerable amount of energy per mole of methane. Besides that, the high heat of methane combustion $39.8 \text{ MJ}\cdot\text{m}^{-3}$, makes the recovery of energy as heat or even electricity an attractive option^{22,23}.

The autoignition temperature of methane is about 580 °C in the presence of air. So, it is important to operate at high temperature values to achieve the maximum conversion into CO₂ and water vapor. Also, the lower explosive limit (LEL) means the minimum compound content inside the mixture to occur the combustion. For methane, the LEL value is 5 % of the total volume in the mixture and the UEL (upper limit) is 15 % volume²⁴.

The most interesting technologies to promote the total thermal oxidation of methane are Regenerative Thermal oxidizer (RTO), Regenerative Catalytic oxidizer (RCO), Recuperative catalytic oxidizer (RecCO), Direct Thermal Oxidizer (DTO) as well as Flare burners. The mindset is to use a thermal oxidation unit after *Carborex*[®] MS to treat the tail gas stream (see **Figure 2.3**) to reduce methane slip while producing CO₂.

RTO, RCO, RecCO, DTO should be used for the operation with methane concentrations lower than 1% (v/v). With a high thermal efficiency of over 95 %, the autothermal operation i.e., combustion without additional heat or fuel, is possible, even for low methane concentrations²³.

On the other hand, the flare equipment is indicated to be used in off-gas streams with methane content (v/v) higher than 5 %. For tail gas streams from biogas upgrading plants in which the methane composition varies between 1.5 % - 2 % v/v in a 3-stage configuration, it might be needed to mix with methane, ethane, propane, or even raw biogas intentionally²⁵. In a 2-stage configuration, the methane slip is usually higher as well as the methane composition. For low slip, flaring is not recommended as the methane composition of the tail gas stream is lower than 0.5 % v/v.

Therefore, it is important to evaluate if the implementation of those technologies suits the tail gas composition after the *Carborex*[®] and if it is cost-effective to add it to the system.

2.5.1 Regenerative Thermal Oxidizer (RTO)

The regenerative thermal oxidizer is applied to reduce trace components, such as volatile organic compounds (VOCs), and hazardous air pollutants (HAP) concentrations, from waste gas of biogas upgrading plants. It is also used for CH₄ removal, according to a proper mix of constraints, mainly, temperature, gas residence time, turbulence, and oxygen ²³.

With this type of equipment, the inlet gas passes into the inlet manifold of the oxidizer. Then it is preheated inside energy recovery chambers, to achieve the required temperature. Afterwards, it is heated in the ceramic beds as they move towards the combustion chambers, where the total oxidation is performed (if needed, supplementary oxygen is added to this chamber) ²⁶.

Since methane is a stable compound, breaking the C-H bond and oxidizing the molecule requires a large amount of activation energy. Thus, the operating temperature within the RTO must be high enough to overcome the energy barrier. As the reaction is highly exothermic, it will release large amounts of energy and maintain the operating temperature (800 °C – 1000 °C) ^{23,27}.

After the total combustion, a heat sink, such as a ceramic bed, is used to lead the treated gas flow out of the combustion chamber. The ceramic bed recovers the energy released by the gas flow to heat the untreated inflow gas. Moreover, with this mechanism, up to 95 % of the heat present in the gas flow can be recovered, resulting in a low output temperature ²⁵.

Figure 2.4 shows an RTO unit composed of two combustion chambers and a switching valve system (direct flow system: black arrows; reverse flow system: orange arrows), which is the general configuration for this type of equipment (It is also possible to have 3-stage combustion chambers). Thus, by continually alternating the direction of the flow, a ceramic bed is alternatively heated and cooled by the outlet gas and inlet gas, respectively ²³.

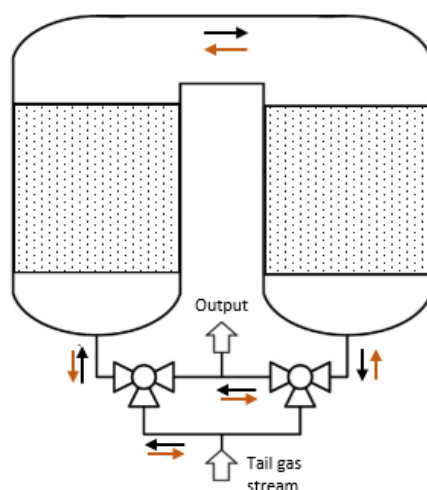


Figure 2.4 - Schematic 2-chambers RTO unit with switch valve system, adaptation²³

It was found that RTO technology presents a high destruction efficiency higher than 97 %, and heat recovery is also quite high (up to 95 %). In addition, almost all vendors offer units to treat a wide range of tail gas flows, from $1000 \text{ Nm}^3 \cdot \text{h}^{-1}$ to $100\,000 \text{ Nm}^3 \cdot \text{h}^{-1}$, as they have solutions for treating large industrial scales. Guarantees are typically given for VOC removal (it might produce NO_x and CO during the process).

A typical range of flow and compositions based on internal information from DMT are given between $180 - 500 \text{ Nm}^3 \cdot \text{h}^{-1}$ with an inlet composition (volume) of 0.1 - 0.9 % CH_4 , 0 - 0.2 % of O_2 and 0 - 0.3 % of H_2S . The RTO operating pressure is set between 5 - 50 mbara, as compressed air is used to oxidize the mixture with a consumption rate of $3 - 4 \text{ m}^3 \cdot \text{h}^{-1}$ (for given operating conditions). At the outlet, it is possible to obtain a flow rate of about $1000 \text{ Nm}^3 \cdot \text{h}^{-1}$ since it is added a secondary air stream at the inlet port of the RTO.

The range price of the equipment is between 190 000 € and 220 000 €, excluding additional equipment. It is also important to account for the annual running costs in terms of electric energy ($0.10 \text{ €} \cdot \text{kW} - 0.5 \text{ €} \cdot \text{kW}$) that would affect the system's *OPEX*.

2.5.2 Regenerative Catalytic Oxidizer (RCO)

The RCO presents the same mode of operation as the RTO. However, it uses a catalytic bed in the middle of two inert beds to reduce the ignition temperature. Therefore, the combustion temperature is achieved in a range between $300^\circ\text{C} - 500^\circ\text{C}$. It is inside the inert beds where the heat regeneration capacity is concentrated. Thus, this technology allows operating at high yields, at almost half of the temperature that the RTOs operate at, hence reducing by half the energy costs. This is because of the catalyst effect. Also, there is no NO_x produced as it can happen when operating at high temperatures²³.

Regarding the catalysts, palladium (Pd) is typically used to oxidize short-chain hydrocarbons, i.e., methane and ethane, while platinum (Pt) is more used for larger molecules. Moving to the metal oxide catalysts, cooper (Cu) with cobalt (Co) or chromium (Cr) have been used in RCO to oxidize isopropyl alcohol, propane, and butane as they have lower prices associated^{23,27}.

The disadvantage of using a catalyst might be due to the poisoning components effect, such as H_2S , as well as the humidity, which negatively affects the lifetime and the efficiency of the catalyst per cycle of usage. Due to this catalyst poison, a biogas pre-treatment step must be ensured to operate at high yields in the sense of removing the trace components that can affect the catalyst's performance¹⁰.

A case study was performed by Moscato et. al., 2018 within the *Resilco S.r.l.* company (Italy) to compare the RTO with the RCO (*Re-CAT RCO*). This report shows that the company uses a quite efficient process with RCO, even for small plants. It is specified that this unit is suited for the treatment of large streams with low concentrations of VOC ($0.8 - 4 \text{ mg} \cdot \text{Nm}^{-3}$). Also, it is possible to treat off-gas flows from

biomethane production between 200 -1000 Nm³·h⁻¹ (small plants), with over 95 % abatement of VOC and CO (methane abatement was not given in the report).

The difference remains in the fact that a heat exchanger with heat recovery is put after the catalytic reactor instead of using the heat exchanger over the ceramic media beds. As a result, the thermal recovery was slightly reduced, 5 % less than the RTO, allowing a high rate of methane destruction and energy recovery ²⁸. In **Figure A.2, Annex A** is possible to understand the flow diagram of the *Re-cat RCO* unit.

It is important to refer that an RTO can be changed to RCO if a catalyst bed is added to the RTO system, with the same basic configuration built.

From DMT's archive, all RCO vendors specifically provide guarantees for methane removal, treating streams provided by biogas upgrading plants. Moreover, this technology is also advised to treat tail gas streams coming from PSA units. There are no quotations available from DMT's global office. However, it was found in the literature that the *Capex* of the system rounds 200 000 €, not accounting for the price of the chosen catalyst ^{25,29}.

The destruction efficiency of this unit is slightly lower than RTO, but it is indicated if the customer aims to achieve almost zero methane slip. With this option, the energy demand is lower since the operating temperature required is less than for RTO's unit, as mentioned before. Besides that, it needs to be accounted for an increase of the *OPEX* due to catalyst replacement after a certain period of usage, due to loss of efficiency.

2.5.3 Recuperative Thermal and Catalytic Oxidizer

While the regenerative options use two/three chamber of ceramic bed (with heat transfer and heat recovery), the recuperative thermal and catalytic oxidizers use only one chamber, and the heat is exchanged directly in one heat exchanger at the discharge of the thermal oxidizer ²⁵.

This technology is an option commercialized by *Spooner industries* (RecTO and RecCO) with 99.99 % of the destruction of HAPs, VOCs, and odorous emissions. However, as the thermal efficiency of RecTO is reduced by 30 % compared with an RTO unit, this means a real thermal efficiency between 40 %-70 %. Despite that, the Spooner RecTO can treat a 150-15 000 Nm³·h⁻¹ achieving 95 % of heat recovery, with low NO_x formation ³⁰

Since the thermal efficiency is low when compared to the RTO and RCO, this type of equipment should not be considered in terms of usage of thermal energy and electrical cost.

2.5.4 Direct Thermal Oxidizer

It is the simplest type of thermal oxidizer, without any type of heat recovery system to recover a portion of the waste heat generated by the combustion process.

The tail gas with mainly CO₂ and traces of methane is added to the inlet port of the thermal oxidizer, which is mixed with air. Then the mixture is burned at the inlet to reach the required operating temperature and goes to the combustion chamber, where total oxidation of methane and other remaining compounds is performed. As a result, the output stream goes to the stack. The electrical energy to provide the necessary heat is not recovered in this type of system³¹. In terms of costs, this solution is less expensive than the others with heat recovery. However, it presents the highest operating costs due to energetic expenses.

Through DMT's Global office, there is available information for treating 900 Nm³·h⁻¹ with approximately 0.6-1.0 % of CH₄ (it can be scaled up to 5 %). The expected destruction of VOC is about 98 % (total methane destruction was not guaranteed) with a total maximum heat released of 8.5 MBtu h from the thermal unit, depending on the tail gas stream composition and flow rate.

2.5.5 Flare

This treatment promotes the total oxidation of methane, VOCs and HAPs that may be present at the tail stream. It is similar to the DTO mechanism, although it is indicated for streams with CH₄ content above 5 % v/v, as referred previously. If this option is considered, there is a need to add air to the biogas mixture. The operating temperature is about 900 °C leading to an output gas of 600 °C. Thus, it is possible to utilize the outlet stream as a heat source for other purposes¹⁰.

In terms of market, there are vendors for large scales [1000 – 12 000] Nm³·h⁻¹ with a maximum fire output of 50 – 70 MW and for small scales [2 -250] Nm³·h⁻¹ with maximum fire output of about 0.8 MW.

2.6 CO₂ Liquefaction

CO₂ liquefaction based on cryogenic distillation is common for flue gases to purify and further liquefy carbon dioxide. The technology can be added downstream of the *Carborex® MS* off-gas outlet producing renewable CO₂ and giving the possibility for a system with zero methane slip. The CO₂ liquefaction downstream a *Carborex® MS* creates an additional revenue stream for the end-user, producing industrial or food-grade CO₂ that can be used in various applications. Moreover, the removed CH₄, can also be recovered in case of integration, therefore minimizing biofuel/product loss.

Figure A.3 (Annex A) exhibits the phases of CO₂ according to temperature and pressure. This technology is well developed in the market and operates in a relatively easy fashion: in the condenser, the CO₂ is liquefied, while the remaining CH₄ stays in the gaseous phase and can be vented to the atmosphere or recycled back to the system, increasing the recovery up to 100 %.

Pentair Haffmans (Netherlands) is already providing a technology using a multi-stage membrane separation process together with a liquefaction unit of CO₂. This unit is capable of separating the CO₂ from

the remaining methane when treating a flow range between 700 to 3 600 Nm³·h⁻¹ for a biogas composition with 55 % CH₄, 44 % CO₂ and 1 % of air³².

For the liquefaction of CO₂, the critical point is the main state of the compound. **Figure 2.5** shows the diagram process when using a liquefaction unit to treat the tail gas composed mainly of CO₂

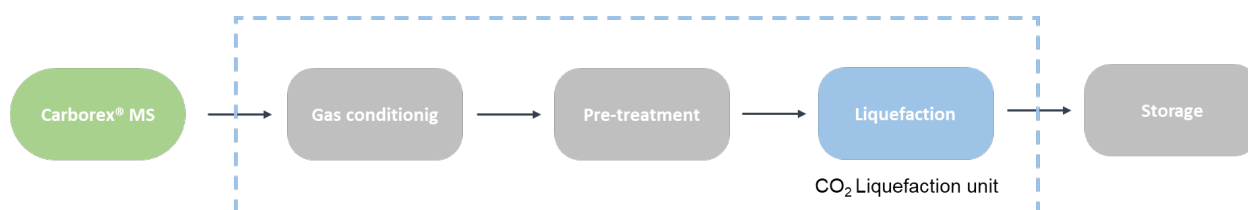


Figure 2.5 - Schematic representation of the off-gas stream from Carborex MS with liquefaction unit

3 Computer Application *Simulation of Gas Separation Modules in Real Time*

During this work, several multistage membrane separation systems were investigated for the 0.2 % methane slip, i.e., applying low temperatures before membrane stage 1 or stage 3, with and without reheating prior to the polishing step (stage 2). The conventional MS design system with 0.5 % slip and the low slip configuration by recycling increasing were considered as reference cases. This work aims to techno-economically evaluate systems to produce H-gas product quality with 0.2 % methane slip, considering a maximum CO₂ content of 2.5 % (v/v) in the product stream. Eventually, a business case was built up comparing the cases.

3.1 Software

The software used was *Simulation of gas separation modules in real time* version 3.5.1 beta for Sepuran membranes, provided by EVONIK Industries, as DMT owns a license for this program. This EVONIK simulator is used to model biogas upgrading processes through membrane separation and so, it fits into the chemical engineering workflow, delivering results in real time. Moreover, it is user-friendly and easy to understand and handle.

3.2 Simulation Setup

When the software is initialized, it shows the basic interface of the program. First, it is important to set up the settings, which are presented below:

Equations of state (EOS): For the modeling, the *Redlich-Kwong* equation of state (EOS) was chosen. The other options available are the *EOS as the ideal state* which does not consider the temperature loss due to expansion (Joule-Thomson effect), and the *EOS of Van der Waals* which is less accurate than EOS of *Redlich-Kwong*.

Viscosity: To approach reality, the viscosity was taken into account. This allowed for the pressure drop across the membrane to be considered.

Standard Conditions: Standard conditions were used, temperature and pressure of 0 °C and 1.01325 bar, respectively, when simulating.

After selecting the proper settings for the models, it was possible to open the simulator's interface, where the modeling took place. Different elements provided by the software were used in the simulation, in order to recreate a biogas upgrading plant through MS process:

A **Flow and pressure controller**, which was set as one single output (full flow sent to one single outlet), meaning that there was no flow backward. This unit presents the following options:

- pressure and temperature control (with dewpoint control): control valve followed by heat exchanger (HE) or compressor\blower followed by an HE.
- *Isobar* and temperature control (with dewpoint control): Acts only as a heat exchanger.
- *Isobar* and *isothermal*: Acts as a simple pipeline.

The pressure is set for upstream(s) but is located downstream(s), while the temperature is set for downstream(s). If the option *Isothermal* is chosen, the pressure is automatically established.

A **membrane** with four connection points, in which it was possible to connect the feed, retentate, permeate, and sweep gas inlet (not used). It exhibits the followed considerations:

- Number of membranes: the number of parallel modules per stage must be set. It is possible to define whether the modules work as *new* or with degradation either in separation capacity or selectivity. The number of membranes affects the separation capacity of the stage.
- Modeling precision: the *finite elements method* was used, by default. 64 elements were assumed for this work. For the same membrane's length, increasing the number of elements leads to more calculations per iteration, enhancing the accuracy of the results. This method was implemented by the software developer. The user did not have access to the mathematical equations behind it.
- Heat transfer between fibers: a standard value of $1 \text{ J}\cdot\text{K}^{-1}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ was predefined for the heat coefficient. This allowed the temperature to drop between upstream and downstream.

A **mix** to simulate the mixer of the streams. In this work, this mix was used to introduce the recycling streams, i.e., permeate flux from stage 2 and product stream from stage 3, both back to the inlet of the compressor unit.

At last, a **gas source unit** was placed before the compressor. The composition of the pre-upgraded gas (feed) was set in this element, as well as its respective flow rate. It took into consideration only the presence of CH_4 , CO_2 , N_2 , and H_2O content. Thus, it was assumed that all other compounds such as VOCs and H_2S (pollutants) were removed during the pre-treatment step after anaerobic digestion. The temperature of the inlet pre-upgraded gas was 25 °C.

Generally, the given flow rate ($F_{dry\ basis}$) and inlet conditions are in dry basis. Therefore, a conversion needs to be made for the wet conditions ($F_{wet\ basis}$), which is based on the equation (3.1) below:

$$F_{wet\ basis} = \frac{F_{dry\ basis}}{(1 - y_{H_2O} \%)} \quad (3.1)$$

Due to the presence of water content ($y_{H_2O} \%$), the biogas flow rate increases. However, the composition (y_i) changes and the content of the other compounds will decrease, given by

$$y_{i,wet\ basis} \% = y_{i,dry\ basis} \times (1 - y_{H_2O} \%) \quad (3.2)$$

To simulate the gas separation process, the main inputs to have in consideration are the following ones:

- Raw biogas inlet flow rate on a wet basis and its composition.
- The inlet temperature of each stage.
- The retentate/feed pressure on each stage.
- The number of membranes and if they work as *new* membranes or with degradation.

3.3 Mathematical modelling

In this project, the simulations were performed considering parallel membrane modules with a crossflow separation mechanism. Each membrane module exhibits a countercurrent configuration. In other words, the flow direction of the gas streams occurs in parallel and in the opposite direction on both sides of the membrane. The overall process is a 3-stage membrane separation system, accounting for two recycle streams, i.e., from the permeate side of stage 2 and retentate of stage 3. Besides that, the transport inside the modules follows the plug flow pattern.

Regarding the global system, taking into account **Figure 2.3**, the material balance is given by equation (3.3), knowing that $F_{f,S1}$ is the compressed biogas, i.e., raw biogas stream ($F_{f,raw\ biogas}$) mixed with the recycle ones, $F_{p,S2}$ and $F_{r,S3}$.

$$\begin{aligned} F_{f,S1} &= F_{r,S1} + F_{p,S1} \\ F_{f,S1} &= (F_{r,S2} + F_{p,S2}) + (F_{r,S3} + F_{p,S3}) \\ F_{f,S1} &= F_{f,raw\ biogas} + F_{p,S2} + F_{r,S3} \\ F_{f,raw\ biogas} \cdot y_{CH_4,f} &= F_{r,S2} \cdot y_{CH_4,r2} + F_{p,S3} \cdot y_{CH_4,p3} \end{aligned} \quad (3.3)$$

The fraction of methane for each stream is given by $y_{CH_4,j}$. The global mass balance was verified by the results after the modeling. Therefore, knowing $F_{f,S1}$ and $F_{f,raw\ biogas}$, it is possible to determine the global recycle, in dry basis ratios.

$$Recycle \% = \frac{F_{f,S1} - F_{f,raw\ biogas}}{F_{f,raw\ biogas}} \times 100 \quad (3.4)$$

This parameter is a key factor for the system's analysis and techno-economic evaluation. Knowing the recycling in each case, it is possible to calculate the power consumption associated with the compressor capacity and the overall system. Moreover, it is required to obtain the defined product quality respecting the maximum methane slip limit (0.2 %) in the exhaust gas.

3.4 Methodology

The modelling part can be divided into two main phases: the parametric study of the operating conditions and the sensitivity study of several configurations.

3.4.1 Parametric study of the operating conditions

In this phase, the sensible range of cooling temperatures was acquired. The operating pressure was fixed at 16.5 bara at the inlet of the systems, following an average operating pressure in the *Carborex® MS*. The necessary steps to remediate the product quality and methane slip when changing the conditions (degradation in the second stage) were investigated. It allowed a better understanding of the system's behavior to changes. Besides that, the product quality was not strictly limited. **Figure 3.1** shows the performed tasks.

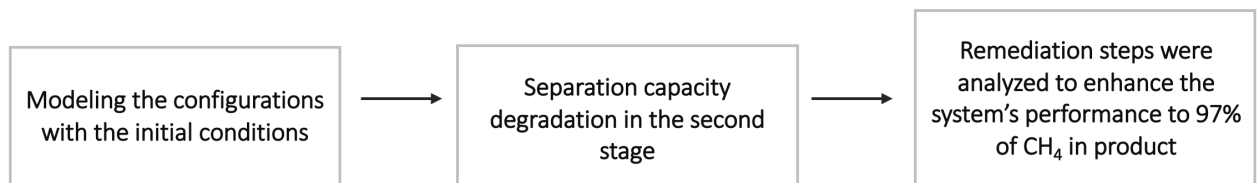


Figure 3.1 - Methodology for the parametric study of the operating conditions

To add extra safety on the system performance (separation capacity), degradation effects were considered in the membranes of stage 2. This action aims to simulate fouling and/or aging effects after a certain operational period, that particularly affect the polishing step, leading to a decrease in the system's performance. Thus, it was considered 10 % degradation in separation capacity (SC) in stage 2 and the results were compared with the operation of *new* membranes. To increase the system's performance, remediation measures had to be taken. Recycling was also investigated, as it is a relevant parameter.

3.4.2 Sensitivity study of several configurations for H-gas grid injection

In this second part of modeling, two different approaches were developed for the analysis and sizing of S1 cooling and S3 cooling proposals, to reach the H-gas quality target (maximum 2.5 % of CO₂ and 0.2 % methane slip):

1. Modeling with pressure fixed at 16.5 bara at the system's inlet for all cases, and heat exchanger on stage 2 set with a constant temperature value of 30 °C, for *new* membranes. The content of CO₂ was not strictly regulated.
2. Modeling with fixed 2.5 % of CO₂ at product stream, for all cases. The pressure at the system's inlet and the temperature of the heat exchanger were changed.

DMT already has standard configurations that were utilized as reference cases to analyze the outcomes of the work. The models assumed specific inlet conditions, i.e., flow rate and compositions, that were

constant for all systems. The membrane's number per stage (for all configurations) was kept the same, as on the reference cases, and constant, to fairly compare the systems.

Finally, to build up the business case, the selected systems from the modeling with fixed 2.5 % CO₂ were economic evaluated and benchmarked with the standard cases from DMT. These configurations were built based on the first approach results.

Figure 3.2 shows the steps that were carried out when modeling. The last step considered the system's turndown to half of the capacity. This last step was only taken for the configurations with fixed 2.5 % of CO₂, to observe if the systems could achieve the required performance, while operating with low pressure values at system's inlet (between 10.5 and 12.5 bara).

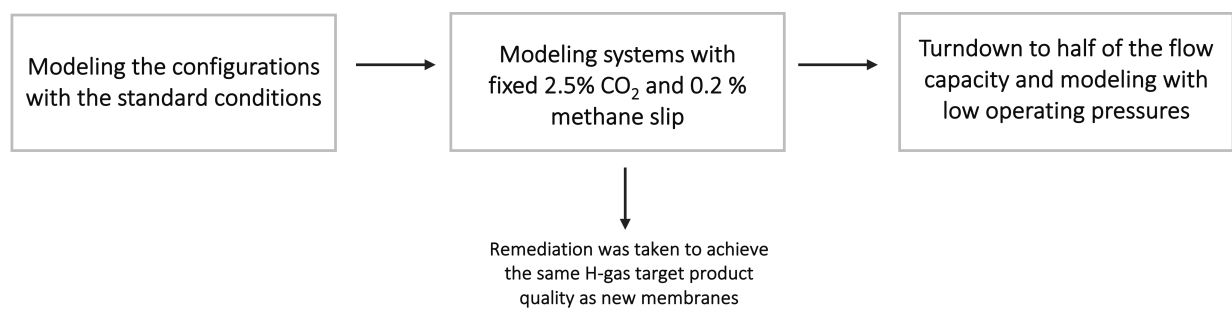


Figure 3.2 - Methodology for the sensitivity analysis of the operational conditions

Alongside these tasks, in the first approach, for the cooling stage 3 with re-heating step proposal, the inlet temperature of the feed biogas was analyzed between 20 °C and 25 °C. This study was made to observe which condition would result in lower recycling.

3.5 Reference cases

Previous works were developed by DMT, namely the standard MS configuration for 0.5 % methane slip and the low slip configuration by recycling increase and with a HE on stage 2 (see **Figure 3.3**). These two configurations are the baselines for the discussion of the results. The inlet conditions and outputs (including the mass balance) obtained from the simulator are reported in **Appendix B**.

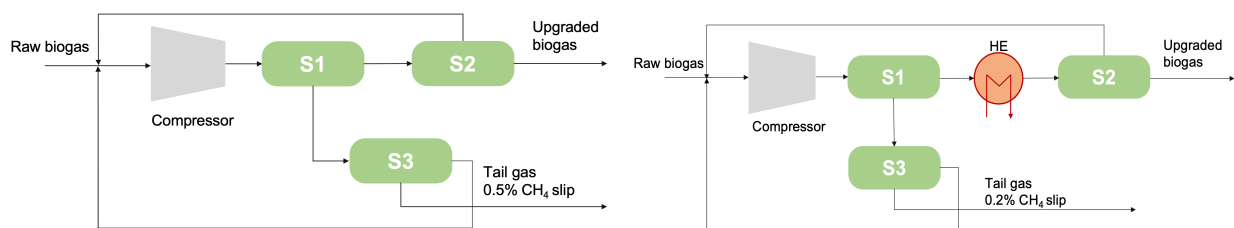


Figure 3.3 - Standard MS configuration with 0.5% methane slip a) and 0.2 % slip case at high recycle b)

Both systems were assembled to treat $1200 \text{ Nm}^3 \cdot \text{h}^{-1}$ (full capacity) dry basis. The feedstock used in the simulations is from an anaerobic digestion plant. **Table 2** shows the inlet biogas composition, considering dry and wet basis. It was assumed that pollutants such as H_2S , VOCs, and other trace compounds typically present in the raw biogas were removed in the pre-treatment step. In it was not needed to place a dryer since there is no cooling step in these systems. Different inlet compositions were not studied in this project, but it would be interesting, depending on the customer's needs.

Table 2 - Raw biogas composition considering the dry and wet basis

	Dry basis (%)	Wet basis (%)
CH₄	55.00	54.95
CO₂	44.50	44.46
N₂	0.40	0.40
O₂	0.10	0.10
H₂O	0.00	0.10

In the *Carborex® MS*, the methane slip (see equation 1) and the product quality are controlled by the pressure regulated loops. According to these values, the set point of the pressure changes to meet the targeted value. This regulation was reflected in the models by manually adjusting the backpressures of stage 3 and stage 2 to achieve the desired values. Therefore, the working pressure on stage 1 was kept in a range between [14-16.5 bara] (high-pressure values) for full flow capacity and in a range of [2-4 bara] for the backpressure on S3.

3.6 Proposed low slip configurations

The proposal configurations were divided into four main cases for the modeling of $1200 \text{ Nm}^3 \cdot \text{h}^{-1}$ dry basis flow rate, composed by the volume fraction presented in Table 2 :

- *Case 1*: Stage 1 cooling with intermediate re-heating before stage 2.
- *Case 2*: Stage 1 cooling without re-heating step.
- *Case 3*: Stage 3 cooling with re-heating step before stage 2.
- *Case 4*: Stage 3 cooling without re-heating step.

Figure 3.4 shows a schematic representation of Case 1. For Case 2, the heat exchanger is not considered.

Figure 3.5 exhibits a schematic representation of Case 3. In Case 4, the re-heating step is not done.

Regarding the parametric study, each case considered a specific number of *new* membranes (between 23 and 26 membranes). Besides that, for the sensitivity study, all cases were built with the same and constant number, i.e., 24 modules, to fairly compare the systems (same surface area for gas separation).

As it is shown in both figures, a dryer is placed after the compressor step. As the pre-treated gas assumed 0.1 % of water content (v/v), the feed stream must be dried to remove water and avoid any condensation in the cooling step. This is regulated by adjusting the dew point within the program, lower enough. If this

action had been neglected, the water flow inside the modules could lead to corrosion and damage the membrane layer and the system.

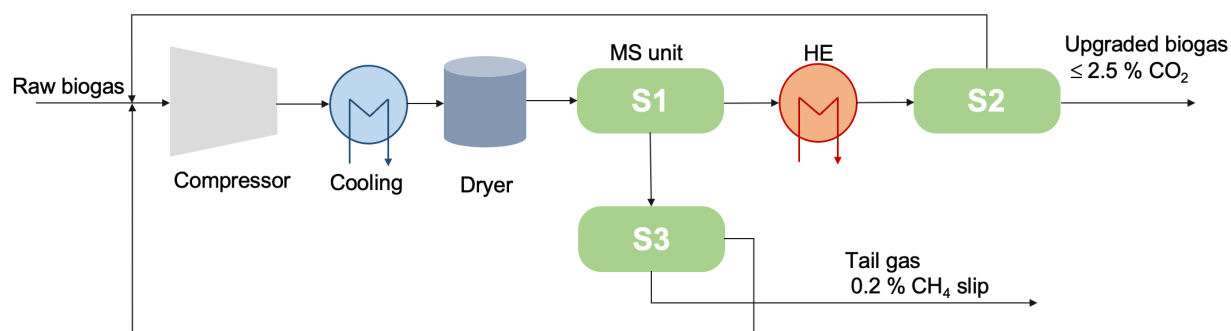


Figure 3.4 - Scheme of low slip case through stage 1 cooling with intermediate re-heating

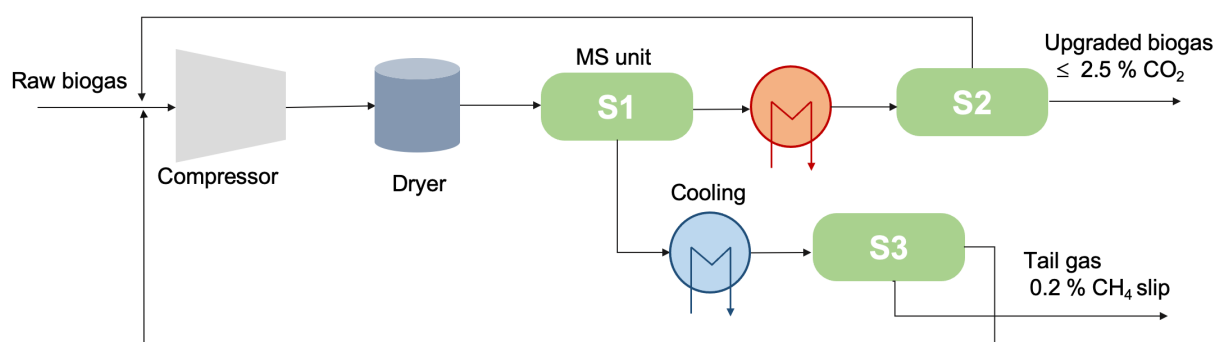


Figure 3.5 - Scheme of low slip case through stage 3 cooling with intermediate re-heating

Thus, in the system's inlet the dew point was set to minus (–) 25 °C to comply with gas phase. For the other stages with temperature controller, the dew point was defined as being the operating temperature minus 15 °C, to prevent condensation of the pair gas compounds

Moreover, the main aspects firstly considered for the simulations of the described cases are summarized in **Table 3**. Due to optimization steps, to achieve the guidelines, some parameters might change.

Table 3 - Initial operating conditions

Initial modeling conditions				
Parameters	Case 1	Case 2	Case 3	Case 4
Membrane counting	26	25	23	23
Pressure system inlet (bara)	16.5			
Pressure S3 (bara)	Automatically regulated			
Temperature inlet S1 (°C)	[1–10]	[1–10]	25	25
Temperature inlet S2 (°C)	30	Isothermal	30	Isothermal
Temperature inlet S3 (°C)	Isothermal	Isothermal	[1–10]	[1–10]

4 Results and discussion

In this chapter, the main part of the performed work is presented and discussed. This section is divided into mainly two sub-sections: Parametric study of different operating conditions to understand the system's behavior; and sensitivity study on several configurations based on the defined ranges, for a specific target of biomethane quality (H-gas grid injection – maximum of 2.5 % of CO₂) and 0.2 % slip. All the results presented were taken from the *Evonik simulator* in steady state.

4.1 Parametric study

4.1.1 Operating inlet temperature of cooling stages

Initially, the four cooling proposals were modeled for different inlet temperatures of the cooling (stage 1, S1, and stage 3, S3) between 1 °C and 10 °C. For each case, the number of membranes was chosen according to the temperature of 5 °C to obtain 0.2 % methane slip with backpressure in the third stage lower than 4 bara. **Figure 4.1** shows the CH₄ volume content in the product stream for the different cases. The cooling temperature range was studied, and the system's behavior was acquired.

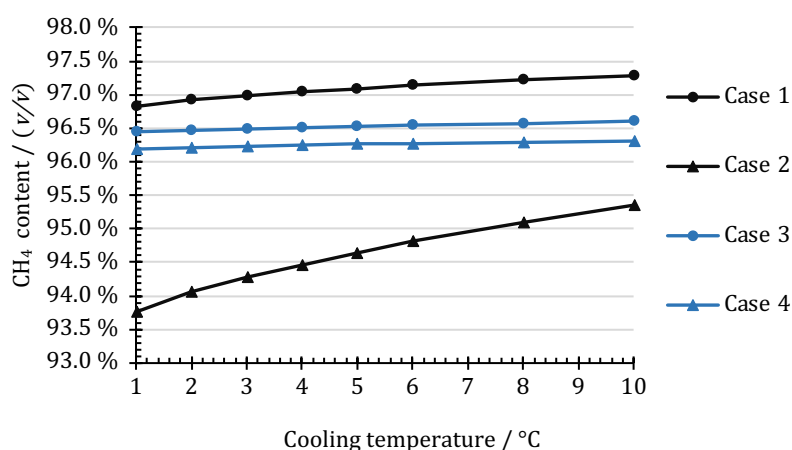


Figure 4.1 - Product quality profile for different cases

First, it was noticed that Case 1 and Case 3 achieve higher product quality, compared with Case 2 and Case 4, due to the intermediate heat exchanger placed before stage 2 (S2). The permeability of the pair gas CO₂/CH₄ is enhanced with the re-heating step before S2, leading to a methane-rich stream at the retentate side and higher recycling. Case 1 and Case 3 have shown an average of 2.41 % and 0.29 % more methane in the product stream than the cases without a heat exchanger, respectively.

In addition, the product quality was enhanced by increasing the cooling temperatures, but first stage cooling was more affected than the third stage proposal. While permeance improves with temperature increase, selectivity is negatively affected. However, due to the trade-off between permeability and selectivity, the latter does not change as significantly as the permeability.

Thus, for Case 1 and Case 2, the bulk separation enhances, leading to higher recycling and better product quality. On the other hand, for Cases 3 and 4, increasing the temperature in S3 leads to more methane on the retentate side (returning to S1), which results in a slight increase in CH₄ content in the product stream.

Figure 4.2 shows recycling rate (a) and backpressure achieved in stage 3 (b) for the different cooling temperatures.

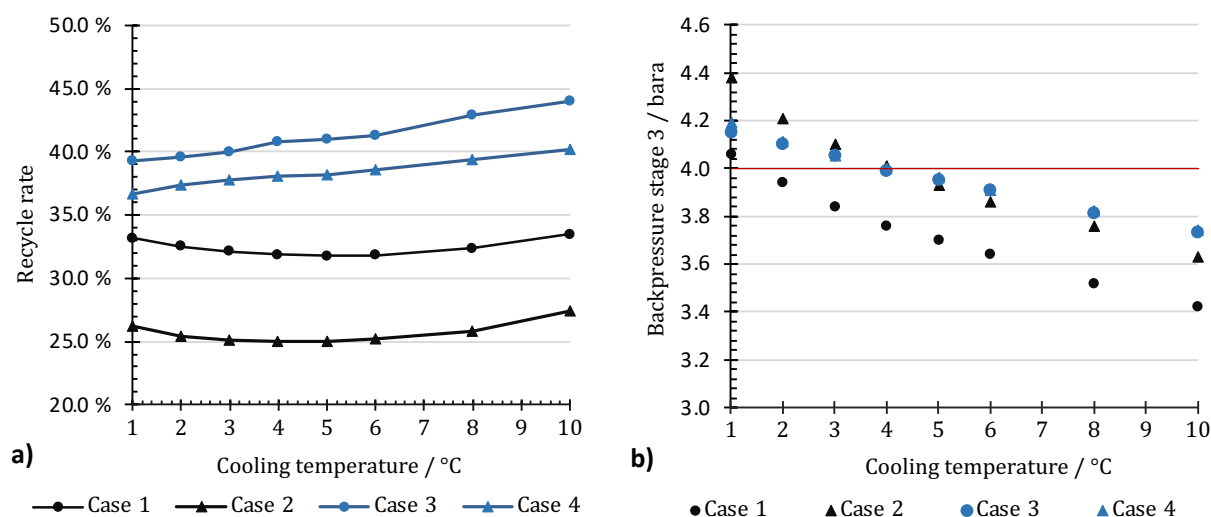


Figure 4.2 - Recycling a) and backpressure in stage 3 b) profile for different cooling temperatures

As seen above, S1 cooling proposal systems exhibited lower recycling than S3 cooling ones (see **Figure 4.2,a**). In addition, Case 1 and Case 3 present a relative difference of 25.6 % and 7.9 % more recycling than Case 2 and Case 4, respectively, as expected. Lower recycling is preferable because it will directly impact the power consumption of the compressor and so the system's operational costs.

At low temperatures (from 10 °C to 1 °C), a reduction of methane slip to values below 0.2 % was verified. This led to adjusting the third stage backpressure to increase the permeate flow and stabilize the slip (as shown in **Figure 4.2,b**). Between 1 °C and 4 °C, most cases exceeded the established limit of 4 bara, defined by DMT, to reduce the possibility of unsafe operation in reality.

In the cases where this situation happens, one more membrane should be added in order to be able to operate below this maximum. Increasing the number of membranes, increases the system surface area for separation, and the driving force is reduced. Between 5 °C and 10 °C, the backpressure limit value was respected for all cases. Also, using a chiller below 5 °C could damage the system since some compounds can be condensed due to Joule Thompson effect and act as a liquid plasticizer that would lead to a separation capacity reduction. Thus, the operating temperature was defined between 5 °C to 10 °C.

4.1.2 Degraded membranes and remediation mechanisms

When operating with membranes, quality issues might occur in the case of membrane degradation in the second stage (e.g., due to fouling/aging). It is essential to understand this event to add extra safety to the

system's performance. With the reduction of separation capacity performance, there is less CO₂ on the permeate side, which goes with the product (worse product quality). 10 % degradation on separation capacity in stage 2 was applied since it is the polishing step of biomethane. When degrading the membrane, remediations steps, i.e., re-heating temperature (Case 1 and Case 3) and membrane number regulation (Case 2 and Case 4) were performed to enhance the product quality to 97 % of methane content.

Figure 4.3 shows the obtained results for the modeling of **Case 1**. As it is possible to see, the product quality a) was higher than 97 % for the set of new membranes and decreased by 0.47 % with 10 % degradation in the second stage. The recycling b) also decreased by 4.4 %.

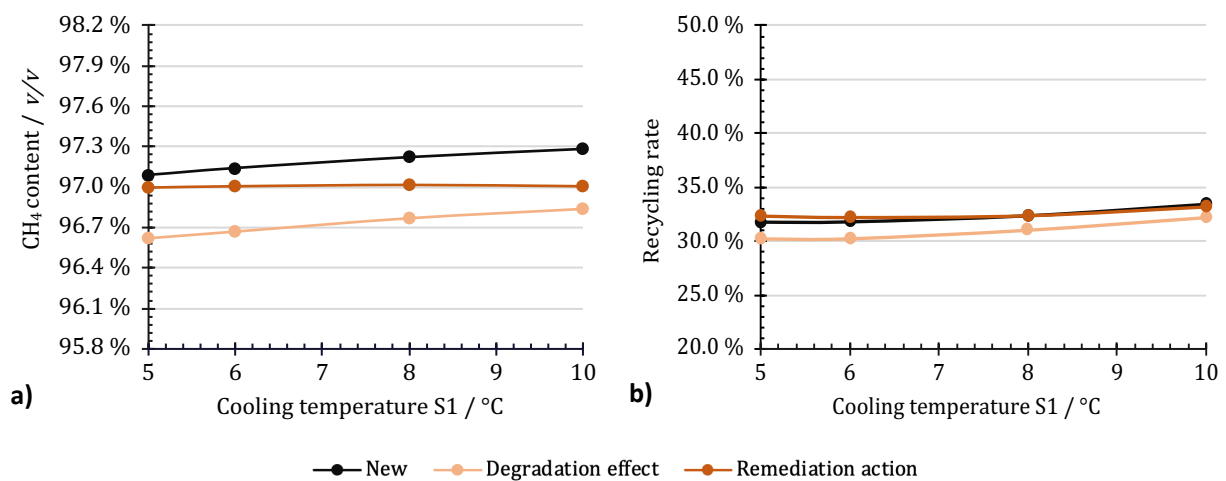


Figure 4.3 - Case 1: Modeling with 10 % degradation on SC in S2: a) product quality; b) recycling rate

For the remediation, the re-heating temperature (before S2) was regulated (initially set at 30 °C) to enhance the system's performance to a fixed value 97.0 % of methane (see Table 4). Since the increase of the first stage cooling temperature led to higher CH₄ content, the amount of energy needed to enhance the quality became lower.

Table 4 – Case 1: Temperature regulation of re-heating step for different cooling temperatures

Cooling temperature first stage / °C	5	6	8	10
Re-heating temperature second stage / °C	37	36	35	33

After remediation, the recycle b) increased to the same rates as initially (with new membranes), with an average of 0.54 % deviation. For Case 1, the backpressure in S3 did not change, as the slip was not affected neither by degradation nor by temperature regulation in stage 2. Thus, it was acknowledged that placing a heat exchanger before stage 2 promotes the decoupling between methane slip and product quality, being easier to regulate the system.

Figure 4.4 shows the results obtained for **Case 2**. In this case, after simulating the aging/fouling effect that leads to the degradation, the system decreased 0.59 % and 4.1 % in product quality a) and recycling rate b), respectively. The system continued to show the same pattern with the increase of the inlet temperature in stage 1. Since no heat exchanger was placed, the membrane's number regulation accomplished the remediation of the system set, initially, with 25 membranes (see **Table 5**).

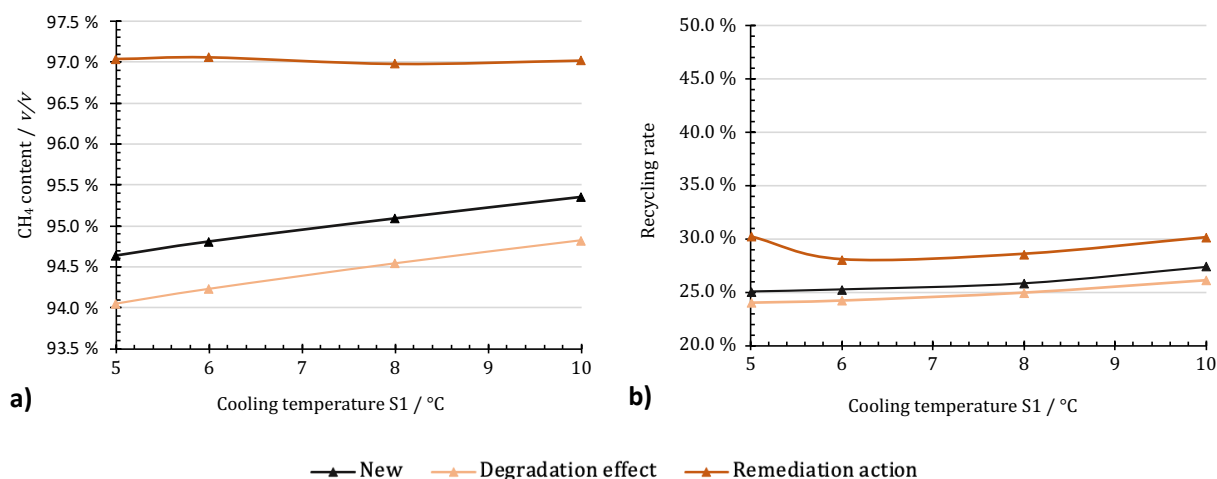


Figure 4.4- Case 2: Modeling with 10 % degradation on SC in S2: a) product quality; b) recycling rate %

The methodology was defined during the modeling part:

- The first step passed through regulating the membrane number in the second stage. (S2) The increase promotes higher permeance flux through the layer, which leads to a rise in product quality and recycling. Keeping constant S1 and S3 configuration, it is obtained more permeance flux in stage 1, with lower CH₄ content, which results in lower methane slip.
- After, the third stage (S3) was regulated. Adding more membranes leads to higher methane slip. It does not significantly affect the product quality (a slight increase was verified).
- At last, the regulation passed through to the first stage (S1). Extra membranes result in higher methane slip (increased permeance flux in S1) and better product quality.

The backpressure in stage 3 was regulated among the allowed ranges (4 bara limit) to respect the 0.2 % of slip. In this case for *new* membranes, the backpressure was set between 3.93 – 3.63 bara. With the remediation step, the backpressure changed from 3.81 to 3.44 bara.

Table 5 – Case 2: total number of membranes after regulation for different cooling temperatures

Cooling temperature first stage / °C	5	6	8	10
Final membrane number	32	32	31	30

As a result of this remediation technique, the CH₄ content, a), was approximately 97.0 % (an average absolute difference of 0.04 % was verified for the points). The relative difference in recycling, b) between

new membranes and remediated ones was 10.7 %. Due to the system's sensitivity, the first point (5 °C) is outside of the expected pattern with a relative difference of 20.7 % for recycling. Thus, it was not considered.

Comparing both **Case 1** and **Case 2**, the regulation through temperature has shown more accuracy due to the decoupling between the polishing stage and methane slip. In Case 1 was relatively easy to meet the targeted value of 97.0 % while keeping methane slip constant. Despite that, the remediated system exhibited more 12.7 % of recycling when compared with Case 2 (in absolute values it means 3.6 % deviation).

The same methodology was performed for the third stage cooling proposals. **Figure 4.5** shows the product quality a) and recycling rate b) profile for different cooling temperatures for **Case 3**. After the degradation step, both a) and b) decreased by 0.53 % and 5.1 % compared with *new* membranes, respectively.

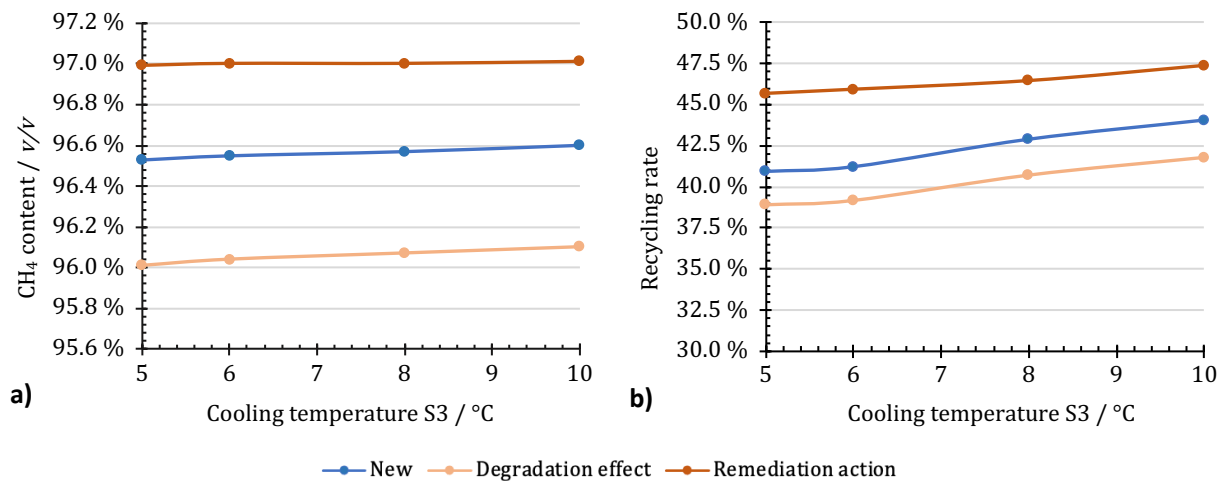


Figure 4.5 - Case 3: Modeling with 10 % degradation on SC in S2: a) product quality; b) recycling rate

The re-heating temperature was changed from 30 °C (initially set) up to the values shown in **Table 6**. Thus, the system's performance was enhanced for the targeted product quality value with no variation. In addition, as previously seen in Case 1, the backpressure in stage 3 did not change. It means that the aging/fouling in stage 2 does not significantly impact the third stage performance (methane slip) when a heat exchanger is placed (decouple function), being advantageous.

Table 6 - Case 3: Temperature regulation of re-heating step for different cooling temperatures

Cooling temperature first stage / °C	5	6	8	10
Re-heating temperature second stage / °C	48	48	47	47

Due to the lower methane content in Case 3, the temperature required for the remediation in this system was relatively higher compared with the remediation made in Case 1. Extra heat to uplift the quality was

needed, leading to a higher recycling rate from the second stage. Therefore, after applying the remedial steps in Case 3, the recycling increased by 9.7 % compared with new membranes.

The last system modeled was **Case 4**. Product profile a) and recycle rate b) are shown in **Figure 4.6**. In a) and b) a reduction of 0.55 % and 4.92 %, respectively, was verified, when applied the degradation in the second stage. The regulation methodology was the same as in Case 2.

Although, in the present case, it was only necessary to set one configuration of membranes since the system has shown more stability alongside the cooling temperature variation. Therefore, between 5 °C and 10 °C, the total number of membranes was enhanced from 23 to 26 membranes.

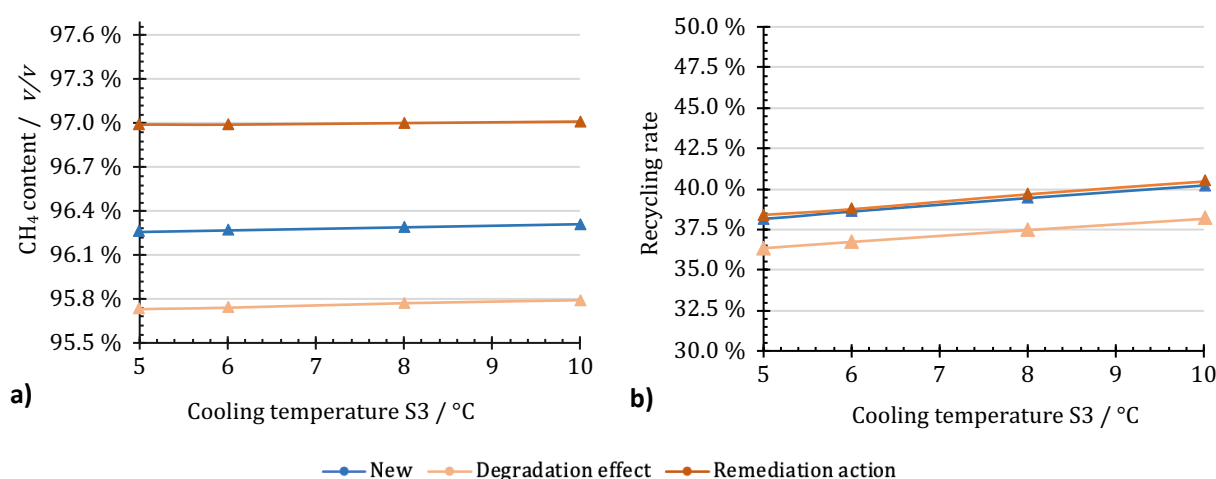


Figure 4.6 - Case 4: Modeling with 10 % degradation on SC in S2: a) product quality; b) recycling rate %

When improving the product quality of the degraded systems (0.01 % of absolute difference from 97.0 %), the recycling slightly increased, deviating 0.6 % from *new* membranes. The remediation through membranes was effective for Case 4, and the system did not face a significant change in the recycle.

In this case for *new* membranes, the backpressure was set between 3.96 – 3.74 bara. With the remediation step, the backpressure changed from 3.65 to 3.45 bara.

Generalizing, for the four cases studied, the remediated systems have shown the same trends as new membranes and degraded ones regarding the recycling rate alongside cooling temperatures. Also, it is verified that the system with the cooling step before the third stage is less prone to changes. Besides that, for all cases, the 0.2 % methane slip was regulated by the backpressure in S3 between the acceptable range. Also, for Case 1 and Case 3, the methane slip and backpressure were not affected by degradation effects on S2.

Summarizing this study, whether the systems exhibit signals of aging or fouling (which leads to a decrease in their performance), it is preferable to regulate through the re-heating temperature (heat exchanger before stage 2). It is easier to set new values of temperature than proceed with assembling extra membranes on site. In addition, remediating through membranes means an increase in the total Capex of

the system, which is a downside. Nevertheless, with temperature regulation the system met the product quality target with more accuracy. Due to this reason, only Case 1 and Case 3 should be considered for further analysis and discussions to develop a product with H-gas quality (fixed 2.5 % of CO₂) and 0.2 % methane slip.

4.2 Sensitivity study of several configurations

In this section, the configurations (Cases 1 and 3) were developed to obtain a final product with a maximum of 2.5 % CO₂ content and 0.2 % methane slip from the system. The systems were built with the same number of membranes (24) to fairly compare the results since the membrane counting is a parameter that affects the separation capacity.

The main goal is to identify which input specifications for each studied configuration result in the requested H-gas product (2.5 % CO₂ and 0.2 % methane slip) with the lower recycling

4.2.1 Case 1: Modeling with standard conditions

For the first approach, the 1st and 2nd reference cases (2.5 % and 2.0 % of CO₂, respectively) were used as guidelines. The standard pressure in stage 1 and temperature before stage 2 was set at 16.5 bara and 30.0 °C, respectively. The product quality and recycle values were acquired for this set of parameters.

According to the results of **Figure 4.7 a)**, the CO₂ content (v/v) reduced as the cooling temperatures in stage 1 increased. With *new* membranes, the product was reduced from 2.54 % (v/v) down to 2.22 % (v/v), approximately. In addition, the recycling (b) for new membranes was comprised between 36.3 % and 35.5 %, being below the 43.8 % of the 2nd reference case (maximum limit) and upper than the standard case (0.5 % of methane slip) with 29.3 % of recycling.

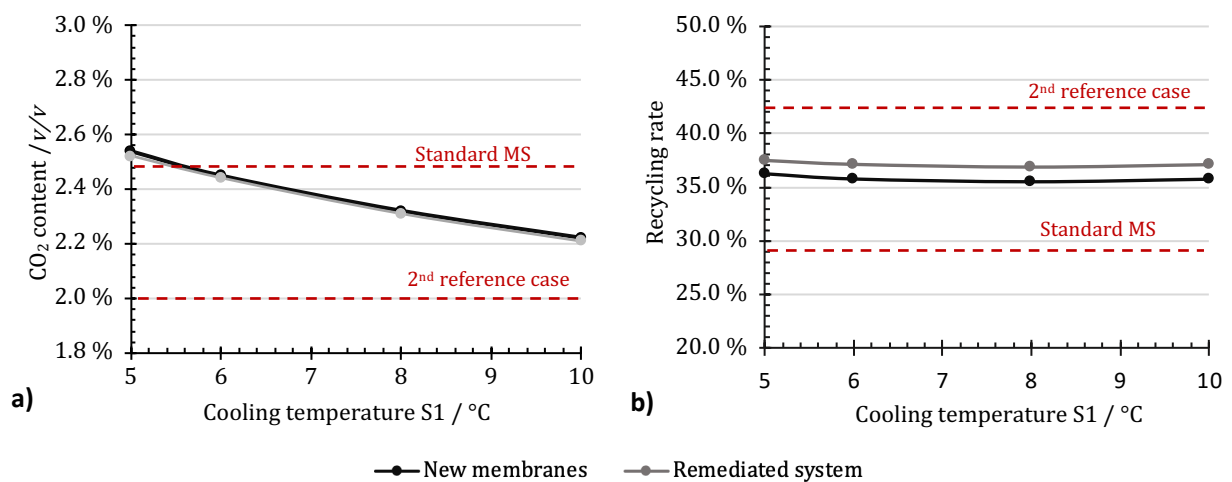


Figure 4.7 – Case 1: product quality a) and recycling b) according to cooling temperatures

Therefore, the recycling exhibited the expected trend (previously observed in the parametric study), i.e., without a significant variation alongside the cooling temperature.

To enhance the performance of the degraded polishing step (S2) and achieve the product quality's original values, the temperature was set at 39 °C. An absolute difference in quality of 0.01 % between the *new* and the remediated membranes was calculated. However, an increase of 3.68 % for the recycling was verified because of the temperature increase in the re-heating step.

Besides that, the methane slip was kept constant due to stage 3 backpressure regulation (the pressure was reduced to keep 0.2 % slip constant), as seen in **Figure 4.8**. For this case, the backpressure exceeded the boundary set for the parametric study, i.e., 4 bara, due to the chosen number of membranes. If the system had been developing with 26 membranes, the pressure would have been reduced (**Appendix C**).

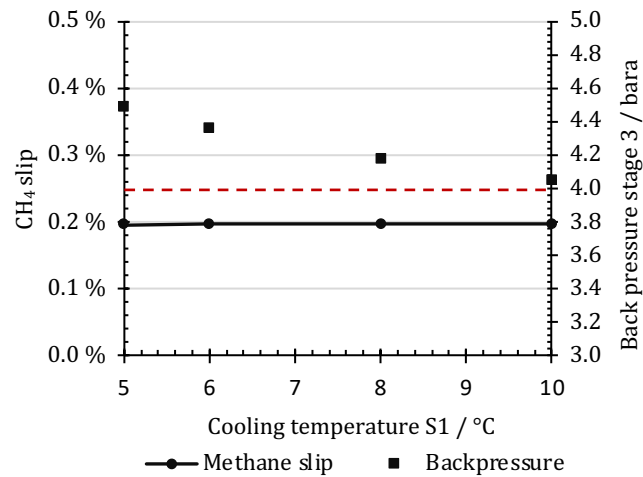


Figure 4.8 – Case1: Methane slip and backpressure in stage 3 for different cooling temperatures in S1

4.2.2 Case 1: CO₂ content fixed at 2.5 % in product stream

Since the CO₂ content was close to the requested value for the previous analysis, the pressure in stage 1 was kept constant (16.5 bara). It was only necessary to change the re-heating temperature in S2 (**Figure 4.9**). The 1st and 3rd reference cases are the guidelines for this modeling.

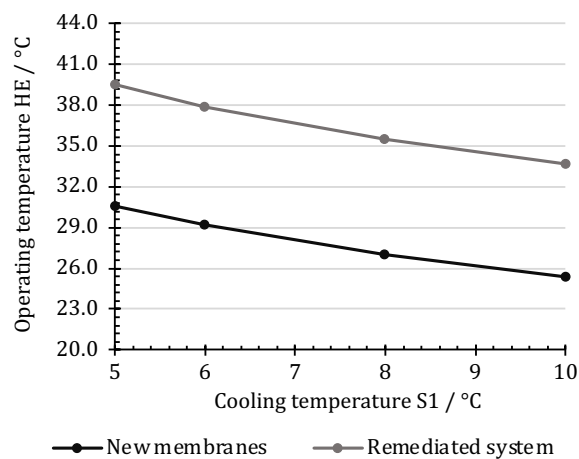


Figure 4.9 – Re-heating temperature regulation on S2 according to S1 cooling temperatures

As seen above, the re-heating temperature step varied from 30.6 °C down to 25.4 °C when operating from 5 °C to 10 °C, respectively. With the increase of first stage cooling temperature, the permeance of CO₂

followed the same trend. Therefore, it was obtained purer biomethane. To stabilize the CO₂ content at 2.5 %, lower re-heating was necessary for the second stage.

Comparing the system with new membranes and 10 % degradation, the re-heating temperature increased by circa 8.6 °C for all simulated points. With that, the system again achieved 2.50 % of CO₂, as shown in **Figure 4.10**. The CH₄ profile was not constant due to trace components, like N₂ and O₂.

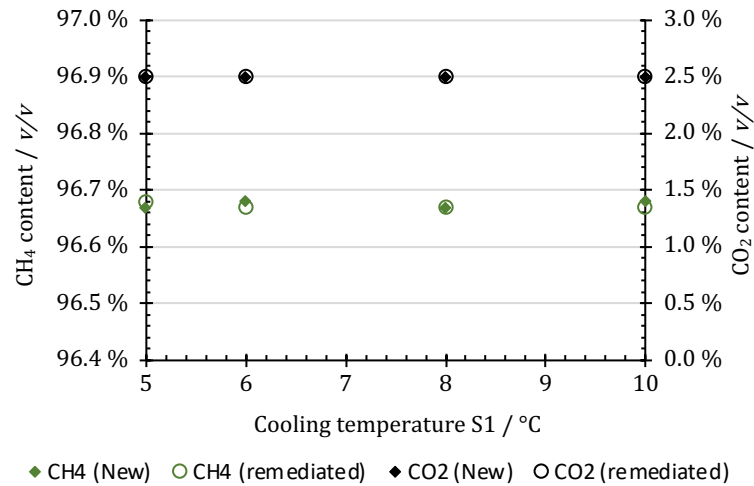


Figure 4.10 - CH₄ and CO₂ content in product stream for new and remediated membranes for different cooling temperatures in S1

Figure 4.11 shows the obtained recycling. As it is possible to see, the system's global recycling exhibited a decreasing trend due to the changes in the operating temperature of the re-heating step (it was varied from 36.51 % to 34.29 %).

The decrease in temperature led to less permeate flux through stage 2, and thus, lower recycling going back to the system's inlet. Also, accompanied by an increase of absolute 8.6 °C, the remediated system presented a deviation of 3.68 % more recycling than new membranes.

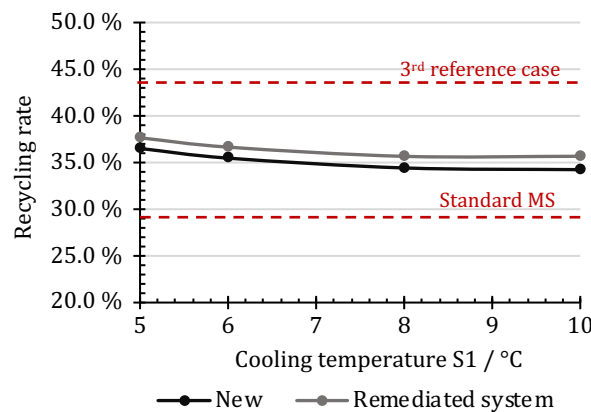


Figure 4.11 - Recycling rate for different inlet temperatures, considering product with 2.5 % CO₂ (v/v)

Thus, acknowledging that low recycling leads to lower power consumption, the optimum configuration for Case 1 is the one in which the cooling temperature of S1 is set at 10 °C, presenting 34.3 % of the recycling rate, with a re-heating temperature set at 25.4 °C.

In **Table 7**, rounded by red squares, are the inputs used by the work's author regarding the operating conditions. In orange, the volume composition of the product quality in stage 2 (retentate) and the volume composition of the tail gas at the permeate side of S3. The backpressure in S3 was not changed.

Considering a gas source consisting of 54.94 % of methane ($659.99 \text{ Nm}^3 \cdot \text{h}^{-1}$), was obtained $518.84 \text{ Nm}^3 \cdot \text{h}^{-1}$ at the permeate side of stage 3 of tail gas, within 0.25 % of methane (v/v). It corresponds to $1.30 \text{ Nm}^3 \cdot \text{h}^{-1}$ of CH_4 in the off-gas stream. Thus, the ratio between the methane in the tail gas and the methane in the gas source is 0.20 %, which is the system's methane slip.

Table 7 - Case 1: Optimum configuration for 2.50% of CO_2 and 0.20 % methane slip for new membranes

description	Gas source	Stage 1 Sepuran Green Cartridge 100x1200 01: SC 3500, S=50, NEW			Stage 2 Sepuran Green Cartridge 100x1200 01: SC 3500, S=50, NEW			Stage 3 Sepuran Green Cartridge 100x1200 01: SC 3500, S=50, NEW		
		Feed	Retentate	Permeate	Feed	Retentate	Permeate	Feed	Retentate	Permeate
port	Raw gas									
press [bar]	16.50	16.50	16.46	4.09	16.46	16.43	1.05	4.09	4.04	1.05
flow [Nm^3/h]	1201.20	1613.72	1031.04	582.68	1031.04	681.30	349.74	582.68	63.90	518.78
Temp [°C]	25.00	10.00	3.70	6.00	25.40	20.30	21.50	6.00	-4.60	4.40
DewP [°C]	14.60	-25.00	-44.50	-31.10	-44.50	-96.20	-59.90	-31.10	-81.20	-44.10
CH ₄	54.94%	47.04%	72.01%	5.01%	72.01%	96.67%	21.06%	5.01%	35.19%	0.25%
CO ₂	44.46%	52.41%	27.25%	94.78%	27.25%	2.50%	78.36%	94.78%	63.76%	99.66%
N ₂	0.40%	0.37%	0.55%	0.06%	0.55%	0.70%	0.25%	0.06%	0.43%	0.01%
O ₂	0.10%	0.17%	0.19%	0.14%	0.19%	0.13%	0.33%	0.14%	0.62%	0.06%
H ₂ O	0.10%	0.01%	0.00%	0.01%	0.00%	0.00%	0.00%	0.01%	0.00%	0.02%

4.2.3 Case 3: Modeling with standard conditions

Firstly, a study of the inlet temperature in stage 1, between 25 °C (A) and 20 °C (B), was made. The pressure in stage 1 and temperature before stage 2 was set at 16.5 bara and 30.0 °C, respectively. The system also considered new membranes and 10 % degradation in stage 2 with remedial step.

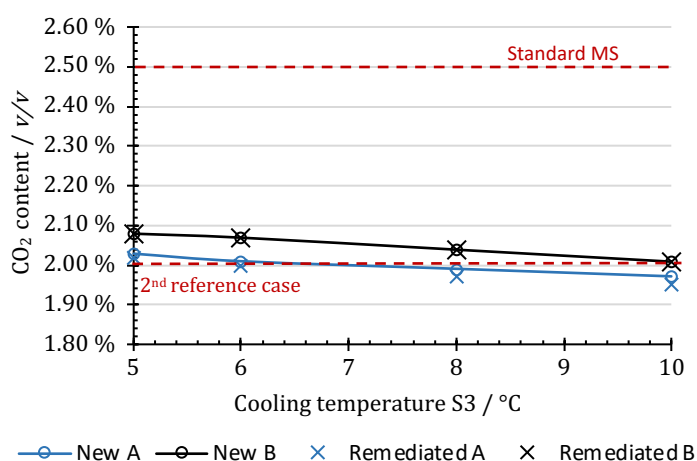


Figure 4.12 – Product quality comparison between A and B for different cooling temperatures in S3

As seen in **Figure 4.12**, both A and B exhibit lower carbon dioxide than 2.50 % for the established conditions, close to 2.0 %. Also, with 20 °C, the content is enhanced by 2.50 % compared to the 25 °C, as more CO₂ goes to S1 downside (retentate). For the degraded cases, stage 2 temperature was increased to 39 °C for both A and B simulations. With that, the performance was fixed into the original ranges. However, a slight difference in system A was verified between the new and the old membranes, but insignificant. System B did not exhibit any difference.

The simulation performed at 25 °C exceeds the established indicative recycling limit (43.8 %, 2nd reference), from 6° C to 10 °C, which is not advised (see **Figure 4.13**). With 20 °C, it was possible to reduce the recycling by 8.64 % (relative difference). Thus, the system worked below the limit for all the simulated points with new and degraded membranes.

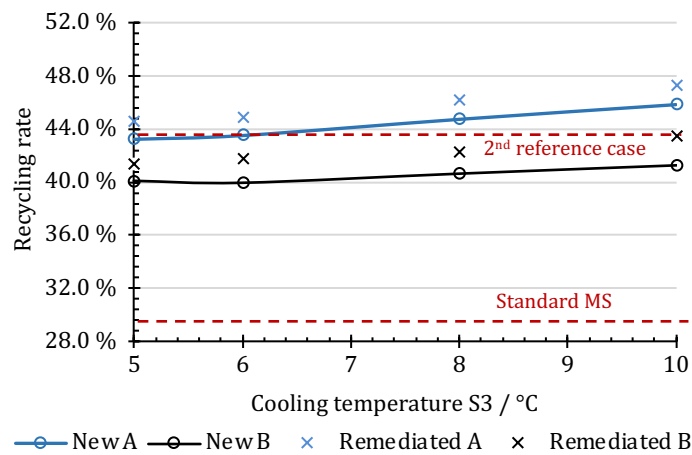


Figure 4.13 – Recycling rate comparison between A and B for different cooling temperatures

Besides that, recycling increased by 3.1 % and 4.2 % for A and B when remediation was taken, respectively. Therefore, both systems would operate with the same compressor since an extra 8 % safety factor is accounted for when sizing the compressor. The backpressure comprised between 4.00 and 3.75 bara and did not change when degradation was applied. Thus, operating at 20 °C (B) in the inlet temperature in stage 1 is the optimum choice since the recycling is lower.

4.2.4 Case 3: CO₂ content fixed at 2.5 % in product stream

As seen previously, with 20 °C set at the S1 inlet, the system could not achieve the content of 2.50 %. Therefore, the operating pressure of stage 1 was changed (the same happened with the 3rd reference case) to 15.81 bara of CO₂ since it was impossible to reach the requested value by only regulating the temperature in the re-heating step. This pressure was constant for all the simulated cooling temperatures. Instead of reducing the first stage pressure, the number of membranes could have been changed. However, to keep constant the surface area of separation, this parameter was not modified.

For the referred stage 1 pressure, the re-heating temperature varied from 31.3 °C to 29.7 °C (**Figure 4.14**). Comparing the system with 5 °C and 10 °C, it was verified an absolute difference of 1.6 °C. This means that

changing the cooling temperature in stage 3 does not significantly impact the polishing step since it requires a minor correction in the set temperature.

The same trend was verified for the degraded system. In this case, the temperature increased by 8.95 °C on average compared with new membranes.

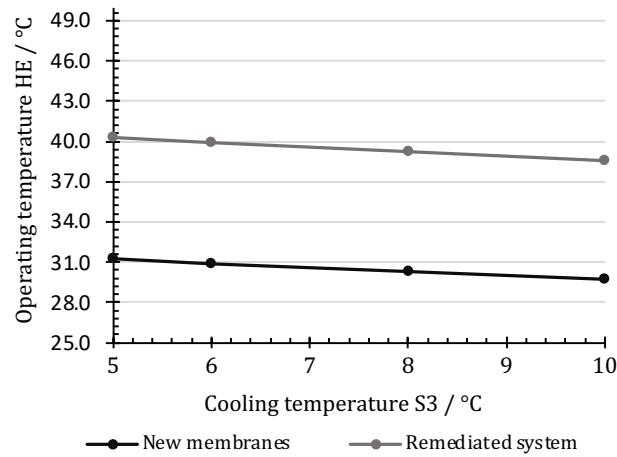


Figure 4.14 - Re-heating temperature regulation on S2 according to S3 cooling temperatures

Through this action, the product stream showed the requested value of CO₂ in its composition (see **Figure 4.15**), i.e., a bio-methane product with 2.5 % of CO₂, 96.67 % of CH₄, 0.70 % of N₂, and 0.13 % of O₂, without water vapor.

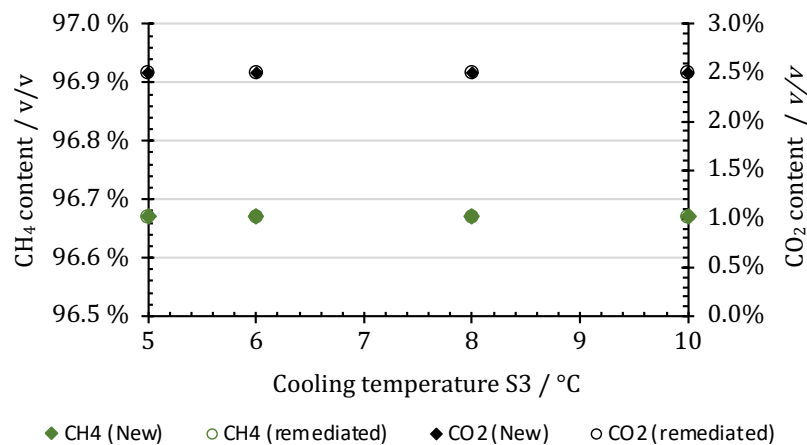


Figure 4.15 - CH₄ and CO₂ content in product stream for new and remediated membranes for different cooling temperatures in S3

In **Figure 4.16** is shown the corresponding recycling values. As seen, the global recycling of the system slightly increased between 5 °C and 10 °C (40.3 % to 41.0 %).

The decrease of the re-heating temperature leads to lower recycling in stage 2. Although, since the backpressure is reduced (varied from 4.00 to 3.78 bara), it is verified an increase in the overall recycling. Also, the system exhibited a 3.2 % deviation between new and degraded membranes.

Since the system with 6 °C of cooling temperature shows the lowest recycling rate, 40.3%, this is the optimum configuration for the Case 3 proposal, in which the re-heating temperature was set at 30.9 °C.

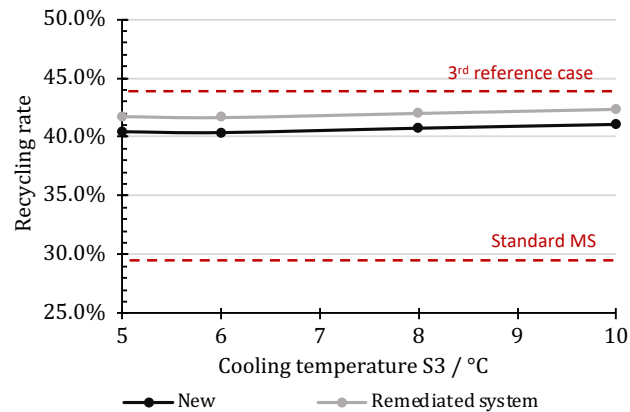


Figure 4.16 - Recycling rate profile for different inlet temperatures, for product with 2.5% CO₂

On the end, comparing this Case 3 with Case 1, for the same H-gas target, the latter presented lower recycling (34.3 %) compared with the third stage cooling (40.3 %), despite the exceeded backpressure limit. This difference is in accordance with what was firstly observed in the parametric study.

In **Table 8**, rounded by red squares, are the inputs used by the work's author regarding the operating conditions. In orange, the volume composition of the product quality in stage 2 (retentate) and the volume composition of the tail gas at the permeate side of S3.

Table 8 - Case 3: Optimum configuration for 2.50 % of CO₂ and 0.20 % methane slip for new membranes.

description	Gas source	Stage 1 Sepuran Green Cartridge 100x1200 01: SC 3500, S=50, NEW			Stage 2 Sepuran Green Cartridge 100x1200 01: SC 3500, S=50, NEW			Stage 3 Sepuran Green Cartridge 100x1200 01: SC 3500, S=50, NEW		
		Feed	Retentate	Permeate	Feed	Retentate	Permeate	Feed	Retentate	Permeate
port	Raw gas	15.81	15.76	4.01	15.76	15.73	1.05	4.01	3.95	1.05
press [bar]	15.81	15.81	15.76	4.01	15.76	15.73	1.05	4.01	3.95	1.05
flow [Nm ³ /h]	1201.20	1684.25	1024.01	660.24	1024.01	681.32	342.69	660.24	141.47	518.77
Temp [°C]	25.00	20.00	14.20	16.20	30.90	26.20	27.30	6.00	-0.90	4.70
DewP [°C]	13.90	-25.00	-44.40	-31.30	-44.40	-94.80	-59.60	-31.30	-68.50	-43.20
CH ₄	54.94%	45.95%	71.85%	5.78%	71.85%	96.67%	22.51%	5.78%	26.08%	0.25%
CO ₂	44.46%	53.49%	27.39%	93.98%	27.39%	2.50%	76.88%	93.98%	73.12%	99.66%
N ₂	0.40%	0.37%	0.55%	0.07%	0.55%	0.70%	0.26%	0.07%	0.31%	0.01%
O ₂	0.10%	0.18%	0.20%	0.15%	0.20%	0.13%	0.35%	0.15%	0.49%	0.06%
H ₂ O	0.10%	0.01%	0.00%	0.01%	0.00%	0.00%	0.00%	0.01%	0.00%	0.02%

Considering a gas source composed of 54.94 % of methane (659.94 Nm³·h⁻¹), at the permeate side of stage 3, was obtained 518.81 Nm³·h⁻¹ of tail gas, composed of 0.25 % of methane (v/v). This corresponds to 1.30 Nm³·h⁻¹ of CH₄ in the off-gas stream. Thus, the ratio between the methane in the tail gas and the methane in the gas source is 0.20 %, which is the system's methane slip.

4.2.5 Turndown to half of the capacity

After performing Cases 1 and 3 with H-gas with fixed content of CO₂, a turndown of the feed flow to half of the original value was applied, i.e., 600 Nm³h⁻¹ dry basis, only considering new membranes. This analysis allowed us to understand the effects on the different parameters, i.e., backpressure in stage 3, re-heating temperature, and pressure in stage 1 if the goal is the H-gas target.

Keeping constant the number of membranes, the feed volumetric flow per surface area is reduced. Therefore, less driving force is needed in stage 1. Thus, Case 1 and Case 3 worked at 11.3 and 11.2 bara, respectively, in stage 1. These values allowed to reach the requested H-gas target.

As seen in **Figure 4.17**, for Case 1, to keep the product quality constant with 2.5 % of CO₂, after the turndown, the re-heating temperature range (a) was reduced as the cooling temperature in S1 increased, from 15.0 °C down to 13.9 °C. However, the variation was not significant (circa 1 °C), as it was verified when operating at full capacity.

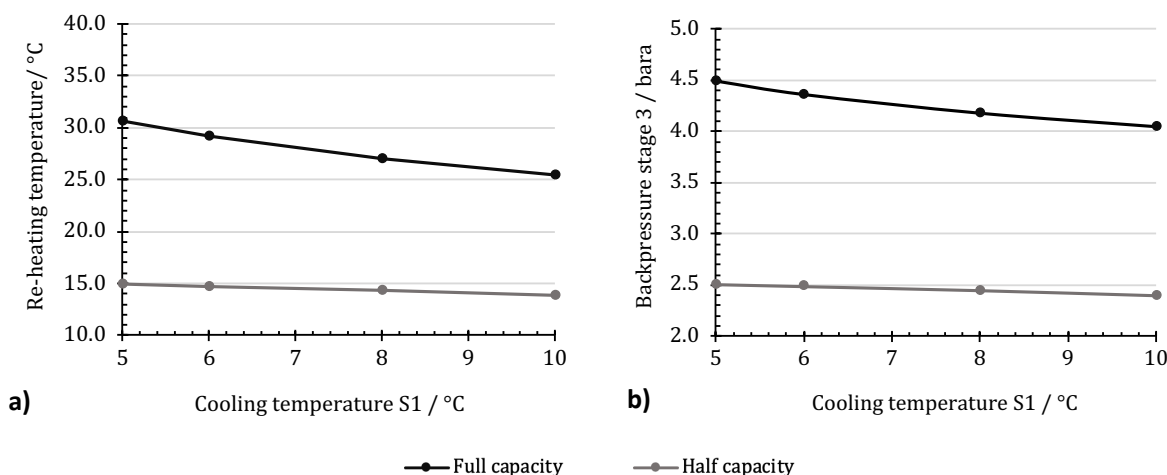


Figure 4.17 – Case 1: comparison of re-heating temperature a) and backpressure in stage 3 b) between system working at full (1200 Nm³h⁻¹) and half (600 Nm³h⁻¹) of the capacity, for new membranes.

This is explained due to the lower amount of flow per surface area, which facilitates the permeation. Hence, it is not necessary to re-heat with higher values of temperature to increase the permeation of CO₂.

The same behavior was exhibited regarding backpressure in the third stage (b). It was reduced from 2.51 bara to 2.40 bara to keep the methane slip constant (0.2 %). Thus, it was acknowledged that higher biogas fields require more pronounced changes when cooling, due to the higher amount of gas per surface area.

Regarding Case 3, with the turndown to half of the capacity, as seen in **Figure 4.18**, the re-heating temperature was set to 15 °C for all the cooling temperatures (a), as it was possible to achieve the 2.50 % of CO₂. This behavior is not the same when operating at full capacity.

The backpressure (b) in stage 3 was comprised between 2.44 bara and 2.34 bara, decreasing as the cooling temperature increased, as well as for the system operating at full capacity.

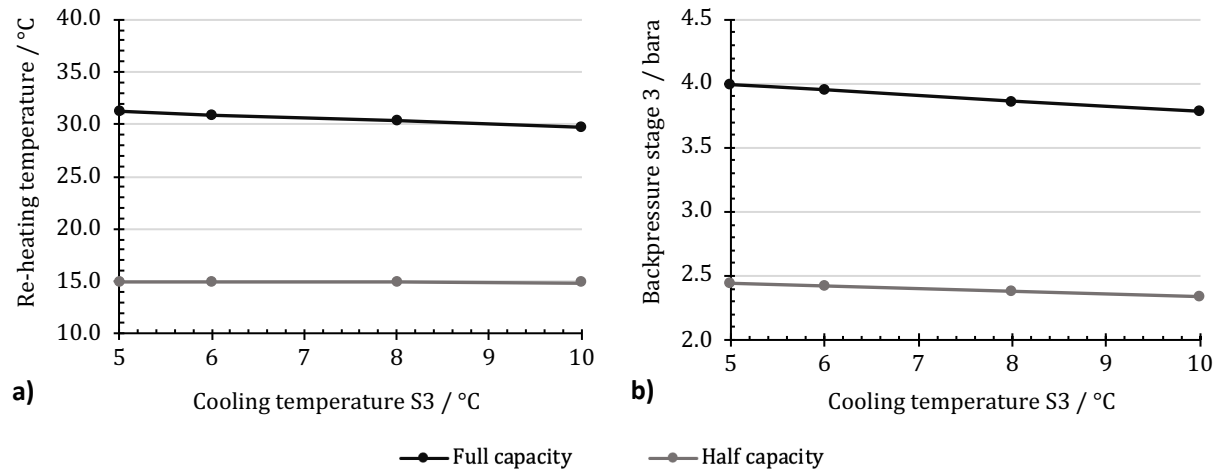


Figure 4.18 - Case 3: comparison of re-heating temperature a) and backpressure in stage 3 b) between system working at full ($1200 \text{ Nm}^3\text{h}^{-1}$) and half ($600 \text{ Nm}^3\text{h}^{-1}$) of the capacity, for new membranes.

Figure 4.19 represents the compressed biogas profile fed in stage 1 after passing through the dryer unit, for Case 1 and 3 proposals. As is possible to see, for both cases, the feed flow in stage 1 tends to increase when operating at half of capacity. This means that also recycling would increase.

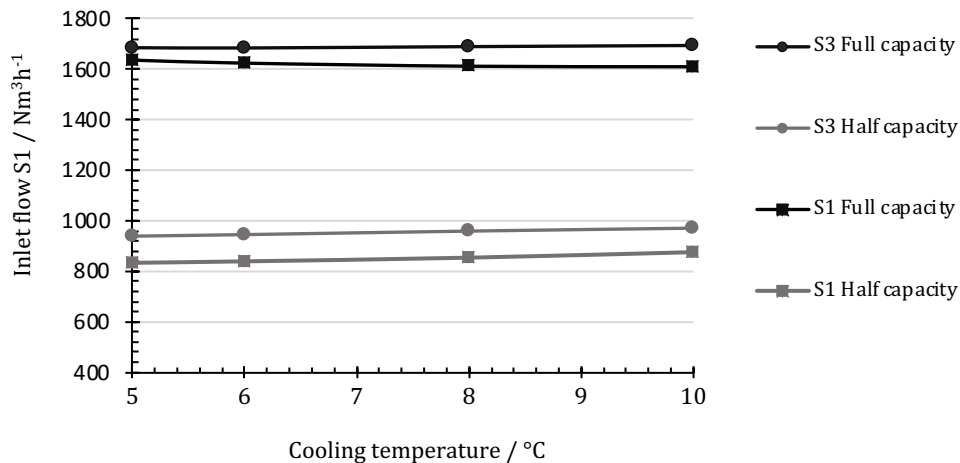


Figure 4.19 - Stage 1 inlet flow profile for Case 1 and Case 3 for different cooling temperatures

In addition, as expected, for both half and full-capacity options, Case 3 exhibits higher inlet flow in stage 1 when compared with Case 1, which means higher recycling rates. Despite that, it was possible to achieve the H-gas target for the modeled configurations. To conclude this study, is possible to work at low pressure if the target is H-gas with 0.25 % CO_2 and 0.2 % methane slip, and it is relatively easy to regulate the system. Case 3 has shown to be less sensitive to cooling temperatures than Case 1. Nevertheless, conjunction between different values of re-heating temperature and stage 1 pressure is also possible, but it needs to be further evaluated to reduce the recycling rates.

4.3 Business case

This chapter aims to investigate the economic feasibility of lowering the methane slip from 0.5 % to 0.2 % with only-membranes and to almost 0 % with the addition of an RTO unit in the tail gas of the process.

A business case has been set up for the techno-economic evaluation of the five configurations. The business case provides the total cost of ownership (TCO), which is composed of capital expenditures (CAPEX) and operational expenditures (OPEX).

The biogas compositions of the 3-multistage MS and the H-gas product (upgraded) are found in **Table 9**.

Table 9 - Concentration inputs for the business case

Carborex® membrane system for H-gas target		
Gas composition	Inlet system	Output
CO ₂ % (v/v)	44.5	2.50
CH ₄ % (v/v)	54.9	96.70
O ₂ % (v/v)	0.1	0.10
N ₂ % (v/v)	0.4	0.70
H ₂ O % (v/v)	0.1	0.00

4.3.1 Business case assumptions

The main assumptions and inputs carried out for the business case are shown in table **Table 10**. The production hours per year were set at 8400 h. The power consumption was determined based on engineering tools within the respective amount of recycling for each system. This parameter affects mainly the system's OPEX.

For the operating of the RTO, an off-gas flow of 522.0 Nm³·h⁻¹ was considered with 11.7 Nm³·h⁻¹ auxiliar biogas. For the total oxidation process, 783 Nm³·h⁻¹ air flow were used. This system consists of a three combustion chambers with a destruction performance of circa 99 % for methane. This information was obtained from DMT internal information regarding thermal oxidizers. The auxiliar biogas was accounted for the total raw materials cost yearly.

Table 10 - Business Case assumptions

Main parameters	Standard MS (0.5 % slip)	0.2 % slip MS (by recycle increase)	Case1 (Cooling ST1)	Case 3 (Cooling ST3)	MS (0.5 %) + RTO (~ 0 % slip)
Gas flow (Nm ³ ·h ⁻¹) wet basis	1201				
Production hours (h)	8400				
Raw biogas treated (Nm ³ ·year ⁻¹)	10 090 080				
Biomethane (Nm ³ ·h ⁻¹)	679	681	681	681	673
Pressure (bara)	16.50	15.81	16.50	15.81	16.5 MS
					0.05 RTO

Recycle	29.3 %	44.0 %	34.3 %	40.4 %	29.3 %
Compressor Power consumption (kW)	318	343	332	335	RTO 3*
					Compressor 318
Depreciation period (years)	15				
Interest (%)	7				
Electricity price (€·kW ⁻¹)	0.1				
Biogas price (€·Nm ⁻³)	0.35				
Biomethane price ((€·Nm ⁻³)	1.4				

* Operating specifications were provided by vendor quotation from DMT internal information.

4.3.2 Results and outputs

Regarding the capital expenditures, the total investment is composed of the *Carborex*[®] base system with additional specific equipment utilized in each case. Besides that, the *Carborex*[®] base-system price was calculated based on specific compressors, accounting with a price correlation, i.e., ratio between the recycle of each case and the recycling of the standard MS (0.5 % slip). This was made since it is important to choose the adequate compressor for each system, which affects the system's CAPEX.

The operating expenditures are composed of the total utilities and the total raw materials costs. These parameters were provided by DMT based on pre-engineering calculations and assumptions, (same for the compressor's power consumption). The total raw materials cost shows the expenses with auxiliary biogas when placing an RTO and the income of slip (methane) recovering, due to the increase of recycling, compared with the standard system.

Both expenditures have been stated as yearly costs and summarized to display the system's yearly TCO for a fair comparison. In addition, the cost for all cases was normalized per volume of biomethane (Nm³) yearly. The difference between each system from the standard MS was quantified.

The main parameters of the business case are summarized in **Table 11**. The values were rounded to simplify the interpretation. A vendor provided the quotation for the RTO unit to approximate this economic evaluation to the market reality.

Table 11 - Business case results

<i>Main parameters</i>	<i>Standard MS (0.5 % slip)</i>	<i>0.2 % slip MS (by recycle increase)</i>	<i>Case1 (Cooling ST1)</i>	<i>Case 3 (Cooling ST3)</i>	<i>MS (0.5 %) + RTO (~ 0 % slip)</i>
TCO summary					
TCO (k€·year⁻¹)	427.1	447.4	438.0	444.7	493.3
Upgrading price (€·Nm⁻³ upgraded gas)	0.0749	0.0783	0.0766	0.0778	0.0873
Annual saving (k€·year⁻¹)	n.a	- 20.3	- 10.8	- 17.5	- 66.1

CAPEX summary (Investment)					
Total CAPEX cost (k€·year ⁻¹)	160.4	179.8	175.8	183.3	190.0
Total investment (M€)	1.58	1.77	1.73	1.80	1.87
Depreciation (k€·year ⁻¹)	105.2	117.9	115.3	120.2	124.6
Interest (k€·year ⁻¹)	55.2	61.9	60.5	63.1	65.4
OPEX summary (Investment)					
Total OPEX cost (k€·year ⁻¹)	266.7	267.7	262.2	261.4	303.3
1. Total raw materials (k€·year ⁻¹)	0.0	- 24.9	-24.9	-24.9	+ 34.4
2. Total utilities (k€·year ⁻¹)	266.7	292.6	287.1	286.3	268.9
Electricity (k€·year ⁻¹)	266.7	288.0	278.8	281.2	268.9
Heat utility (k€·year ⁻¹)	n.a	4.6	8.1	5.0	n.a
Cool utility (k€·year ⁻¹)	n.a	n.a	0.2	0.1	n.a

Relatively to the TCO, the systems are listed next, from the cheapest up to the most expensive yearly: Standard MS (0.5 % slip), low slip by cooling the first stage, low slip by cooling third stage, low slip by recycling increase, and standard with RTO unit for off-gas treatment (as shown in **Figure 4.20**). The TCO is comprised between 427.7 k€·year⁻¹ up to 493.3 k€·year⁻¹ (66.1 k€·year⁻¹ difference).

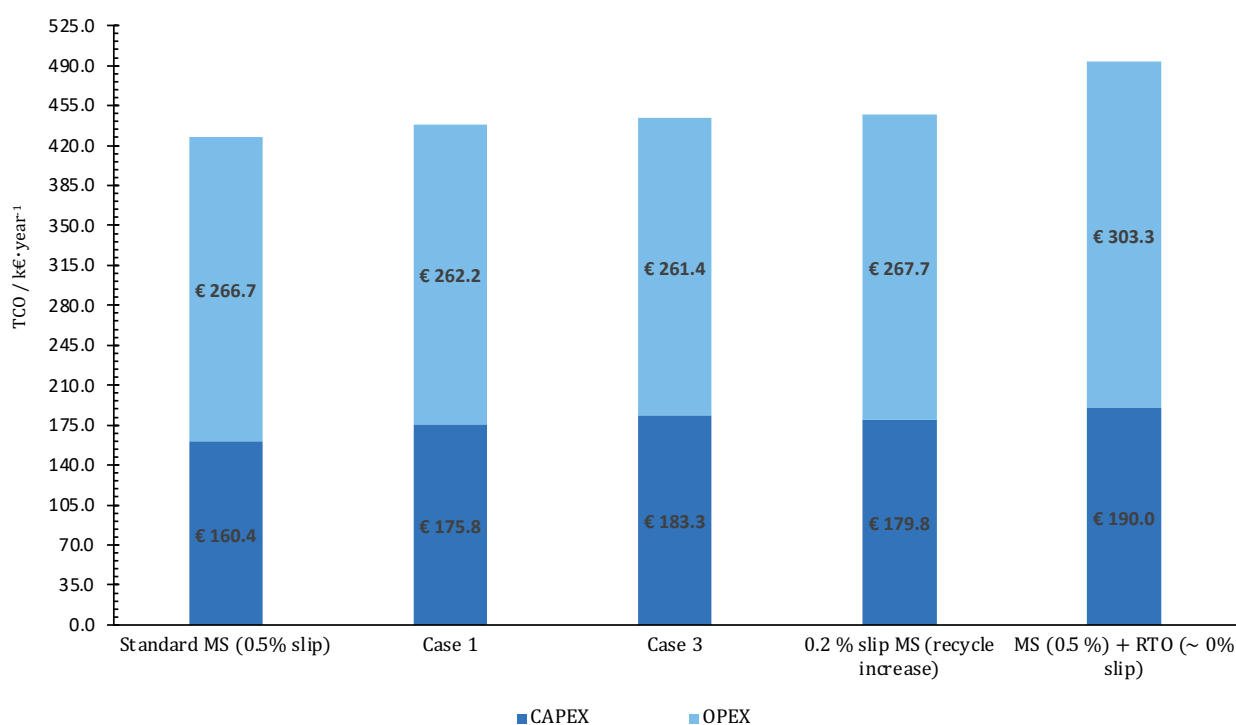


Figure 4.20 - Comparison between the different biogas upgrading configurations

The standard case (0.5 % slip) has the lowest associated CAPEX in the system, however the OPEX is similar to the 0.2 % slip MS by recycle increase, and so, higher than the cooling system proposals. The standard case with an extra RTO unit (~ 0% slip) is principally affected by the usage of auxiliary biogas (plus

34.4 k€·year⁻¹ in raw material costs) and by the total investment of the extra equipment (RTO unit with auxiliary units that entails).

As it is possible to see in **Figure 4.20**, the key parameter for TCO remains in the OPEX's systems (60.6 % average weight). This is because of the raw materials cost and total utilities, but mainly due to the electricity cost associated with the power consumption of the compressor (see values in **Table 11**).

Case 1 has the lowest CAPEX (175.8 k€·year⁻¹) among the low slip cases configurations (due to the lowest recycling rate). However, the OPEX's is similar (slightly higher than) as Case 3. The *0.2 % slip MS by recycle increase* shows a higher OPEX than the previous systems. Overall, *0.2 % slip MS Case by recycle increase* deviates absolute 9.8 k€ and 2.7 k€ yearly (TCO) from Case 1 and 3, respectively. The option of RTO presents the highest CAPEX and OPEX in comparison with all low slip cases.

Observing only this economic evaluation, the *first stage cooling* proposal (Case 1) seems to be the most attractive if the client is obliged to comply with a 0.2 % methane slip. This is also proved through the upgrading price, i.e., the price for upgrading the raw biogas into a revenue product and the deviation from the standard MS (**Figure 4.21**).

The upgrading price of Case 1, Case 3, 0.2 % slip MS by recycle increase, and the MS 0.5 % + RTO show a deviation of 2.2 %, 3.8 %, 4.4 % and 16.5 %, respectively, from the standard MS case. In absolute values, it means an extra 10.8, 17.5, 20.3, and 66.1 k€·year⁻¹ in the TCO, for each configuration, respectively (see annual savings in **Table 11**).

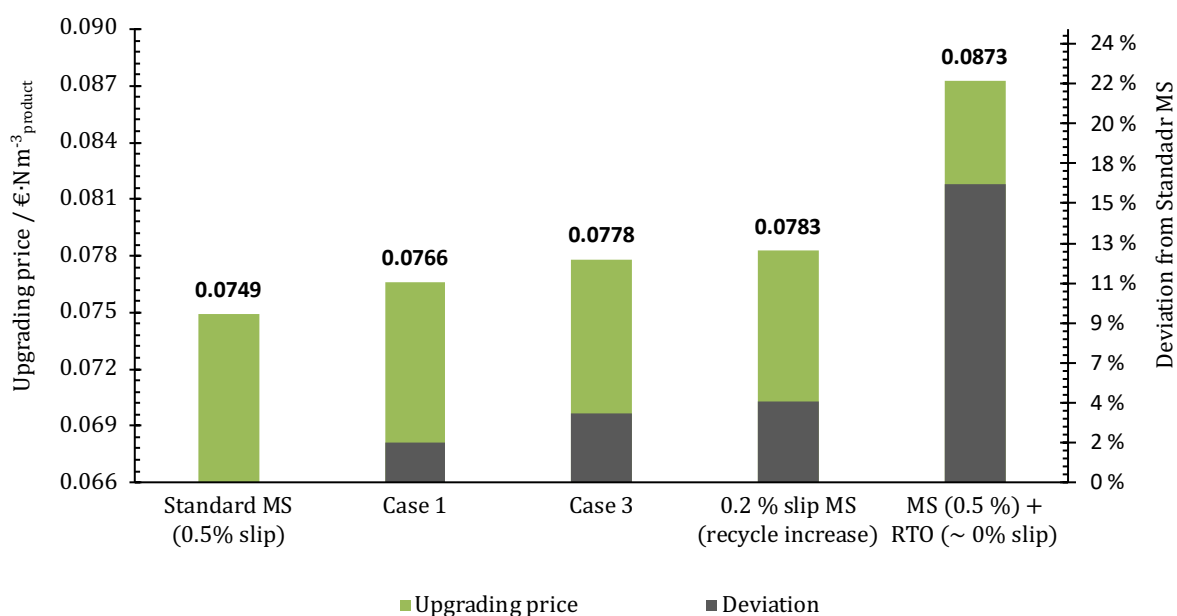


Figure 4.21 - Upgrading price and deviation from Standard MS 0.5% slip

However, even though the *0.2 % slip system by recycle increase* (3rd reference case) has the highest OPEX and biogas upgrading price among the low slip configurations (0.0783 €·Nm³), the price is still competitive

due to the placement of only one heat exchanger. As a result, it has less maintenance concerns when used on-site as opposed to Cases 1 and 3, which have been modified to include a dryer and a cooling unit that may get damaged or in need of replacement

Through this business case it is possible to understand the difference between the low slip configurations and the option of placing an RTO. Moreover, the total investment of Case 1 and Case 3 accounts for circa 34 % and 30 % of margin price, until the systems reach the same biogas upgrading price as the standard case with the RTO unit.

Also, using an RTO after the process has associated extra 55.3 k€ (more than Case 1), 48.6 k€ (more than Case 3) and 45.8 6 k€ (more than low slip case by recycle increase) yearly. This means the thermal oxidizer technology does not outstand against the low slip system built with the same number of membranes.

5 Conclusion

Methane is a significant component of natural gas and bio-methane, having a more detrimental effect than carbon dioxide. CH₄ emissions must be strongly regulated to improve air quality and slow climate change. Some countries, like Germany and Sweden, already applied stricter legislations towards reducing the CH₄ emissions, which has an immediate impact on the biogas upgrading industry. The goal of this project is to determine and optimize several configurations of DMT's *Carborex*[®] MS with a methane slip of 0.2 %.

In this work, several configurations were built and analyzed for the development of a low slip system (0.2 %) with determined biomethane quality of CO₂ ≤ 2.5 %, as typical value for injecting it to the H-gas grid. Hence, a business case was built up to economically evaluate the different options while benchmarking DMT's standard system (0.5 % slip) and the typical application of placing an RTO to treat the off-gas stream from the traditional *Carborex*[®] MS.

Initially, a parametric study was performed. It was concluded that the cooling temperature, whether in the first or third stage, must be set between 5 °C and 10 °C. Operating values below 5 °C can lead to condensation of compounds, membrane module corrosion, system instability, and a decrease in efficiency. Also, when the system shows signs of degradation (aging/ fouling effect), remediating the performance through re-heating temperature regulation is preferable than changing membrane number. The quality is enhanced with more accuracy since temperature directly affects the permeability and selectivity (Arrhenius's law).

Also, by adding a heat-exchanger for re-heating purposes prior to stage 2, it was obtained a decouple effect between the product quality and methane slip, i.e., the regulation of one does not affect the other.

The development of an H-gas product quality with 0.25 % CO₂ and 0.2 % slip was accomplished for both first (Case 1) and third (Case 3) stage cooling systems, after the sensitivity analysis. First-stage cooling has lower recycling compared with the third-stage cooling proposal, although it is more sensitive to changes when modeling. Regarding Case 3, 20 °C is the preferable inlet temperature of first stage. Values below that were not taken since it was applied a safety margin in operating conditions to not get any condensation in the membranes.

For the cases with intermediate heat exchanger prior second stage, the re-heating temperature and the first stage pressure must be regulated to achieve the product targets. There is a correlation between these two parameters. The methane slip is automatically controlled through backpressure and is not impacted by degradation.

For the first and third stage cooling, the operating cooling temperatures that resulted in the lowest recycling were 10 °C and 6 °C, respectively. For steady state operation after degradation, the product quality and methane slip should be close to the initial values, as it was verified.

The business case has shown that the best case among the low slip offers is the first stage cooling proposal, developed alongside this work. However, it accounts for more maintenance risks due to the extra units (cooling unit, dryer, intermediate exchanger) than the low slipcase already developed by DMT.

Benchmarking with the Standard *Carborex*® MS, if the client is obliged to comply with low slip values, there is no considerable deviation in terms of extra costs yearly. The first stage cooling system would spend more 10.8 k€ yearly than the standard case (TCO). Besides that, the OPEX is the key factor for the price increase of the configurations.

In addition, placing an RTO after the standard *Carborex*®, instead of considering low slip configurations, is not feasible due to the extra costs associated with this thermal oxidizer (equipment, raw materials). It would also mean the destruction of revenue products (methane). It would not be possible to recover it after the process. However, since there is no membrane system capable of reaching ~ 0.0 % methane, this option is an option if the client is obliged to meet the target (0.0 % methane emissions).

Nevertheless, the option of placing an RCO might be a better option than RTO, since the set operating temperature is lower, and the oxidation reaction is improved using a catalyst. The raw material cost needs to account for the selected catalyst and for the replacement after a certain period of usage. Thus, future work should consider a business case with an RCO.

At last, the objectives specified at the start of the internship were attained throughout the work conducted at DMT Environmental Company. Economically, the low slip configuration with first stage cooling has proven to be the solution for the requested biogas upgrading process.

Although, efforts on reducing the operational costs are needed for case 3 and case 1, i.e., the recycling and power consumption can be optimized through changes in the embedded parameters. Hence, for future work is important to study the effect of different number of membranes for each configuration, to understand if lower values of recycling are possible to achieve.

Still, membrane separation technology is a feasible technique for the biogas upgrading process while meeting the established market targets of low slip. Although, it needs further improvement and researching. Thus, it is essential to be connected to the R&D department, to find the best cost-effective process for the company.

6 Assessment of the work done

6.1 Objectives Achieved

The performed goals for this work are listed below:

- Overview of biogas upgrading technologies, mainly membrane separation and off-gas treatment technologies, such as thermal oxidizer units for methane removal.
- Design and modeling of a membrane separation process with the software *Simulation of gas separation modules in real time*
- Understand the system behavior for different cooling temperatures and get sensibility with the application and the different parameters involved in the overall process.
- Parametric study of a specific range of cooling temperatures for several 0.2 % slip configurations.
- Analysis of membrane degradation and system's behavior response
- Study of different remedial steps to enhance system's performance: regulation of re-heating temperature and number of membrane modules.
- Design and modeling low slip (0.2 %) configurations for H-gas product with maximum 2.5 % of CO₂, using the simulator.
- Business case of several configurations and benchmark them with the standard *Carborex® MS* (0.5 % slip). An economic evaluation of a standard *Carborex®* system with an RTO placed for tail treatment.

6.2 Other Work Carried Out

Through the internship, it was possible to have contact with a real biogas upgrading plant, where a specific membrane skid was tested for a client. This gave a broader insight into the technical aspects of the *Carborex®* system.

6.3 Future work

Further research must be done on the subject. Regarding the off-gas treatment, the implementation of an RCO needs to be studied, as well as its impact on the Standard *Carborex® MS* system cost. The catalyst would play an important role in the performance of the unit. Regarding the cooling stage configurations, they are a promising alternative. However, it is important to test the data on-site and validate the results. Also, the proposed configurations should be studied, varying the number of membranes.

6.4 Final Assessment

Throughout the development of this work, I was able to get deeper into the renewable energies market and industrial biogas upgrading plants. This experience has guided me to new challenges and a will of getting more experience in the field. Also, working as an intern at the R&D department was truly enriching, as it is a healthy and friendly environment, where values such as teamwork, transparency, and responsibility are present. This project allowed me to develop a strong interest in the development of renewable energy technologies and large industrial plants where membrane separation is applied.

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Annex A - Complementary figures of SOA

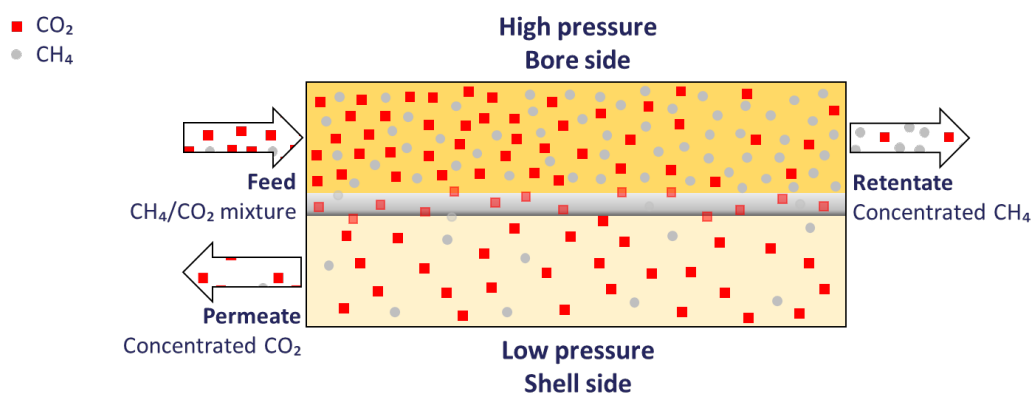


Figure A.1 - Separation mechanism of CO₂/CH₄ in a polymeric membrane, counter-current system ¹⁵

Table 12 - Joule-Thomson coefficient at 30 °C and 10 bar²¹.

Constituent	Joule-Thomson coefficient / K·bar ⁻¹
H ₂	-0.03
N ₂	0.20
O ₂	0.26
CH ₄	0.42
CO ₂	1.05
C ₃ H ₆	1.95
C ₃ H ₈	2.03

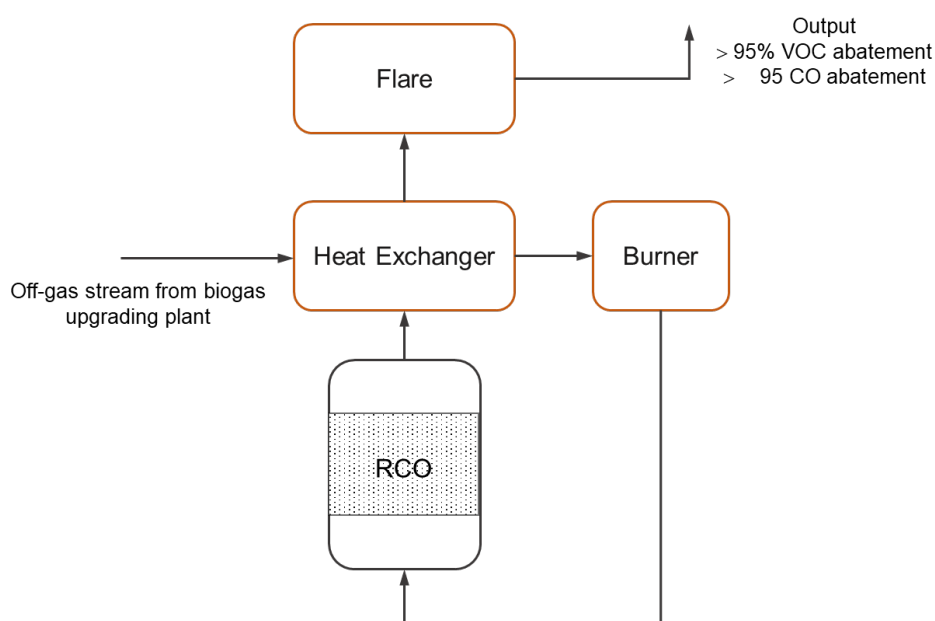


Figure A.2 - Schematic adaptation from Resilco RCO system ²⁸

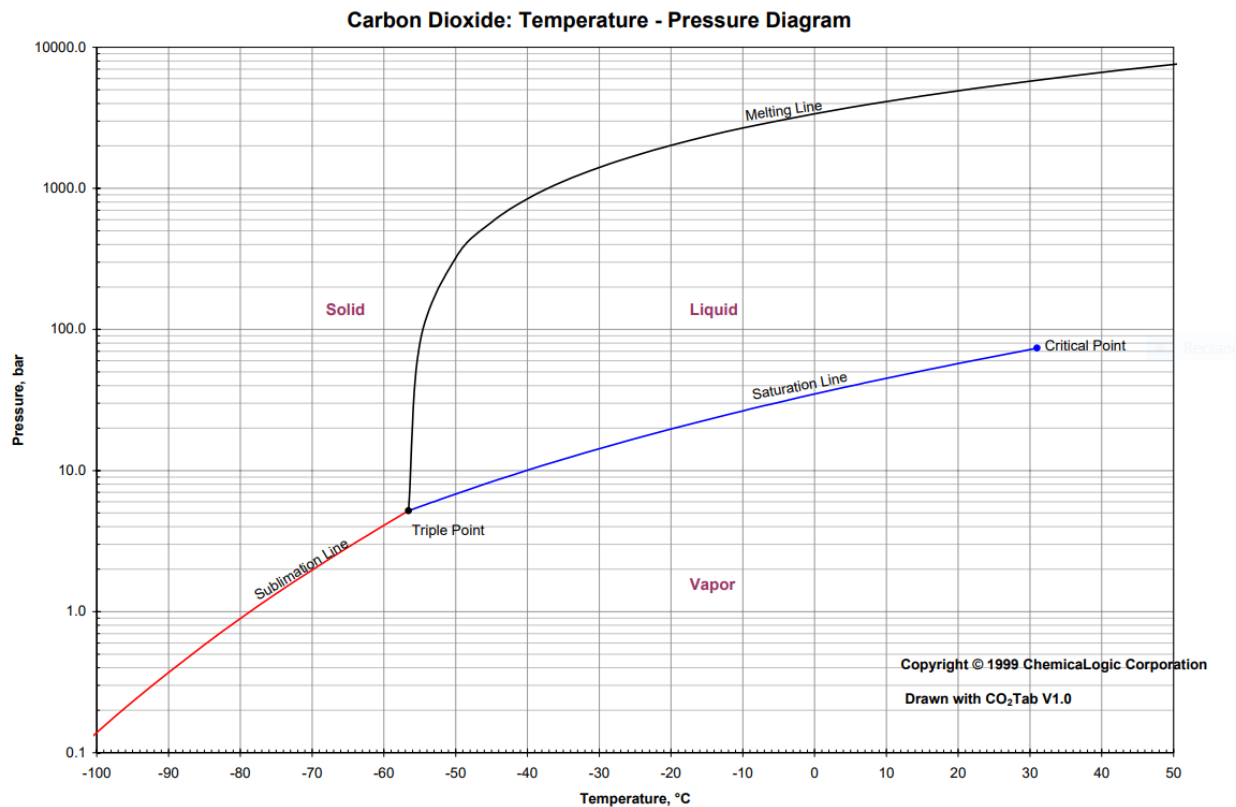


Figure A.3 - Phases diagram of CO₂ P vs. T

Appendix A – Scientific background of membrane separation

The flux through the membrane for a certain species is determined by both solubility (S_i) and diffusivity (D_i), as well as the driving force. i.e., partial pressure difference (Δp_i) on both sides of the membrane, given by equation (A.1):

$$N_i = D_i S_i \frac{\Delta p_i}{\delta} \quad (\text{A.1})$$

Where, the two properties, diffusivity, and solubility can be expressed through permeability coefficient, $P_i = (S \times D)_i$. The unit commonly used for this parameter is the barrer, as 1 barrer is $3,35 \times 10^{-6} \frac{\text{mol}}{\text{m s Pa}}$ in SI units. In addition, the division of permeability by membrane thickness (δ), gives the permeance (Q_i), expressed in *gas permeation unit* (GPU), as 1 GPU is equal to $3,35 \times 10^{-10} \frac{\text{mol}}{\text{m}^2 \text{ s Pa}}$. Thus, the flux depends on membrane specifications (permeance) and the process conditions (applied pressure), $N_i = \text{GPU} \cdot \Delta p_i$.

A common term used to discuss membrane specifications is the separation capacity (SC_i), which also factors in the membrane surface area (A) and is expressed by $SC_i = Q_i \cdot A$, in units of GPU·m².

Also, an important performance indicator is membrane selectivity. It quantifies the difference between the permeability of two different species and it can be expressed by equation (A.2):

$$\alpha_{CO_2/CH_4} = \frac{(S \times D)_{CO_2}}{(S \times D)_{CH_4}} = \frac{P_{CO_2}}{P_{CH_4}} = \frac{SC_{CO_2}}{SC_{CH_4}} \quad (\text{A.2})$$

Thus, a membrane that has a CO₂/CH₄ selectivity of 50, should theoretically let 50 molecules of CO₂ through for every molecule of CH₄. Nevertheless, in practice, it is the difference in partial pressure of feed and permeate side that drives the flux, as it was said.

Appendix B – Reference cases data

Through the reference cases, was possible to understand if the results of the modeled configurations are between the guidelines of the systems already developed.

The *standard MS* configuration (**1st reference case**) accounts for 0.5% methane slip and 2.5% of CO₂ on product quality. Through *Evonik Simulator*, the data needed for results discussion was obtained, as is shown in **Table 13**. The input conditions are flagged.

Table 13- Standard MS simulation for 0.5 % methane slip without safety factors accounted.

description	Stage 1 Sepuran Green Cartridge				Stage 2 Sepuran Green Cartridge				Stage 3 Sepuran Green Cartridge			
	100x1200				100x1200				100x1200			
conditions	01: SC 3500, S=50, NEW				01: SC 3500, S=50, NEW				01: SC 3500, S=50, NEW			
port	Inlet	Feed	Retentate	Permeate	Feed	Retentate	Permeate	Feed	Retentate	Permeate	Feed	Retentate
press [bar]	16,50	16,50	16,46	4,02	16,46	16,43	1,05	4,02	3,96	1,05	4,02	3,96
flow [Nm ³ /h]	1201	1553	938	615	938	679	259	615	93	522	615	93
temp [°C]	25,0	25,0	19,1	21,1	19,1	14,7	15,9	21,1	12,8	19,7	21,1	12,8
DewP [°C]	14,6	10,0	-17,3	1,3	-17,3	-76,5	-34,6	1,3	-55,4	-14,9	1,3	-55,4
CH ₄	54,9%	49,3%	76,5%	7,9%	76,5%	96,7%	23,3%	7,9%	48,8%	0,6%	7,9%	48,8%
CO ₂	44,5%	50,1%	22,8%	91,7%	22,8%	2,5%	76,1%	91,7%	50,1%	99,1%	91,7%	50,1%
N ₂	0,4%	0,4%	0,6%	0,1%	0,6%	0,7%	0,3%	0,1%	0,6%	0,0%	0,1%	0,6%
O ₂	0,1%	0,2%	0,2%	0,2%	0,2%	0,1%	0,3%	0,2%	0,5%	0,1%	0,2%	0,5%
H ₂ O	0,1%	0,1%	0,0%	0,2%	0,0%	0,0%	0,0%	0,2%	0,0%	0,2%	0,2%	0,0%

Therefore, this standard case presents 2.5% of CO₂ content in the product stream, meaning a product quality of 96.7% of methane. The system accounts for a 29.3% recycle rate in dry basis ratio. To achieve low slip, the backpressure of stage 3 must be reduced. However, since there is no temperature control in stage 2 (*standard MS*), the product quality decreases, and more CO₂ permeates the membrane.

Aiming low slip, a heat exchanger between S1 and S2 was previously studied at DMT. Nevertheless, this re-heating step was accompanied by an increase in recycling. There were used two references regarding the re-heating step.

For the **2nd reference case**, the pressure at stage 1 and the operating temperature of the heat exchanger before stage 2 were set constant, 16.5 bara and 30 °C, respectively.

The outcome data and the inputs are shown in **Table 14**. The inlet conditions are flagged by red squares. For those conditions, it was obtained a product quality of 2.0 % of CO₂ (97.2% of product quality). The system presented 43.8 % recycle.

A **3rd reference case** was built, with fixed 2.5% of CO₂ in the product stream. The inlet conditions were changed (pressure at stage 1 and temperature of the heat exchanger on stage 2).

Thus, a final product with 96.7% of CH₄ was obtained. The recycle was 44.0% (upper limit of recycle). **Table 15** provides the mass balance and data from the modelling. Inputs are flagged as well.

Table 14 - Low slip configuration for 0.2% methane slip and product stream with 2.0% of CO₂

	Stage 1				Stage 2				Stage 3			
	Sepuran				Sepuran			Sepuran				
	Green				Green			Green				
	Cartridge				Cartridge			Cartridge				
description	Gas source	100x1200		8	100x1200		8	100x1200		8		
conditions	01: SC 3500,				01: SC 3500,			01: SC 3500,				
	S=50, NEW				S=50, NEW			S=50, NEW				
port	Raw gas	Feed	Retentate	Permeate	Feed	Retentate	Permeate	Feed	Retentate	Permeate		
press [bar]	16,50	16,49	16,45	3,68	16,45	16,43	1,05	3,68	3,59	1,05		
flow [Nm³/h]	1201	1727	986	740	987	678	310	740	216	523		
temp [°C]	25	20	13	15,3	30	25,5	26,5	15,3	11,3	14,5		
DewP [°C]	14,5	5	-25,9	-5,2	-25,9	-85,6	-43,4	-5,2	-34,8	-17,6		
CH4	54,9%	45,1%	74,8%	5,4%	74,8%	97,2%	25,9%	5,4%	17,8%	0,3%		
CO2	44,5%	54,3%	24,4%	94,3%	24,4%	2,0%	73,4%	94,3%	81,6%	99,5%		
N2	0,4%	0,4%	0,6%	0,1%	0,6%	0,7%	0,3%	0,1%	0,2%	0,0%		
O2	0,1%	0,2%	0,2%	0,2%	0,2%	0,1%	0,4%	0,2%	0,4%	0,1%		
H2O	0,1%	0,1%	0,0%	0,1%	0,0%	0,0%	0,0%	0,1%	0,0%	0,2%		

Table 15 - Low slip configuration for 0.2% methane slip and product stream with 2.5% of CO₂

	Stage 1				Stage 2				Stage 3				
	Sepuran Green Cartridge				Sepuran Green Cartridge				Sepuran Green Cartridge				
	100x1200				100x1200				100x1200				
	01: SC 3500, S=50, NEW				01: SC 3500, S=50, NEW				01: SC 3500, S=50, NEW				
description	Gas source												
conditions													
port	Raw gas	Feed	Retentate	Permeate	Feed	Retentate	Permeate	Feed	Retentate	Permeate			
press [bar]	15,81	15,81	15,76	3,64	15,76	15,73	1,05	3,64	3,55	1,05			
flow [Nm³/h]	1201	1730	999	731	999	681	318	731	211	520			
temp [°C]	25	20	13,5	15,7	28,7	24,2	25,3	15,7	11,7	14,9			
DewP [°C]	13,9	5	-24	-4,8	-24	-81,7	-41,5	-4,8	-34,4	-17,1			
CH4	54,9%	44,5%	73,3%	5,2%	73,3%	96,7%	23,2%	5,2%	17,3%	0,3%			
CO2	44,5%	54,9%	25,9%	94,5%	25,9%	2,5%	76,2%	94,5%	82,1%	99,5%			
N2	0,4%	0,4%	0,6%	0,1%	0,6%	0,7%	0,3%	0,1%	0,2%	0,0%			
O2	0,1%	0,2%	0,2%	0,2%	0,2%	0,1%	0,4%	0,2%	0,4%	0,1%			
H2O	0,1%	0,1%	0,0%	0,1%	0,0%	0,0%	0,0%	0,1%	0,0%	0,2%			

Appendix C – Case 1: Sensitivity study of membrane number in the third stage.

Regarding the modeling of Case 1 with standard conditions (section 4.2.1), for *new* membranes, the backpressure exceeded 4 bara for all the tested cooling temperatures, to keep constant 0.2 % methane slip. The system was built with 24 membranes. However, by enhancing the number of membranes in the third stage, the backpressure was reduced 16.4 % (**Figure C.1**).

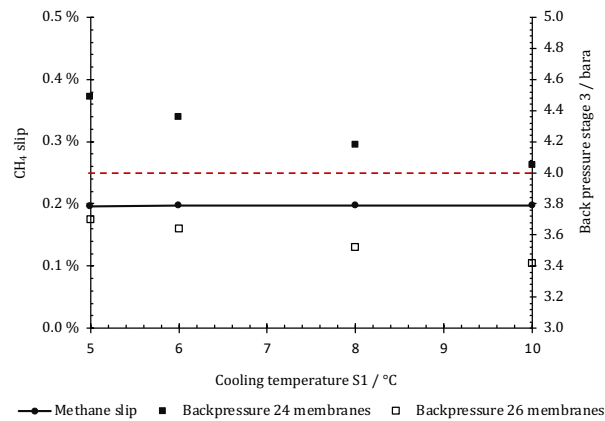


Figure C.1 – Methane slip and backpressure in stage 3 profile with cooling temperature in S1

Adding more membranes in the third stage led to an increase in the surface area. In addition, the separation capacity was enhanced as well the permeance flux, leading to more methane slip. To keep this value constant (0.2 % slip), the backpressure was reduced below 4 bara (lower driving force), as expected. For this effect, two more membranes in S3 were added.

The increase of membranes in the third stage also impacts the product quality (a) and recycling rates (b), **Figure C.2**.

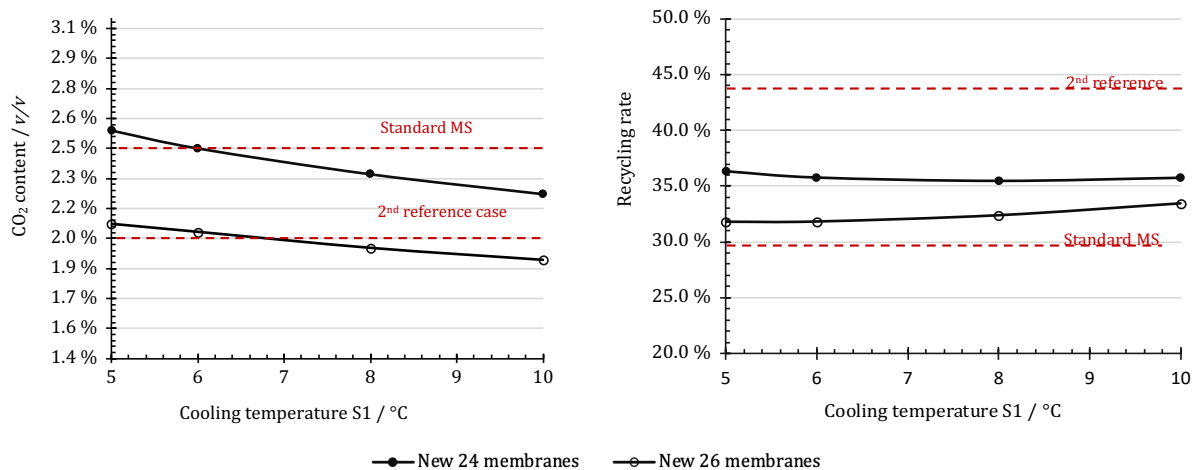


Figure C.2 - Case 1: product quality a) and recycling b) according to cooling temperatures

The product quality (a) followed the same trend for both systems. However, lower CO₂ content was obtained in the product stream for the system with extra membranes. Due to the backpressure decrease, and enhancement of separation capacity, more methane is recycled back to the system's inlet, leading to product quality improvement.

Besides that, the recycling rate was also affected by changing the membrane number. As the permeance flux increases in the third stage, a lower range of recycling is observed. Although of what was expected, this parameter increased alongside the cooling temperatures. Backpressure regulation has more impact in the gas behavior than the cooling effect. Reducing the backpressure led to more retentate flow going back to the beginning of the system, resulting in the recycling increase.

This study has shown that is important to model different systems varying the membrane number. Nevertheless, this system was not considered for the business case. The goal is a fair comparison of all systems, accounting for the same number of membranes (24).

