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METHANE AND CO₂ RECOVERY FROM THE PURGE STREAM TO DESIGN A CLOSED-LOOP FOR THE BIOGAS UPGRADING PLANT

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MASTER THESIS IN CHEMICAL ENGINEERING
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Master in Chemical Engineering

***Methane and CO₂ Recovery from the Purge Stream
to Design a Closed-Loop for the Biogas Upgrading
Plant***

Master dissertation

of

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Developed within the course of dissertation

held in

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Abstract

As the European Union sets ambitious targets to overcome climate crisis, biogas upgrading is increasingly recognized as a promising and sustainable approach for electricity generation and renewable vehicle fuel production. Additionally, the CO₂ generated during biogas upgrading can be captured, treated, and supplied to industries by adding a liquefaction plant, thereby preventing its release into the atmosphere and contributing to the EU's efforts in creating a greener and more resilient future.

This project aimed to recover the purge stream from the CO₂ liquefaction unit creating a closed loop system. For that, several strategies were studied in this project such as the addition of a membrane where the retentate, mostly CH₄, was connected to the biomethane stream while the permeate, CO₂-rich stream, was connected to the compression unit, in the CarboCap. Another strategy was adding a second condenser or a simply recycle flow and connecting them into the compression unit in the Carborex MS, as the flow being recycled in these two cases has significant amount of CO₂ and CH₄. Therefore, the membrane system in the biogas upgrading plant was considered a 2-stage or 3-stage.

In pursuit of the most viable scenario, various parameters were assessed, including the temperature of the main condenser in the liquefaction unit, the pressure on the first stage of the membrane system, and the variation in the composition of both the biogas and tail gas. These simulations were conducted by DMT Environmental Technology, considering projects on a global scale. The simulations aimed to achieve two methane concentration levels in the biomethane: 90 % and 97 %, as some countries mandate higher methane concentrations.

The evaluation of results considered several key factors, including the purity of CO₂ in the liquid flow to the client, CO₂ recovery, CH₄ recovery, flow rate of recycling, power consumption, and unit cost. Among the evaluated configurations, the second condenser exhibited the best performance in recovering the purge; however, due to its high investment cost, it was not prioritized. The membrane system and recycling tie-in demonstrated favorable results for both the 2-stage and 3-stage configurations, regardless of the methane concentration in the biomethane stream. Furthermore, it was found that operating the second condenser at a minimum temperature of -30.0 °C enables the condensation of a significant amount of CO₂, therefore, higher temperatures are preferred.

Keywords (theme):

biogas upgrading plant, liquefaction unit, purge flow, ChemCAD, integration system

Resumo

À medida que a União Europeia estabelece objectivos ambiciosos para contornar a crise climática, a purificação do biogás é cada vez mais reconhecida como uma abordagem promissora e sustentável para a produção de eletricidade e de combustível renovável para veículos. Além disso, o CO₂ gerado durante a purificação do biogás pode ser capturado, tratado e fornecido às indústrias através da adição de uma unidade de liquefação, evitando assim a sua liberação para a atmosfera e contribuindo para os esforços da UE na criação de um futuro mais verde e mais resiliente.

Este projeto teve como objetivo recuperar o fluxo de purga da unidade de liquefação de CO₂, criando um sistema de circuito fechado. Para tal, foram estudadas várias estratégias neste projeto, tais como a adição de uma membrana em que o retentado, maioritariamente CH₄, era ligado ao fluxo de biometano, enquanto o permeado, fluxo rico em CO₂, era ligado à unidade de compressão, no CarboCap. Outra estratégia foi adicionar um segundo condensador ou simplesmente reciclar o fluxo e ligá-los à unidade de compressão no Carborex MS, uma vez que o fluxo a ser reciclado nestes dois casos tem uma quantidade significativa de CO₂ e CH₄. Por conseguinte, o sistema de membranas na unidade de purificação do biogás foi considerado 2 estágios ou 3 estágios.

Na procura do cenário mais viável, foram avaliados vários parâmetros, incluindo a temperatura do condensador principal na unidade de liquefação, a pressão no primeiro estágio do sistema de membranas e a variação na composição do biogás e do gás residual. Estas simulações foram realizadas pela DMT Environmental Technology, considerando projectos à escala global. As simulações tiveram como objetivo atingir dois níveis de concentração de metano no biometano: 90% e 97%, uma vez que alguns países exigem concentrações de metano mais elevadas.

A avaliação dos resultados considerou vários factores-chave, incluindo a pureza do CO₂ no fluxo líquido para o cliente, a recuperação de CO₂, a recuperação de CH₄, o caudal de reciclagem, o consumo de energia e o custo unitário. Dentre as configurações avaliadas, o segundo condensador apresentou o melhor desempenho na recuperação da purga, porém, devido ao seu alto custo de investimento, não foi priorizado. O sistema de membranas e a adição do reciclo apresentaram resultados favoráveis tanto para a configuração de 2 estágios quanto para a de 3 estágios, independentemente da concentração de metano no fluxo de biometano. Além disso, verificou-se que o funcionamento do segundo condensador a uma temperatura mínima de -30.0 °C permite a condensação de uma quantidade significativa de CO₂, pelo que se preferem temperaturas mais elevadas.

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

A handwritten signature in black ink, featuring a large, stylized 'R' and 'D' followed by a horizontal line and a small flourish.

3rd July 2023

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Notation and Glossary

N_i	Flux through the membrane	$\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
D_i	Diffusivity	$\text{m}^2\cdot\text{s}^{-1}$
C_i	Concentration of the substance	$\text{mol}\cdot\text{m}^{-3}$
x	Distance	m
L_i	Permeability	$\text{mol}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$
l	Membrane thickness	cm
p_i^o	Partial pressure of component i in the feed side	bar
p_i^l	Partial pressure of component i in the permeate side	bar
S_i	Solubility	$\text{kg}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}$
y_i	Molar fraction of i in the permeate	
x_i	Molar fraction of i in the retentate	
Q	Permeance	GPU
$\dot{Q}$	Heat transfer	$\text{W}\cdot^\circ\text{C}^{-1}$
$\dot{m}$	Mass flow rate	$\text{kg}\cdot\text{h}^{-1}$
C_p	Heat Capacity	$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
T	Temperature	$^\circ\text{C}$
U	Overall heat transfer coefficient	$\text{W}\cdot\text{m}^{-2}\cdot^\circ\text{C}^{-1}$
A	Area	m^2
E_a	Activation energy	$\text{J}\cdot\text{mol}^{-1}$
R	Gas constant	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
L	Liquid CO ₂ to client	$\text{Nm}^3\cdot\text{h}^{-1}$
F	Biogas feed	$\text{Nm}^3\cdot\text{h}^{-1}$
P	Biomethane stream	$\text{Nm}^3\cdot\text{h}^{-1}$
$x_{F\text{CO}_2}$	CO ₂ composition in the biogas feed	
$x_{L\text{CO}_2}$	CO ₂ composition in liquid CO ₂	
$x_{F\text{CH}_4}$	Methane composition in the biogas feed	
$x_{\text{H}_2\text{O}}$	Water composition in the biogas feed	

Greek Letters

$\alpha_{A/B}$	selectivity	
λ	Latent heat	J
ΔF	Driving force	bar

Indexes

i	index or counter
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List of Acronyms

GHG	Greenhouse Gases
CO ₂	Carbon Dioxide
CH ₄	Methane
NO ₂	Nitrogen Dioxide
H ₂ S	Hydrogen sulphide
N ₂	Nitrogen
O ₂	Oxygen
H ₂	Hydrogen
H ₂ O	Water
SO _x	Sulfur oxides
NO _x	Nitrogen oxides
He	Helium

1 Introduction

1.1 Framing and presentation of the work

According to the Food and Agriculture Organization of the United Nations (FAO) and United States Environmental Protection Agency (EPA), from 18 % to 24 % of global greenhouse gases (GHG) emissions are produced by agriculture. Greenhouse gases consist mainly of carbon dioxide (76 %), methane (16 %), nitrous oxide (6 %) and the residual amount (2 %) of hydrofluorocarbons, perfluorocarbons and sulfurhexafluoride. The presence of CO₂ and CH₄ in the atmosphere contributes to the overheating of the earth as these gases retain infrared rays from the sun [1-3].

To overcome this problem, two main arrangements were established. Firstly, the European Green Deal, focuses on the climate neutrality by cutting emission by 50 % until 2030 and by zero until 2050. Afterwards, the Paris Agreement was established internationally to withhold temperature increasement below 2 °C and invest in actions to increase the goal to 1.5 °C [4].

Moreover, from the engineering perspective, biogas upgrading is an attractive renewable technology to prevent global warming by decarbonizing the agricultural and gas industry. Biogas, mainly composed of methane (CH₄) and carbon dioxide (CO₂), is produced through anaerobic digestion. This renewable energy source can be further processed through upgrading, where impurities are removed, resulting in biomethane. The purified biomethane, with its high methane content, can be integrated into the natural gas grid, used as a vehicle fuel, or applied in various traditional natural gas applications, offering a cleaner and more sustainable energy alternative [5-7].

During the biogas upgrading process, a byproduct, also known as tail gas, is generated and predominantly composed of up to 99 % of carbon dioxide. Given the demand for liquid CO₂ in the industry, a post-treatment unit is typically implemented to recover the CO₂-rich tail gas and convert it into a liquid form. This allows for efficient utilization and commercialization of the captured CO₂, addressing both the need for liquid CO₂ and minimizing the release of greenhouse gases into the atmosphere [8].

Normally, in a liquefaction plant, a significant volume of liquid CO₂ is produced, but a small fraction of the CO₂ introduced into the plant does not undergo condensation and is released into the atmosphere. However, to address this challenge, industries have been actively investing in the development of a closed-loop process to recover and recycle the uncondensed CO₂ within the system. By implementing this alternative approach, the uncondensed CO₂ is captured, preventing its release into the atmosphere, and enabling its reuse, thereby promoting a more sustainable and environmentally friendly operation.

The project aims to analyse various strategies for recovering the purge stream, the uncondensed CO₂ from the liquefaction unit, through a closed-loop process. The strategies involve the implementation of a membrane, a condenser, or a simple recycle stream. Thus, the study focused on:

- Identify the most suitable configuration for an integrated upgrading and CO₂ liquefaction process.
- Model several systems setups.
- Drafting a base reference case for the CO₂ liquefaction unit.

1.2 Presentation of the company

DMT Environmental Technology is a company with a focus on green technology contributing to the transition to a more sustainable world. Thus, DMT has offices in the Netherlands, Canada and the United States of America wherein the main products are Carborex® MS, Sulfurex® and CarboCap®.

Carborex® MS is an advanced biogas upgrading system that utilizes membrane technology to separate and purify biogas, transforming it into high-quality biomethane. The biomethane can be directly supplied to the natural gas grid or used as a vehicle fuel, depends on the client requirement. Carborex® MS is known for its high efficiency, compact design, and operational flexibility, making it an ideal solution for biogas upgrading in various applications, such as agricultural, industrial, and municipal waste treatment plants.

Sulfurex® is another cutting-edge technology developed by DMT, specifically designed for gas desulphurization. It effectively removes hydrogen sulphide (H₂S) from biogas, ensuring compliance with strict emission regulations and preventing corrosion in downstream equipment.

CarboCap® is a liquefaction unit to treat and recover the residual gas from Carborex® MS. CarboCap® employs advanced chemical at high pressure and negative temperature in order to liquefy the CO₂ molecules. The captured CO₂ can be used in various applications, including in food industry, refrigerated transport and in agricultural production.

DMT Environmental Technology is investing in an integrated system that combines Carborex® MS and CarboCap® to produce biomethane and liquid CO₂. This approach offers several advantages for customers, as it increases revenue and improves methane recovery.

1.3 Contribution of the author to the work

This dissertation was carried out at the Technology Office of DMT Environmental Technology headquarter. The work investigated the best unit operation to recover the purge from the CO₂ liquefaction unit and establish operational boundaries. The company aims is to obtain a high methane and CO₂ recovery while maintaining a robust and cost-effective system.

Hence, a study was performed on different system designs (for both 2-stage and 3-stage membrane systems with a variety of setups for system integration/recycle tie-ins). The scenarios investigated are:

- Recycle tie-in directly to the compression unit in the biogas upgrading plant.
- Addition of a second condenser where the uncondensed CO₂ is sent back to the compression unit in the biogas upgrading plant.
- Additional membrane stage where the permeate is sent to the CO₂ liquefaction unit inlet, while the retentate is connected to the biomethane stream in the biogas upgrading plant.

In addition, a study was conducted on different parameters sensitivity, such as temperature, pressure, biogas compositions and tail gas composition, was executed to achieve the optimized scenario.

To evaluate the feasibility of the best scenarios, an economic perspective was set as parameter alongside engineering criteria to achieve a more accurate and real optimization. All simulations were carried out using the chemical software ChemCAD and with assistance from DMT employees.

1.4 Presentation of the dissertation

This thesis was elaborated in accordance with the structure to be considered the most appropriate for presenting and understanding the different scenarios and theories involved. This work is organized into six chapters.

1. Introduction: A brief description of the project presentation, goals and framework is provided. Also included is a brief introduction of DMT.

2. Context and state of the art: Overview of methane composition through different sources. The main DMT products, Carborex® MS and CarboCap®, are presented including its main units to produce biomethane and liquid CO₂, respectively.

3. Materials and Methods: The software utilized by the author is explained in this chapter. The main considerations applied in the simulation over the scenarios are described.

4. Results and discussion: Discussion of the obtained results for the different scenarios and an evaluation between the scenarios is provided. 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 aligned with the feasibility of the project.

6. Assessment of the Work: Final review, limitations of the project and proposes future works on this topic.

7. References: Provide a list of all references consulted during the writing of this thesis.

Annexes and Appendices: contain additional information.

2 Context and State of the art

2.1 Biogas Overview

Biogas, an environmentally sustainable gas, is produced through anaerobic digestion, which takes place at various sites including sewage treatment plants, landfills, and manure processing facilities. Its composition predominantly comprises CO₂ and methane, accompanied by minor proportions of H₂S, N₂, O₂, H₂, and water vapor. Table 1 provides a comprehensive overview of the biogas composition.

It is important to note that the raw biogas produced through anaerobic digestion is not suitable to be utilized directly as renewable biogas. Before its application, the raw biogas needs to undergo a cleaning or upgrading process.

Table 1. Biogas composition according to the production source [9, 10].

Compound	Concentration /%			
	Sewage Sludge	Landfill	Wastewater	Overall Basis
CH ₄	60 - 70	35 - 65	55 - 58	50 - 75
CO ₂	34 - 38	30 - 45	32 - 50	25 - 50
H ₂ O	1 - 7	1 - 5	1 - 5	0 - 10
N ₂	0 - 2	5 - 15	< 1	0 - 15
O ₂	< 1	0 - 1	< 1	0 - 3
H ₂	< 1	0 - 5	< 1	0 - 5
H ₂ S	< 1	< 1	< 1	< 1

Biogas upgrading techniques enhance its quality and energy content by adjusting the gas composition. The methane concentration increases by removing impurities and separating CO₂, resulting in a higher calorific value. In addition, it is crucial to remove H₂S and N₂ to prevent corrosion and production of SO_x and NO_x, respectively. Also, a dewatering process is mandatory to avoid condensation. Upgrading optimizes biogas for applications such as heat, electricity, or injection into the natural gas grid.

Nowadays, several industrial methods using chemical or physical techniques are applied to separate and concentrate CH₄ on the biomethane stream. Traditional methods such as pressure swing adsorption (PSA) and water scrubbing are still applied in the market therefore membrane technology is the new upcoming and innovative technique to upgrade biogas. Membrane technology offers several advantages over PSA and water scrubbing, such as lower energy consumption, reduced equipment size, require less water usage, and have lower maintenance requirements. Therefore, the lifetime of a membrane is still short when compared to other upgrading techniques [11, 12].

The minimum methane concentration in biogas is determined based on the composition of the raw materials within each country. For instance, the Netherlands produces biomethane with a methane

content of 90 %, primarily due to the significant nitrogen content in the gas. On the other hand, Belgium has managed to reach methane concentrations of up to 97 % in their biomethane stream. As a result, the European Union is currently assessing a proposal to establish a minimum methane requirement for all of Europe.

The biogas upgrading plant generates a tail gas stream that exhibits a high concentration of CO₂. To enhance the efficiency and avoiding emitting CO₂ into the atmosphere, a CO₂ liquefaction unit is integrated into the plant. This unit plays a pivotal role in transforming the CO₂-rich stream into a liquid state, opening up possibilities for storage, transportation, or further industrial applications.

By efficiently converting the tail gas into liquid CO₂, the plant gains a valuable commodity that can be monetized in various ways. The liquid CO₂ can be sold to industries that require it as a raw material or used in the production of food and beverages such as a solvent for extracts or hop flavors process in the food and beverage industry [13].

2.2 DMT Engineering Plants

2.2.1 Carborex® MS

DMT Environmental Technology has developed a new promising biogas upgrading plant, named Carborex® MS, based on membrane technology. In fact, a membrane acts as a barrier allowing specific compounds to permeate through it while other compounds remain retained on it. The fastness of permeation of biogas components through a non-porous membrane is illustrated in Figure 1 wherein the water vapors and hydrogen diffuse faster than nitrogen and methane.

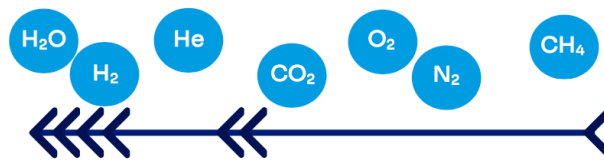


Figure 1. Relative permeation rates of components wherein rapidity increases from right to left [14].

The separation is based on molecular size and chemical affinity between the gas and the membrane. Thus, the gas diffusion occurs under a pressure driven by Fick's Law, which can be written under partial pressure. Equation 1 can be used to describe the Fick's Law where the N_A is the flux through the membrane, D_A is the diffusivity, C_A is the concentration of the substance while x is the distance. In addition, the flux through the membrane can be written wherein L_A is the permeability, l represents the membrane thickness and p_A^o and p_A^l are the partial pressure in the feed and permeate side, respectively.

$$N_A = -D_A \frac{dC_A}{dx} = \frac{L_A}{l} (p_A^o - p_A^l) \quad (1)$$

The key performance of membrane separation is the rate of permeation which is described by the movement of gas through the membrane under a partial pressure derived from the feed site and permeate side. The permeation mechanism is divided in Knudsen diffusion, molecular sieving, solution diffusion, sorption-diffusion, and capillary coalescence. The selected membranes work under the sorption-diffusion phenomena for many biogas upgrading companies, including DMT.

From a material standpoint, process efficiency is determined by permeability, which refers to the amount which a component permeate through the membrane by a unit of area, time, and pressure. In simpler terms, it is the ratio of the product permeating flux and membrane thickness and the driving force or is equal to the product of diffusivity and sorption, as described in Equation 2. The pressure difference is written as ΔF_A while the diffusivity and sorption is represented by D_A and S_A , respectively

$$L_A = l \frac{N_A}{\Delta F_A} = D_A S_A \quad (2)$$

In addition, selectivity is crucial in determining the separation performance, as it directly correlates to the sorption/diffusion of the desired gas compared to the non-desired gas. Thus, the selectivity can be written as the ratio of the permeabilities for two different gases species A and B, which are P_A and P_B , respectively. The selectivity is presented as the ratio of the molar fraction of A in the permeate, y_i , and the retentate side, x_i , as seen in Equation 3. In the biogas perspective, A represents CH₄, and B is CO₂ [15].

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{y_A x_B}{y_B x_A} \quad (3)$$

Besides that, in industrial application, permeance is also a notorious parameter that associates with the ease each substance have to pass through the thickness of the membrane and is represented as the permeability over the membrane thickness, shown in Equation 4 [16].

$$Q_A = \frac{L_A}{l} \quad (4)$$

Moreover, membranes are categorized into configuration modules: flat, tubular, plate and frame, spiral wound, and hollow fiber, as well as materials such as inorganic, polymeric, and composite membranes. They can also be symmetric or asymmetric. Nowadays, polymeric hollow fiber is the most applied in the biogas industry due to its high selectivity performance and high temperature and mechanical strength. However, the application of membrane technology is limited to moderate flow rates, as performance decrease with the increment of feed flow also, more modules are required to treat higher flow rates. Regarding membrane supplies, Evonik and Air Liquide are the leading suppliers in the market.

As represented in Figure 2, before the biogas goes into the multi-stage membrane system it is required a cleaning step to remove pollutants such as oxygen, hydrogen sulfide, nitrogen, hydrogen and water vapor to avoid damage in the pipeline. The first step is performed by an activated carbon column filter.

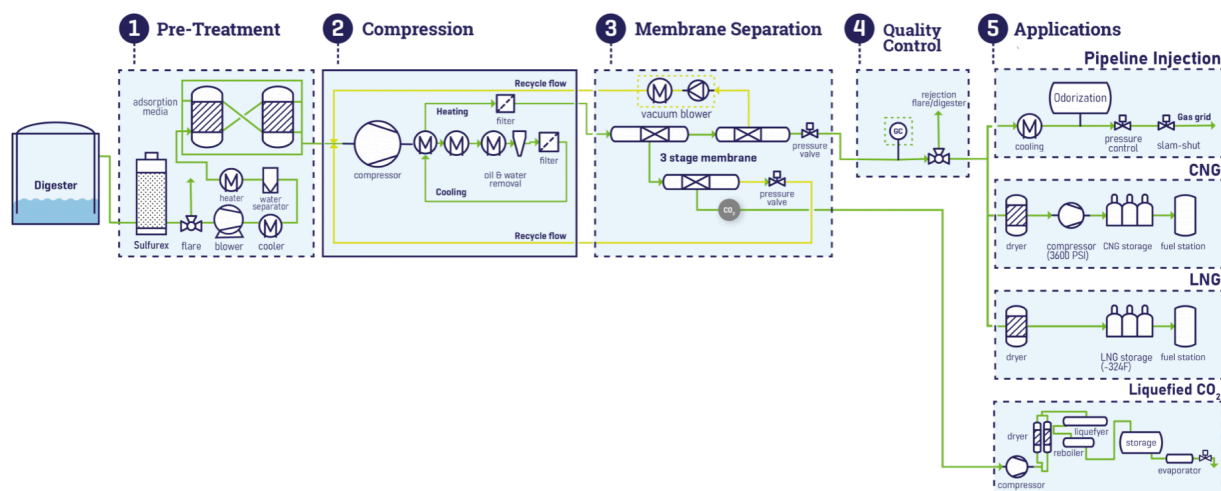


Figure 2. Schematic representation of DMT biogas upgrading plant Carborex® MS, adapted from [17].

Once the biogas is free from H₂S and other pollutants, the gas goes to the compression stage to be pressurized up to 18 bar followed by an air-cooled compressor and condensate discharge to reach temperatures between 25 °C and 40 °C before entering the membrane.

In the multi-stage membrane system, DMT Environmental Technology designs two plants regarding the membrane model: 2-stage and 3-stage. In the 2-stage biogas plant, the biogas enters the first membrane where the retentate stream will be treated on the second stage while the permeate is sent to the liquefaction unit as contains mainly CO₂. The retentate of the second stage is the biomethane stream while the permeate is recycled back to the first stage. The scheme of 2-stage can be visualized in Figure 3.

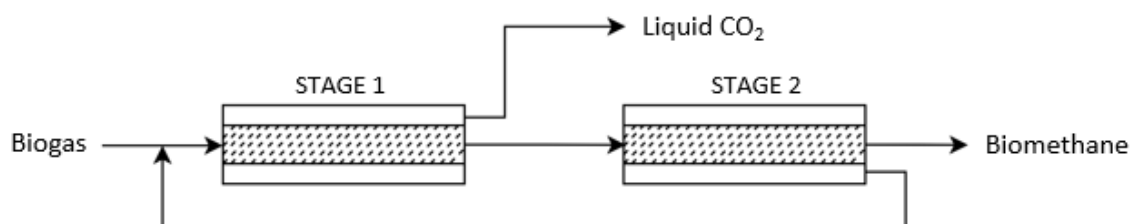


Figure 3. Schematic representation of a 2-stage membrane system to treat biogas.

Due to the high amount of CH₄ on the permeate stream provided by the first stage, a three-stage is proposed by adding one membrane stage to polish the tail gas which is represented in Figure 4. With that, the permeate of the third stage consists of a purer CO₂-rich stream to be dropped in the liquefaction unit while the retentate is recycled back to the first stage for methane recovery. This stage is more established in European projects once the European legislation requires a higher level of purity of biomethane.

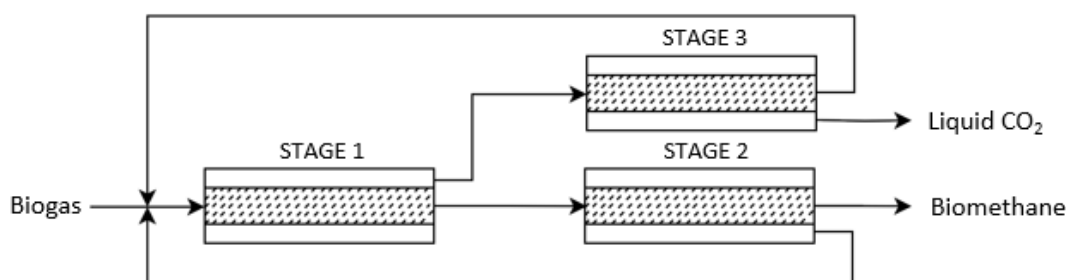


Figure 4. Schematic representation of a 3-stage membrane system to treat biogas.

2.2.2 CarboCap

The increase in the CO₂ emission rate has set companies, including DMT, to innovate and develop a strategy to recovery the tail gas from the biogas upgrading plant. Converting the tail-gas into liquid allows not only reduce emissions to atmosphere but also increase the company revenue. The integrated system of Carborex® MS and CarboCap is represented in Figure 5.

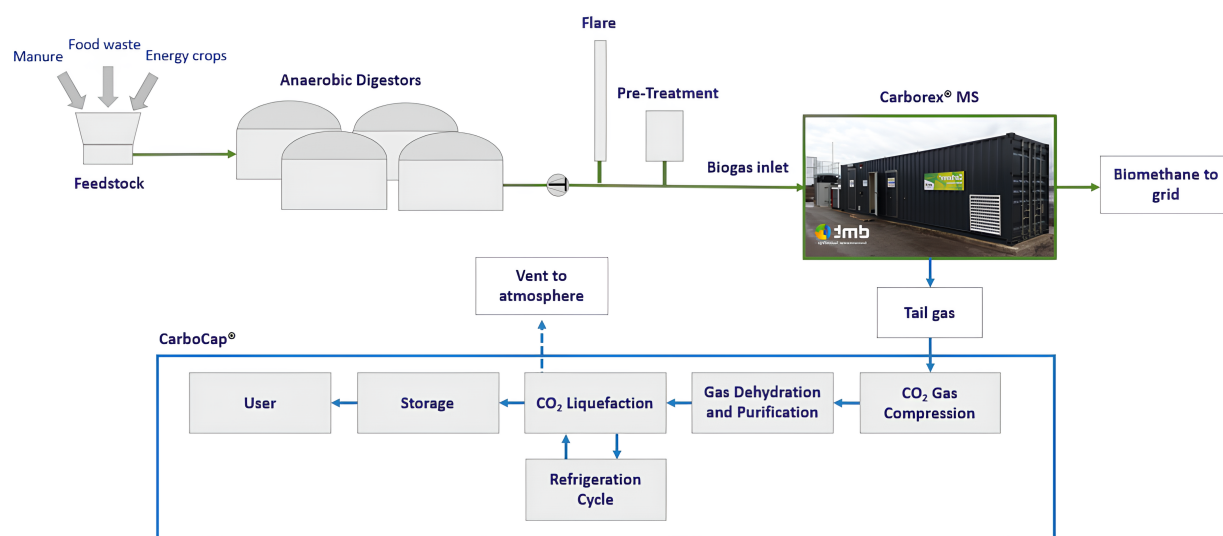


Figure 5. Schematic representation of the integrated system.

Before entering the liquefaction part, the tail gas requires to be compressed to obtain a higher pressure thus a pre-treatment such as dehydration is required. Then, the CO₂ liquefaction occurs in two main unit in CarboCap: condenser and cryogenic distillation.

The condenser, also referred to as a heat exchanger, is a crucial unit in the operation that facilitates the condensation of gas molecules by extracting heat from the stream. In industrial processes, the design of a condenser is tailored to achieve the desired product composition, often necessitating the incorporation of a refrigeration unit.

The condenser receives the stream from the top and releases it from the bottom. During this process, the cooling fluid interacts with the feed stream, facilitating heat exchange. To ensure adequate cooling and the release of latent heat, the refrigeration unit must be appropriately designed to provide sufficient power and heat. Thus, DMT has invested in a plate and shell condenser in its plants.

The calorific power that the cooling stream receives is equal to the calorific power released in the condensation which is described in Equation 5. The left hand of the equation is regarding the cooling fluid wherein the mass flow of the cooling fluid is represented by $\dot{m}$, C_p is the heat capacity while T_{out} is the room temperature and T_{in} is the temperature of the fluid. The right hand is related to phase variation where the λ is the latent heat while $\dot{m}$ is the vapor mass flow rate.

$$\dot{m}_{CoolingFluid} C_{p,CoolingFluid} (T_{out} - T_{in}) = \dot{m}_{vapor} \lambda_{vapor} \quad (5)$$

In addition, the basic equation which describes the heat transfer between two fluids is given by Equation 6. The heat transfer is nominated as $\dot{Q}$ wherein the overall heat transfer coefficient is represented by U . Thus, A is the area of the condenser and ΔT is the temperature difference between the hot and cold fluids [18].

$$\dot{Q} = U A \Delta T \quad (6)$$

Alongside the condenser, the cryogenic distillation plays a vital role as a separation technique in which applies low temperatures to separate components based on their different condensation points.

The operational mechanism of cryogenic distillation involves introducing it into a distillation column, utilizing countercurrent vapor-liquid flow for separation. Components with similar boiling points can be separated effectively by exploiting the temperature difference created during pre-cooling and expansion. The process requires careful control of temperature, pressure, and flow rates to optimize separation efficiency and achieve desired purity levels.

During the CO₂ liquefaction process, methane is released at the top of the column due to its lower condensation point alongside a small amount of non-condensed CO₂. The cryogenic column operates at the CO₂ saturation conditions of temperature and pressure depicted in Figure A.1. CO₂ undergoes condensation as it progresses through the column and is collected at the bottom. This separation process is visually represented in Figure 6 offering a clear representation of the mechanism involved. Due to the low operating temperatures, a refrigeration system is required.

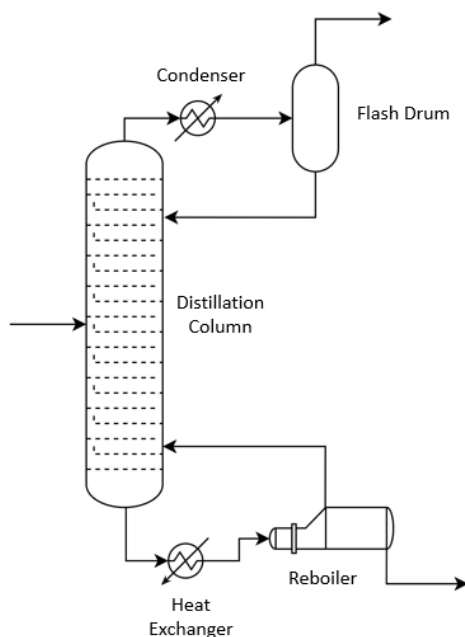


Figure 6. Cryogenic distillation setup for CO₂ liquefaction

Several designs are established, such as packed bed, anti-sublimation, and structured packing to force contact between vapor and liquid. Optimizing the column density increases residence time, leading to improved efficiency. The cryogenic method allows to achieve of a high-purity liquid product that satisfy CO₂ purity legislation. However, due to the exceptionally low dew point of CO₂, there is a significant increase in energy consumption [19].

DMT developed a new strategy on the liquefaction unit to deal with the CO₂-rich stream from Carborex® MS. The concept is to cool down the stream leading to the condensation of CO₂ while methane remains gaseous. The tail gas provided from the biogas upgrading facility is at a low pressure and a conditioning step is required to increase the pressure up to 20 bar. After that, a pre-treatment is followed to remove small amounts of pollutants, such as VOC's and water vapor to avoid damage and freezing along the unit. Then, DMT set a carbon-based drying system to dehydrate the gas before sending it to two pressure-temperature swing adsorption (PTSA) column to execute in a continuous way and remove pollutants.

Additionally, in the CO₂ liquefaction unit developed by DMT Environmental Technology, which operates as an open-loop system, a purge stream is presented releasing minor quantities of CH₄ and non-condensed CO₂ into the atmosphere. This emission is commonly known as slip and is calculated by comparing the molar flow in the purge stream to the molar flow in the inlet stream. Equation 7 represents this correlation, where the variable i can be replaced with either CO₂ or CH₄ depending on the particular gas under consideration.

$$Slip_i (\%) = \frac{\text{Molar flow rate of } i \text{ in purge stream}}{\text{Molar flow of } i \text{ in feed stream}} \quad (7)$$

In order to meet the purity requirements proposed by the food industry and provide the most accurate liquid CO₂, the product stream from the liquefaction unit must have at least: 99 % v/v CO₂ purity, 20 ppm v/v of water vapor, 30 ppm v/v of oxygen and 50 ppm v/v of total volatile hydrocarbon [20].

3 Computer Application ChemCAD

Simulation and modelling strategies are essential to develop or optimize chemical processes and software tools are extensively used to achieve faster designs. DMT invests in an annual license of ChemCAD to run the engineering simulations as its more user-friendly and intuitive compared to other software such as Aspen.

In this study, ChemCAD was used to simulate several scenarios for the recovery of the purge stream of the liquefaction unit and identify the most suitable setups. Setting up the model for running the simulations followed the following steps: selecting thermodynamics models, selecting chemical compounds; specifying engineering units; adjusting variables input.

3.1 Thermodynamics Models

Setting up a thermodynamic model is crucial once it enables accurate calculations and predictions of the system's behaviour. Thus, selecting the most suitable thermodynamic package for enthalpy and equilibrium-K satisfy reliable results avoiding convergence problems.

The PRSV thermodynamic method consists of the Peng-Robinson (PR) cubic equation with a significant improvement of Soave-Redlich-Kwong (SRK) to provide more accurate predictions over vapor-liquid equilibrium, enthalpy and phase behavior [21].

The use of PRSV (Peng-Robinson Soave-Redlich-Vapor) equation of state in simulating the process of CO₂ liquefaction is advantageous since it provides a reliable forecast result for the conditions typically encountered in the liquefaction process.

The negative temperatures involved in CO₂ liquefaction, often below its critical temperature, necessitate an equation of state capable of handling the non-ideal behavior and phase transitions that occur. Additionally, the high pressures employed in the liquefaction process further contribute to the non-ideal behavior of CO₂. Thus, the PRSV is well-suited for modeling CO₂ liquefaction because it considers important factors such as intermolecular interactions, molecular size, and the presence of multiple phases [22, 23].

3.2 Component Selection

Once the appropriate thermodynamic method is chosen, the subsequent procedure involves incorporating the components that will be engaged in the process. Biogas is a renewable gas that can be obtained from different sources, including landfills, manure, wastewater and others, therefore, a variety

of CH₄ and CO₂ composition was considered, as detailed in Table 2. As most typical composition 50.17 % of CH₄ and 40.43 % of CO₂ has been applied in several scenarios.

In addition, it was considered that no hydrogen was entering in the feed stream to avoid convergence issues. For all simulation the biogas inlet flow was set at 1000 Nm³·h⁻¹.

Table 2. Biogas composition variation for input data

Component	Composition /%						
	Study 1	Study 2	Study 3	Study 4	Study 5	Study 6	Study 7
CH ₄	52.17	46.17	48.17	50.17	54.17	56.17	58.17
CO ₂	40.43	46.53	44.54	42.54	38.54	36.54	34.54
N ₂	0.37	0.37	0.37	0.37	0.37	0.37	0.37
O ₂	0.09	0.09	0.09	0.09	0.09	0.09	0.09
H ₂ O	6.83	6.83	6.83	6.83	6.83	6.83	6.83

3.3 Simulation Units

After selecting the thermodynamics model and components, the final step is selecting the operating units and setting the parameters.

The units studied in this project were incorporated within the framework of an existing process flow diagram in ChemCAD. Hence, all three units were add to the same process flow diagram where dividers were introduced to direct the flow towards a particular unit and bypass the units not. Figure A.1 illustrates the existing process flow diagram, wherein the green box represents the Carborex® MS system, while the liquefaction unit, also referred to as CarboCap, is gray. Moreover, these units were strategically positioned after the main condenser in the liquefaction unit, to effectively treat the non-condensed flow emitted from it.

For the membrane configuration, also known as “stage X”, the membrane modules were the same as present in the membrane system in Carborex. The membrane unit added consisted in a hollow-fiber type operating at counter current as provide large membrane surface area per unit volume, good flexibility and easily handling [24, 25] .

In order to obtain the optimal operating conditions and evaluate the feasibility of the process it is required to add the permeance data to the simulations. This information allows the user to analyze the degree of separation achieved and the composition of the streams. Thus, by adding the permeance data it is possible to study the effect of varying parameters such as pressure, temperature and membrane properties.

One alternative way to obtain the permeance is by the Arrhenius equation. The Arrhenius equation correlates that the permeance of a substance is exponentially dependent on the activation energy and inversely related to the temperature. As shown in Equation 8, the permeance is increased when a higher operating temperature is preferred [26]. The permeance are represented by Q_i and Q_0 while R is the gas constant, E_a is the activation energy and T is the temperature.

$$Q_i = Q_0 \exp\left(\frac{-Ea}{RT}\right) \quad (8)$$

The information related to Q_0 and Ea was provided by the supplier while the Q_i was adjusted according to DMT standards.

In these base cases, the purge stream was released into the atmosphere without undergoing any treatment or modifications within the process. This approach was taken to establish a benchmark and evaluate the potential impact of where to locate the recycle stream from the added unit in further simulations. By examining the base cases, it provides a reference point for comparison against alternative scenarios where measures are implemented to address the treatment of the purge stream. The base cases for the 2-stage model are represented by Figure 7.

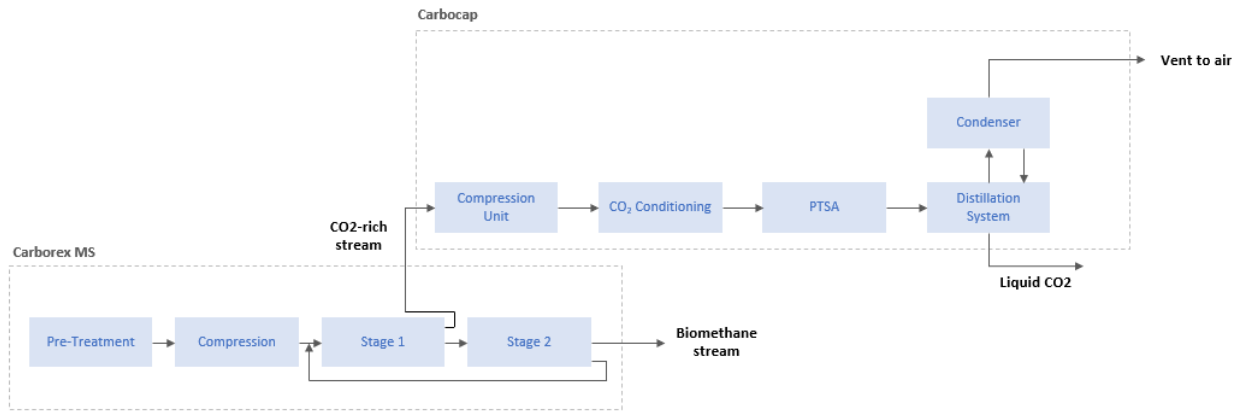


Figure 7. Block diagram for the base configuration in a 2-stage model

For the 3-stage model, the base scenario is stated in Figure 8.

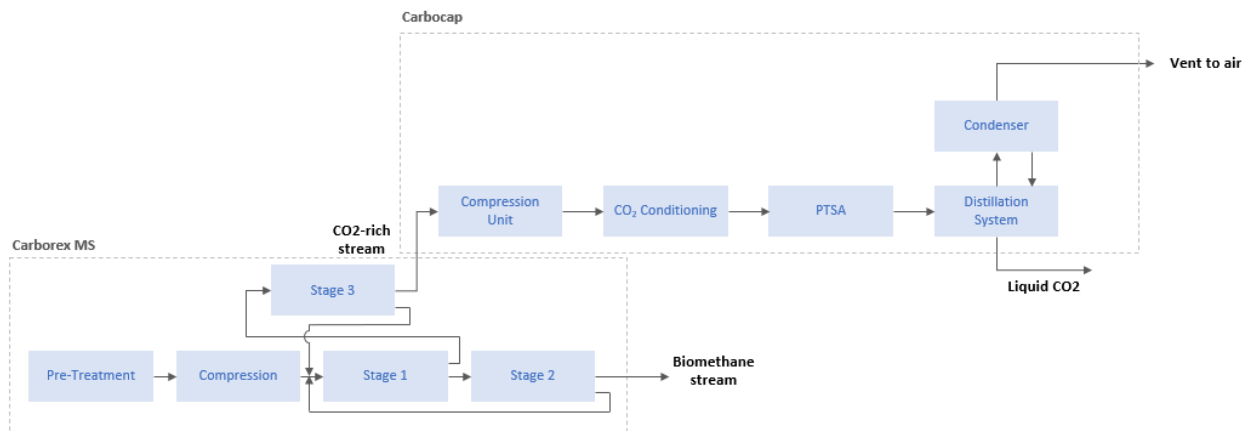


Figure 8. Block diagram for the base configuration in a 3-stage model.

For the recycle tie-in configuration, no equipment addition was required. Therefore, the strategy to close the loop was to connect the exit of the main condenser to the compression unit, located in the Carborex. Figure 9 shows the block diagram for 2-stage model.

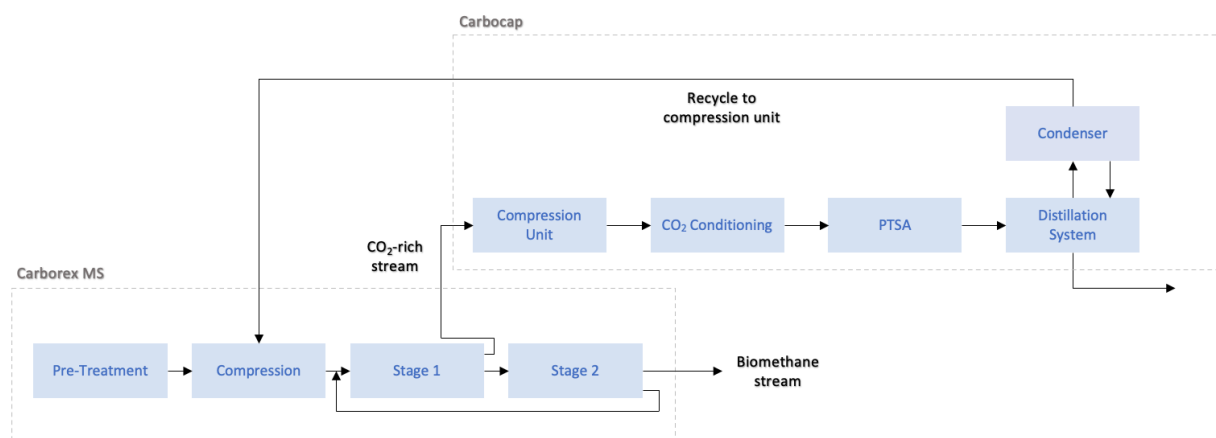


Figure 9. Block diagram for recycle tie-in configuration in a 2-stage model.

The 3-stage setup for the recycle tie-in configuration are presented in Figure 10.

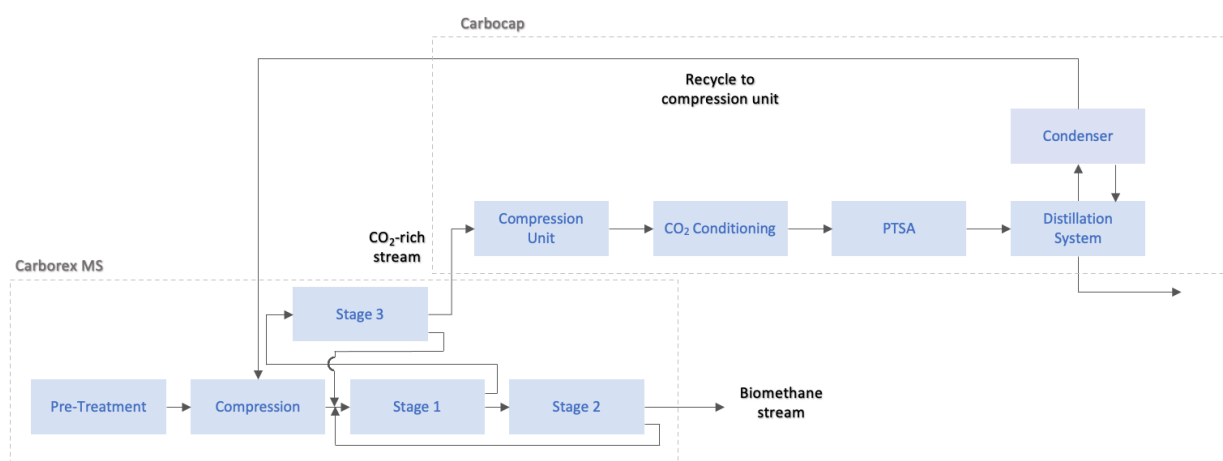


Figure 10. Block diagram for recycle tie-in configuration in a 3-stage model.

Another proposed strategy by DMT to recovery non-condensed CO₂ on the purge stream is adding a second condenser to cool down the gas stream from the first condenser. The liquid CO₂ outlet will flow down to the cryogenic distillation while the remaining non-condensable gas will be recycled to the compression unit, in Carborex.

The second condenser consists of a fixed head exchanger type with carbon steel material and is connected to a closed-loop refrigeration unit using a refrigerant. The condensation temperature is pre-set to -42.5 °C, two and a half degree above the maximum operating temperature of the first condenser, in order to condensate the maximum amount of CO₂ available. Figure 11 illustrate the block diagram for the 2-stage model.

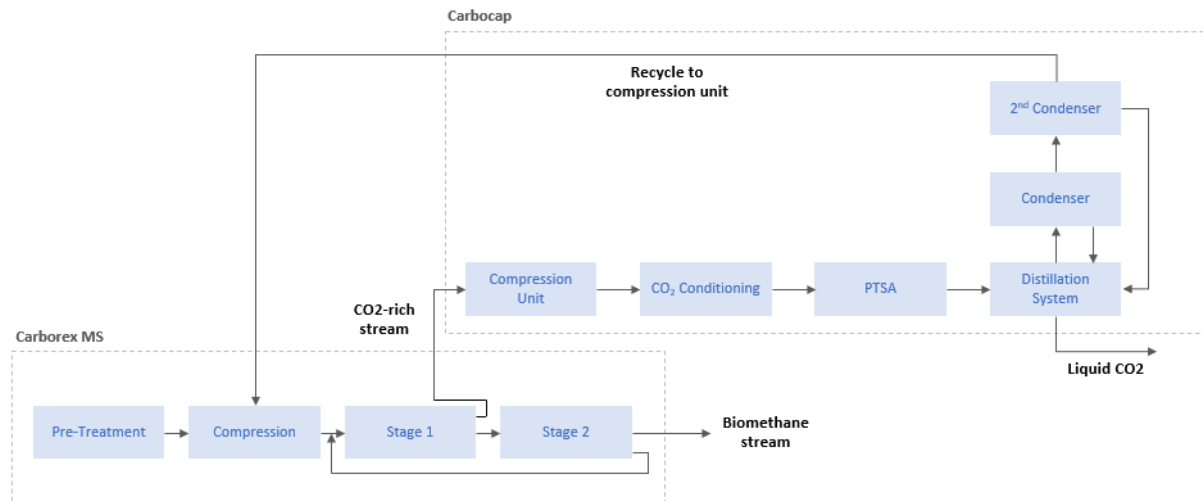


Figure 11. Block diagram for second condenser configuration in a 2-stage model.

In addition, the 3-stage model setup considering the second condenser are illustrated by Figure 12.

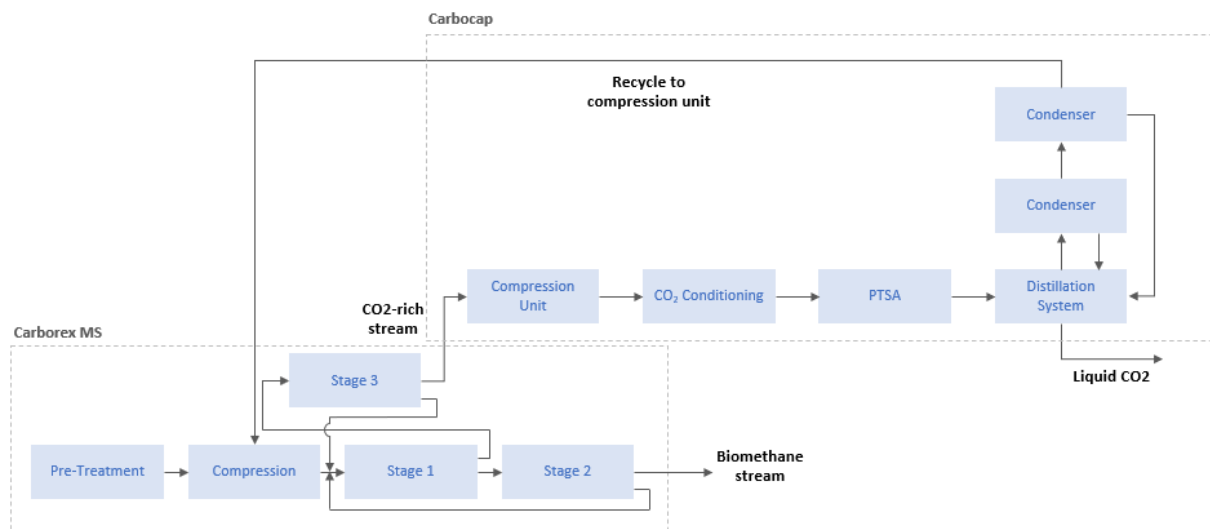


Figure 12. Block diagram for second condenser configuration in a 3-stage model.

Thus, for the membrane configuration, the permeate flow of the stage X was connected to the entrance of the liquefaction unit as this flow is mainly composed of CO₂. At the same time, the retentate flow, composed mainly by methane and small amounts of CO₂ is connected to the biomethane stream instead of the compression unit. This was established as the flow rate on the retentate side is small and the high content of methane made it not being necessary to be treated again. Figure 13 display the membrane configuration setup for 2-stage model.

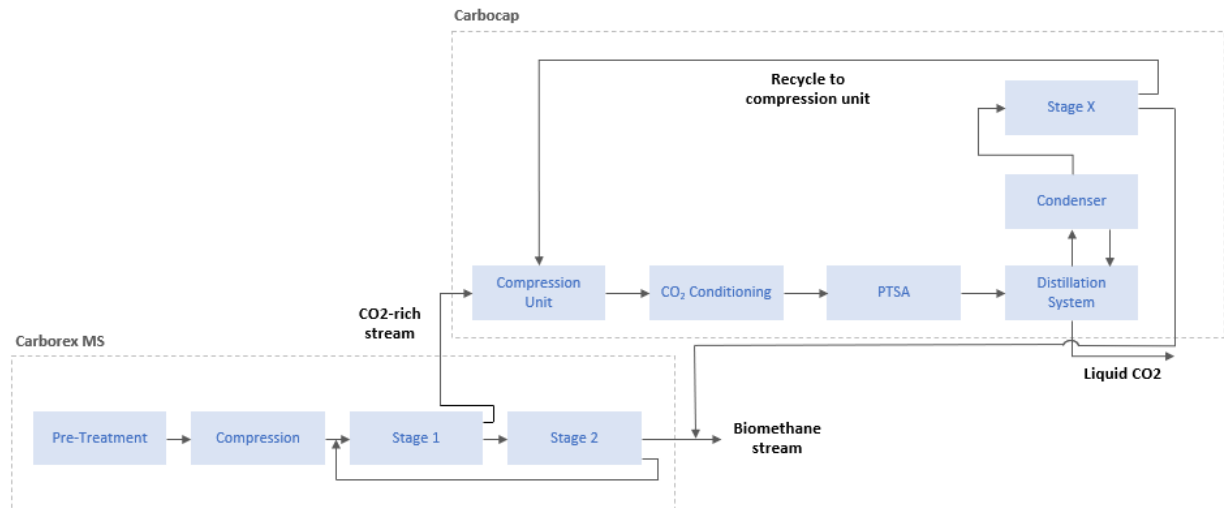


Figure 13. Block diagram for the membrane configuration in a 2-stage model.

The membrane configuration for the 3-stage model is shown in Figure 14.

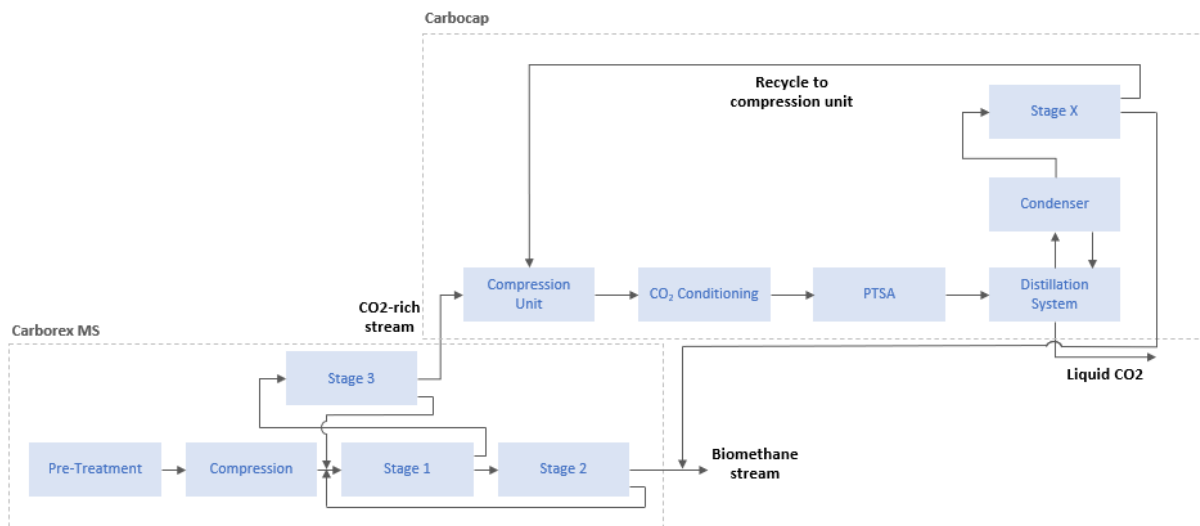


Figure 14. Block diagram for the membrane configuration in a 3-stage model.

In the 2-stage membrane simulations, the permeate pressure of the liquefaction membrane was adjusted to match the permeate pressure of stage 1 in the upgrading unit. Conversely, in the 3-stage model, the permeate pressure of the liquefaction membrane was set equal to the permeate pressure of stage 3.

3.4 Simulation Variables

To study the recovery of the purge stream of the upgrading plant, three types of variables were applied: adjustment variables, study variables and control variables.

- The adjustable variables consist of variables modified in ChemCAD to achieve the values of the control variables. The adjustable variables consisted of:
 - Number of membranes in the membrane system.
 - Pressure in the permeate side for the membrane stages.
 - Heat in the reboiler of the cryogenic column.

Note: The membrane configuration scenarios require additional adjustment such as:

- Number of membranes of the stage X.
- Pressure in the permeate side for the membrane of the stage X.
- The study variables are user-defined variables which allow the study of the behaviour of this variable in the system. The study variables consisted of:
 - Temperature of the main condenser.
 - Feed pressure of stage 1.
 - Biogas composition.
 - Tail gas composition.
- The control variables serve to guarantee that the outputs are in accordance with the proposed DMT study. The control variables consisted of:
 - Methane concentration in the biomethane stream.
 - Methane concentration in the tail gas.

Figure B.1 schemes the flow chart which describes the strategy adopted to run the simulations to introduce the variables.

The simulations conducted in this study were categorized into three major cases wherein for each of them all three units, stage X, condenser and recycle tie-in, were evaluated:

- First case examined the variation of the condenser temperature.
- Second case analysed the changes in the biogas composition.
- Third case investigated the variations in the tail-gas composition.

To investigate the variation of condenser temperature, the methane biogas composition for this study was set as study 1, from Table 2. Thus, Table 3 displays the control variables and the study variables wherein the temperature of the primary condenser varies across -40.0 °C, -37.5 °C, -35.0 °C, -32.5 °C, -30.0 °C, -27.5 °C, and -25.0 °C.

Table 3. Variables ranges for the study 1 evaluate to analyse the temperature behaviour.

Study	1							
Membrane Model	2-stage				3-stage			
Feed Pressure /bara	16.5	16.5	10.5	10.5	16.5	16.5	10.5	10.5
Temperature	-40 — -25	-40 — -25	-40 — -25	-40 — -25	-40 — -25	-40 — -25	-40 — -25	-40 — -25
Composition in biomethane /%								
CH ₄	97	90	97	90	97	90	97	90
CO ₂	2	9	2	9	2	9	2	9
Composition in tail gas /%								
CH ₄	5	5	5	5	0.5	0.5	0.5	0.5
CO ₂	95	95	95	95	99	99	99	99

To investigate the variation in biogas composition, studies 1 to 7, from Table 2, were chosen. Additionally, the study variables and control variables utilized in this analysis are presented in Table 4.

Table 4. Variables ranges for the study 1 to 7 to analyse the methane variation in the biogas flow.

Study	1 - 7			
Membrane Model	2-stage		3-stage	
Pressure /bara	16.5	10.5	16.5	10.5
Temperature	-27.5	-27.5	-27.5	-27.5
Composition in biomethane /%				
CH ₄	97	90	97	90
CO ₂	2	9	2	9
Composition in tail gas /%				
CH ₄	5	5	0.5	0.5
CO ₂	95	95	99	99

In order to examine the variation of methane concentration in the tail-gas, study 1 was selected to as the biogas composition. The study variables and control variables are presented in Table 5.

Table 5. Variables ranges for the study 1 evaluation to analyse the methane variation in the tail gas.

Study	1	
Membrane Model	2-stage	3-stage
Pressure /bara	10.5	10.5
Temperature	-40	-40
Composition in biomethane /%		
CH ₄	97	97
CO ₂	2	2
Composition in tail gas /%		
CH ₄	3	0.4
	4	0.5
	5	0.55
	6	0.7
	7	0.85
	8	1
	9	-
CO ₂	96	99
	95	99
	94	98
	93	98
	92	98
	91	98
	90	-

3.5 Optimization Boundaries Methodology

The optimization methodology was performed to identify the most viable scenarios and boundaries. The analysis focused on assessing various parameters, such as:

- Recycle flow rate.
- CO₂ recovery.
- CH₄ recovery.
- Investment cost
- Power consumption.

The maximum acceptable recycle flow rate was set at 9.5 % of the biogas inlet flow to the upgrading unit to avoid disturbance. Thus, a higher flow rate requires larger equipment in the upgrading plant, such as vessels, pumps, and pipelines.

The recovery parameter evaluates, quantifies, and measures the efficiency and effectiveness of a process. Specifically, for CO₂ recovery, it involves comparing the amount of CO₂ present in the liquid CO₂ flow exiting the liquefaction unit to the amount of CO₂ in the biogas, presented by Equation 9. Similarly, the CH₄ recovery consists in analyzing the methane composition in the biomethane stream exiting the Carborex® MS unit and comparing it to the methane composition in the biogas, presented by Equation 10.

In addition, dividing the recovery by $(1 - x_{H_2O})$ allows normalizing the mass flow rates to a dry basis, eliminating the contribution of water. By performing so, the analysis and comparison of the composition and quantities of the dry flow is more accurate.

$$Recovery_{CO_2} = \frac{\frac{L x_{LCO_2}}{F x_{FCO_2}}}{(1 - x_{H_2O})} \quad (9)$$

$$Recovery_{CH_4} = \frac{\frac{P x_{PCH_4}}{F x_{FCH_4}}}{(1 - x_{H_2O})} \quad (10)$$

The investment cost includes the prices of membranes A and B, which are installed in Carborex® MS and CarboCap, respectively. Additionally, new units such as the second condenser are added. The price of membrane B is denoted as X euros, while membrane A is priced at 2.7 times that of membrane B due to its larger area. The inclusion of the second condenser incurs a financial cost equivalent to 9.23 times the price of membrane B. Power consumption is specifically associated with the compressors in Carborex® MS and CarboCap.

The selection of the most feasible scenarios was divided into categories:

- Condenser temperature optimization

In this step, the analysis was done for the scenarios in which the primary condenser temperature varied. This evaluation took into consideration the membrane model (2-stage or 3-stage), methane concentration in the biomethane stream (90 % or 97 %) and both operating pressure (16.5 bara or 10.5 bara). The main goal of this category is to find the most suitable temperature range.

- Unit selection for the variation of methane concentration in the biogas flow

In this step, the analysis was made for the scenarios in which the methane concentration in the biogas varied. The evaluation was made considering the membrane model (2-stage or 3-stage), the methane concentration in the biomethane stream (90 % or 97 %), the operating pressure (16.5 bara or 10.5 bara). For each concentration, ranging from 48.17 % to 56.17 % of methane entering the upgrade unit, the best unit was obtained.

- Unit selection for the variation of the methane concentration in the tail-gas

In this step, the analysis was done for the scenarios in which the methane concentration in the tail-gas varied. For each concentration, ranging from 3 % to 9 % or 0.4 % to 1.0 %, of methane entering the CO₂ liquefaction unit, depending on the membrane setup. The analysis was done for the methane concentration in the biomethane stream of 97 %, operating at the high and low pressure (16.5 bara or 10.5 bara). This category was carried out twice considering the 2-stage and 3-stage membrane setup.

4 Results and discussion

In this chapter, the main results from ChemCAD simulations are presented and discussed. Hence, this section is divided into two sub-sections: 2-stage and 3-stage. For both sub-sections, the sensitivity analysis was performed under different configurations to evaluate the studied variables behaviour.

4.1 2-Stage

4.1.1 Temperature Behaviour

The sensitivity study to analyse the temperature variation of the primary condenser was performed for the case of 90 % methane in the biomethane stream and 5 % methane in the tail-gas. Additionally, an analysis was done for comparison purposes using the case of 97 % methane in the biomethane stream and 5 % methane in the tail-gas. Both studies were performed for operating pressures of 16.5 bara and 10.5 bara. The study conducted at temperatures of -25.0 °C exhibited low process efficiency due to the high temperature and lack of pressure to condensate the CO₂ resulting in convergence issues in ChemCAD. Consequently, it was determined that the evaluation of the study's feasibility was not viable.

The purity of the liquid CO₂ stream must be greater than 99.90 % to be acceptable to the food industry. As shown in Figure 15, for the membrane and recycle tie-in configurations, the purity increases with increasing temperature once less methane is condensed along with the CO₂. Thus, the operating temperature of -40.0 °C and -37.5 °C demands more heat fed to the reboiler, illustrated in Figure 15, to evaporate part of the condensed methane before it exits along with the liquid CO₂. The second condenser configuration achieved 99.99 % of purity with 0.01 % of methane for all operating temperatures once the operating temperature of -42.5 °C allowed large amount of uncondensed CO₂ from the first condenser to condense.

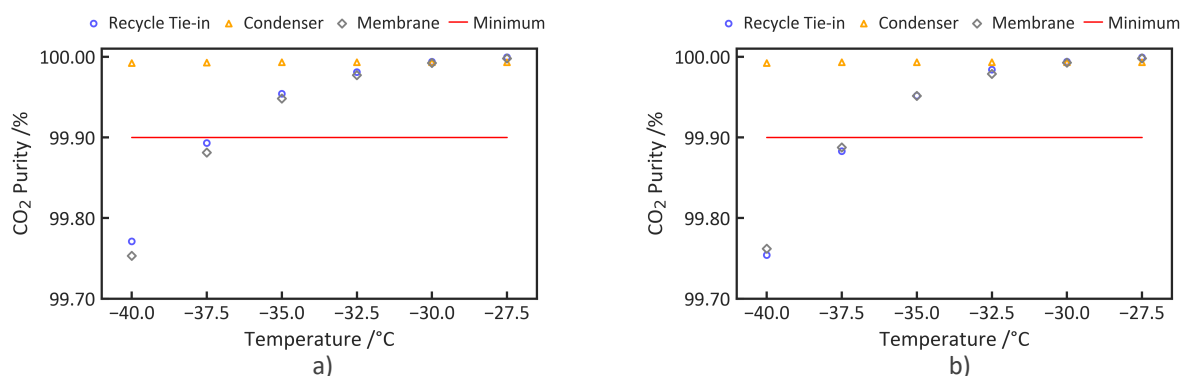


Figure 15. CO₂ Purity for temperature behaviour study in 2-stage model and 90 % of methane in biomethane wherein
a) high pressure b) low pressure.

As no heat was added in these scenarios, Figure 15 is mainly displaying the lack of reboiler heat duty to compensate the overcooling and therewith capturing of inerts in the liquefaction unit. If extra reboiler heat input would have been used, the quality could have been maintained.

As seen in Table 6, Table 7 and Table 8, the variation in the feed pressure does not cause a significant variation in the output flows of the upgrading facility. Therefore, the produced flow of biomethane and liquid CO₂ was the same for the three units studied. Nevertheless, the decrease from 16.5 bara to 10.5 bara directly affects the number of membranes needed at Carborex® MS. The decreased pressure leads to a lower pressure difference of the membrane system in Carborex® MS, reflecting on the separation efficiency.

Increasing the temperature from -40.0 °C to -27.5 °C directly affects the retentate and permeate flow. Higher operating temperatures in the main condenser led to an increase in the amount of non-condensed CO₂ and CH₄. As seen in Table 6, regardless of the operating pressure, temperatures higher than -30 °C are unfeasible due to generating of a recycle flow above the limit imposed by DMT. Therefore, scenarios 3, 4, 21 and 22, are suitable for implementation as the flow rate is satisfactory.

Table 6. Membrane simulation data for temperature behaviour study in 2-stage model and 90 % of methane in biomethane.

Parameters	Main Condenser Temperature /°C											
	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5
Pressure	High						Low					
Biomethane /Nm ³ ·h ⁻¹	621.4	621.9	622.8	621.9	621.7	623.1	620.3	621.6	623.2	623.1	622.2	623.2
Tail gas /Nm ³ ·h ⁻¹	398.3	398.6	398.6	400.9	398.6	398.6	402.9	402.9	402.9	405.9	401.6	405.4
Stage 1 Modules /unit	2	2	2	2	2	2	4	4	4	4	4	4
Stage 2 Modules /unit	2	2	2	3	2	2	7	7	7	7	7	8
Liquid CO ₂ /kg·h ⁻¹	742.2	741.7	740.5	742.5	743.1	740.1	744.7	742.5	739.8	739.9	741.9	739.9
Stage X												
Module /unit	1	1	1	2	2	2	1	1	1	1	1	2
Pressure /bara	1.1	1.1	1.1	1.1	1.1	1.1	2.2	2.2	2.2	2.2	2.2	2.2
Permeate Flow /Nm ³ ·h ⁻¹	31.8	39.6	50.0	65.1	107.2	164.5	31.2	38.9	49.2	63.2	108.4	164.7
Retentate Flow /Nm ³ ·h ⁻¹	19.7	20.6	21.4	22.8	20.3	21.7	23.2	24.5	26.1	29.0	23.8	28.5
Simulation Index												
Scenario	1	2	3	4	5	6	19	20	21	22	23	24

As expected, the same behaviour on the membrane configuration was seen in the recycle tie-in configuration. As presented in Table 7, the recycle flow increased along with the temperature increase due to non-condensed CO₂ and CH₄ throughout the process. The addition of the recycle tie-in required more modules on the Carborex® MS membrane system when operating at 10.5 bara as the tie-in location is directly connected to the compression unit, in the upgrading unit, increasing the flow rate entering the membrane system. Furthermore, recycling is not characterized as an exciting strategy for temperatures in the primary condenser higher -32.5 °C due to a large recycled flow. Furthermore, for more extreme temperatures, -40.0 °C and -37.5 °C, it is necessary to add heat to the reboiler. In this case, the most attractive scenarios are: 9 and 27.

Table 7. Recycle tie-in simulation data for temperature behaviour study in 2-stage model and 90 % of methane in biomethane.

Parameters	Main Condenser Temperature /°C											
	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5
Pressure	High						Low					
Biomethane /Nm ³ ·h ⁻¹	620.9	622.4	623.6	623.2	623.3	621.0	622.1	623.2	621.8	621.0	623.6	622.3
Tail-gas /Nm ³ ·h ⁻¹	436.1	443.8	455.1	476.8	522.8	706.1	429.8	437.8	454.1	491.7	523.6	673.5
Stage 1 Modules /unit	3	3	3	3	3	4	4	4	4	5	5	6
Stage 2 Modules /unit	4	4	4	4	4	4	7	7	7	7	7	6
Liquid CO ₂ /kg·h ⁻¹	743.1	741.0	738.9	739.8	739.6	744.6	741.0	739.2	742.5	743.7	739.4	741.5
Recycle Tie-in												
Flow Rate /Nm ³ ·h ⁻¹	57.0	66.2	78.6	100.1	146.1	327.0	51.9	61.0	75.9	112.6	147.3	295.7
CH ₄ Composition /%	38.4	33.5	28.3	22.9	17.2	11.2	38.4	33.5	28.3	22.9	17.2	11.2
CO ₂ Composition /%	60.0	65.1	70.5	76.2	82.1	88.3	60.0	65.1	70.5	76.2	82.1	88.3
Simulation Index												
Scenario	7	8	9	10	11	12	25	26	27	28	29	30

The second condenser configuration also required more modules, as presented in Table 8, within the membrane system at 16.5 bara as the recycle flow goes back to the compression unit, in the Carborex. The recycle remained constant since the second condenser operating at -42.5 °C achieves a high conversion rate of the non-condensed CO₂ coming from the first condenser. Therefore, all unit are suitable to recover the purge.

Table 8. Condenser simulation data for temperature behaviour study in 2-stage model and 90 % of methane in biomethane

Parameters	Main Condenser Temperature /°C											
	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5
Pressure	High						Low					
Biomethane /Nm ³ ·h ⁻¹	621.7	621.7	621.7	621.7	621.7	621.7	622.8	622.8	622.8	622.8	622.8	622.8
Tail-gas /Nm ³ ·h ⁻¹	429.9	429.9	429.9	429.9	429.9	429.9	425.8	425.8	425.8	425.8	425.8	425.8
Stage 1 Modules /unit	3	3	3	3	3	3	4	4	4	4	4	4
Stage 2 Modules /unit	4	4	4	4	4	4	7	7	7	7	7	7
Liquid CO ₂ /kg·h ⁻¹	743.2	742.5	742.4	742.8	742.6	742.7	740.9	740.9	740.7	740.6	741.1	740.6
2 nd Condenser												
1 st Condenser Gas Flow /Nm ³ ·h ⁻¹	58.6	68.3	82.9	106.5	151.9	274.0	55.1	64.2	77.8	100.1	142.8	257.2
2 nd Condenser Gas Flow /Nm ³ ·h ⁻¹	51.7	51.6	51.7	51.7	51.7	51.7	48.5	48.5	48.5	48.5	48.6	48.5
Simulation Index												
Scenario	13	14	15	16	17	18	31	32	33	34	35	36

The biomethane flow contains 9.0 % to 9.4 % of CO₂ which represents 55.89 Nm³·h⁻¹ to 58.62 Nm³·h⁻¹ sent to the grid, regardless of the configuration and pressure setup leading to an average recovery of 86.85 %. The amount of CO₂ sent to the grid directly affects the CO₂ recovery as is represented in Figure 16.

The CH₄ recovery, presented in Figure 17, increased as the operating temperature increased once more methane was being recycled back instead of being condensed alongside the CO₂. Besides the high recovery when operating at -30 °C and -27.5 °C, the elevated recycle flow within these simulations made it unfeasible.

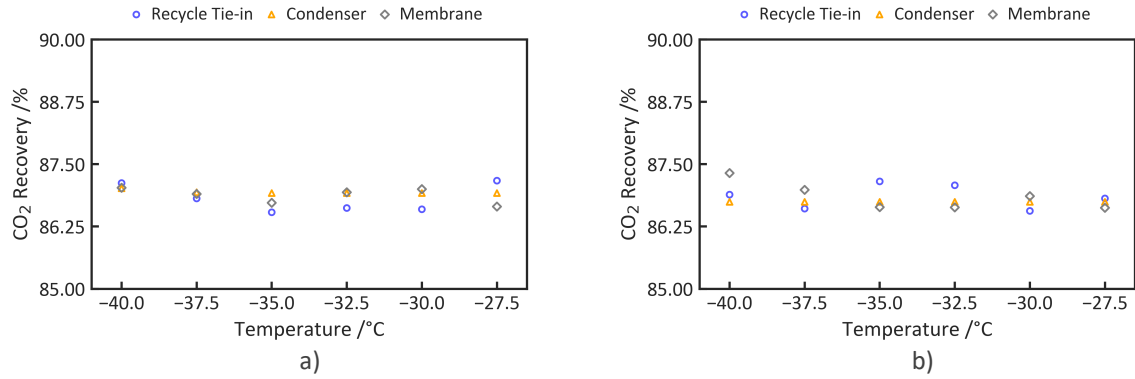


Figure 16. CO₂ Recovery for temperature behaviour study in 2-stage model and 90 % of methane in the biomethane wherein
a) high pressure b) low pressure

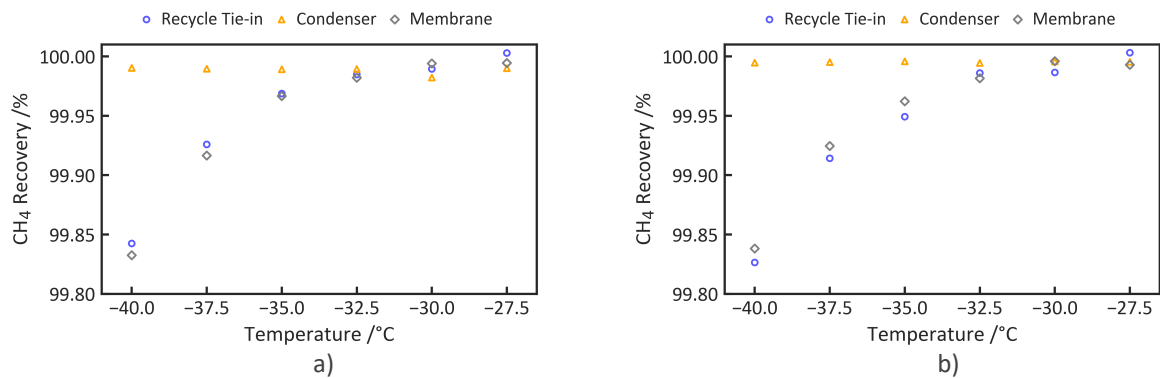


Figure 17. CH₄ Recovery for temperature behaviour study in 2-stage model and 90 % of methane in the biomethane wherein
a) high pressure b) low pressure

The power consumption is directly related to the amount of flow entering the compressors and is shown in Figure 18. As for the membrane and recycle tie-in configuration, the recycle flow is higher, thus the feed flow in the stage 1 increases. Consequently, higher is the permeate flow from the stage 2 to be recycled to the compression unit. The second condenser showed a constant behaviour as the recycle flow remained constant leading to a stable permeate flow from stage 2. The configurations under high pressure consumed from 10.07 % to 16.10 % more power than the lower pressure.

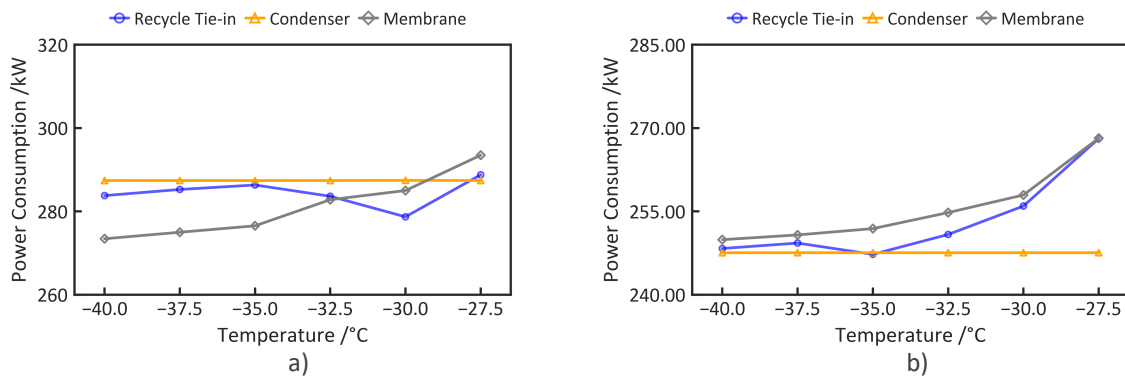


Figure 18. Power consumption for temperature behaviour study in a 2-stage model and 90 % of methane in the biomethane wherein a) high pressure b) low pressure

Overall, as the membrane configuration and the recycle tie-in configuration showed positive results to recover the purge, the second condenser was set as non-priority. When comparing scenario 3, 4, 21, 22, 9 and 27, the most interesting ones are 21 and 27 as combined lower power consumption with great recovery and flow rates, as seen in Table G.1.

A study with 97 % of methane in the biomethane stream was evaluated and compared with 90 % of methane in the biomethane stream.

The purity presented the same behaviour as for the simulation under 90 % of methane in the biomethane stream, as shown in Figure C.1. This is since the inlet composition of the tail-gas was the same, around 94.5 % of CO₂ and 5 % of methane, regardless of methane concentration on the biomethane stream. The simulation under 97 % showed a slightly higher purity for both pressure configurations as the tail-gas increased hence the proportion of CO₂ entering the CarboCap increased from 10 % to 14 % considering all unit configurations.

In the simulations conducted, it was observed that a biomethane flow with 97 % methane concentration resulted in a lower overall biomethane flow compared to a flow with 90 % methane concentration. This signifies the need for improved separation efficiency, which was achieved by using a greater number of membranes in the 97 % methane concentration scenario. In parallel, it was noted that the recycle flow was higher when the biomethane had a 97 % methane concentration compared to a 90 % methane concentration. This information are represented in Table C.1, Table C.2, Table C.3.

For all unit configuration, the number of membranes was higher when operating at 10.5 bara than 16.5 bara. The pressure difference directly affects the efficiency of the membrane as higher pressure generates higher pressure difference within the membrane.

For the membrane configuration, the retentate and permeate flow rates were affected by the temperature increase due to the non-condensation of CH₄ and CO₂. As seen in Table C.1, regardless of the operating pressure, temperatures exceeding 30 °C are not feasible due to generating a great amount of recycle flow. Consequently, scenarios 38 and 57 are suitable for implementation as their flow rates meet the desired criteria.

On the recycle tie-in configuration, the recycle flow increased as the temperature increased as molecules of CO₂ and CH₄ remained in gaseous state. As illustrated in Table C.2, the recycle tie-in is not considered a favourable strategy for temperatures higher than -32.5 °C in the primary condenser due to the significant volume of recycled flow. Therefore, the most interesting scenarios are 45 and 63.

The second condenser condenses great amount of CO₂ due to the operating temperature of -42.5 °C leading to a stable recycle flow regardless the operating temperature of the first condenser. All scenarios are set to evaluation once the recycle flow is below the limit, seen in Table C.3.

As seen in Figure C.2, when the concentration of methane increases from 90 % to 97 %, the recovery of CO₂ increased once the liquid CO₂ to the client is higher. Thus, the concentration of CO₂ sent to the grid varies from 1.8 % to 2.4 % on the biomethane stream leading to a flow of 10.24 Nm³·h⁻¹ to 13.89 Nm³·h⁻¹, for all units and pressure setup.

The CH₄ recovery presented the same behaviour as the simulation under 90 % of methane in the biomethane stream. Hence, as the amount of methane in the product is approximately the same for both simulations, the recovery reaches similar values, as illustrated in Figure C.3.

The power consumption increased as the methane concentration in the biomethane stream increased from 90 % to 97 %. As seen in Figure C.4, the tail-gas increased leading to a higher recycled flow and higher permeate flow from stage 2. As expected, the scenarios under 16.5 bara consumed more power than 10.5 bara leading to an increase between 10.67 % and 14.83 %, regardless the unit configuration.

Since the membrane configuration and the recycle tie-in configuration demonstrated favorable outcomes in reclaiming the purge, the secondary condenser was designated as a non-priority component. The most suitable scenarios are 63 for the recycle tie-in configuration followed by 57 for the membrane configuration, as seen in Table G.2.

4.1.2 CH₄ concentration in biogas flow

The study of methane concentration variation in the biogas stream was proposed to simulate the recovery of the purge under different biogas source for the 2-stage setup. This sensitivity study focused on the scenario of 90 % of methane in the biomethane stream and 5 % of methane entering the liquefaction unit, at low pressure. Further, the previous study was compared with 97 % of methane in the biomethane stream and 5 % of methane entering the liquefaction unit at high pressure.

The rise in methane concentration in the biogas stream of the upgrading unit directly influences the decrease in net CO₂ production, as there is less CO₂ entering the system while the purity reaches the minimum required by Europe of 99.90%, as seen in Figure 19.

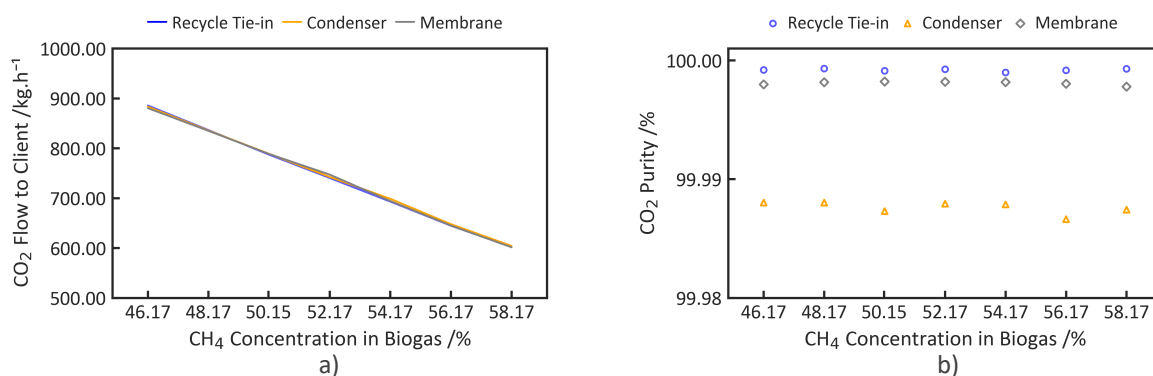


Figure 19. a) Liquid CO₂ and b) CO₂ purity for the biogas composition study in 2-stage model and 90 % of methane in biomethane

The membrane configuration achieved the lowest number of modules compared to the recycling tie-in and the condenser configuration due to the location of the recycling stream in the process. Also, the CO₂ being recycled directly to the liquefaction unit allows for a minor loss of CO₂ in the plant. In addition, the membrane configuration allows a higher biomethane stream rates when compared to the addition of the second condenser and the recycle tie-in. However, as the methane concentration increases, lower is the recycle flow once the tail-gas decreases, as seen in Table 9.

Hence, the recycle flow rate surpasses the limit set by DMT. To address this issue, it is necessary to raise the operating temperature of the condenser to a minimum of -35.0 °C for the methane concentration in the biogas from 46.17 % to 50.17 % while for higher concentration such as from 52.17 % to 58.17 %, the condenser temperature should be set as minimum -32.5 °C. This was evaluated as scenario 76 has the same input as scenario 22 where the difference relies on the main condenser temperature. This temperature decrease will facilitate enhanced CO₂ condensation.

Table 9. Membrane simulation data for biogas composition study in a 2-stage model and 90 % of methane in biomethane.

Parameters	CH ₄ Concentration in Biogas /%						
	46.17	48.17	50.17	52.17	54.17	56.17	58.17
Pressure	Low						
Biomethane /Nm ³ ·h ⁻¹	551.8	574.8	598.6	622.8	646.5	671.5	693.6
Tail-gas /Nm ³ ·h ⁻¹	472.7	449.8	425.5	403.1	370.9	347.4	350.1
Stage 1 Modules /unit	4	4	4	4	3	3	3
Stage 2 Modules /unit	5	5	5	8	7	8	8
Liquid CO ₂ /kg·h ⁻¹	880.4	834.9	788.5	747.2	694.2	645.1	601.5
Stage X							
Module /unit	3	3	3	3	3	2	1
Pressure /bara	1.3	1.4	1.8	2.0	1.0	1.0	1.1
Permeate Flow /Nm ³ ·h ⁻¹	208.3	207.2	199.0	182.9	173.6	154.3	109.6
Retentate Flow /Nm ³ ·h ⁻¹	24.5	24.6	24.1	26.0	17.4	18.9	43.7
Simulation Index							
Scenario	73	74	75	76	77	78	79

As in the membrane configuration, the recycle flow exceeds the limit required by the DMT when the recycle tie-in strategy is implemented, as shown in Table 10, due to the operating temperature of the condenser. To improve the feasibility of scenarios 80 to 86 by reducing the recycled flow, it is necessary to decrease the first condenser temperature to at least -32.5 °C.

Table 10. Recycle tie-in simulation data for biogas composition study in a 2-stage model and 90 % of methane in biomethane.

Parameters	CH ₄ Concentration in Biogas /%						
	46.17	48.17	50.17	52.17	54.17	56.17	58.17
Pressure	Low						
Biomethane /Nm ³ ·h ⁻¹	549.3	574.1	599.2	623.0	647.1	671.6	693.4
Tail-gas /Nm ³ ·h ⁻¹	820.6	799.1	714.6	694.2	611.8	591.0	572.5
Stage 1 Modules /unit	7	7	6	6	5	5	5
Stage 2 Modules /unit	4	4	4	4	5	5	5
Liquid CO ₂ /kg·h ⁻¹	885.8	836.5	787.1	740.4	693.0	644.6	601.9
Recycle Tie-in							
Flow Rate /Nm ³ ·h ⁻¹	369.9	373.3	313.8	317.4	259.0	262.5	265.8
CH ₄ Composition /%	11.2	11.2	11.2	11.3	11.3	11.3	11.3
CO ₂ Composition /%	88.3	88.3	88.3	88.3	88.3	88.3	88.3
Simulation Index							
Scenario	80	81	82	83	84	85	86

The addition of the 2nd condenser at -42.5 °C condenses around 81.13 % of the inlet flow allowing the recycle flow to reach the lowest level when compared to the membrane and recycle tie-in configuration and is presented in Table 11. All scenarios are scalable and to obtain a lower energy consumption, therefore, for scenarios 91, 92 and 93, the condenser temperature might be increased to -40.0 °C as a strategy to save energy consumption while the flow rate is below the limit.

Table 11. Condenser simulation data for biogas composition study in a 2-stage model and 90 % of methane in biomethane.

Parameters	CH ₄ Concentration in Biogas /%						
	46.17	48.17	50.17	52.17	54.17	56.17	58.17
Pressure	Low						
Biomethane /Nm ³ ·h ⁻¹	550.0	574.3	598.0	621.6	644.1	670.1	692.2
Tail-gas /Nm ³ ·h ⁻¹	512.3	484.6	452.9	430.4	404.3	368.5	347.5
Stage 1 Modules /unit	5	5	4	4	4	3	3
Stage 2 Modules /unit	7	7	8	8	8	6	6
Liquid CO ₂ /kg·h ⁻¹	883.3	835.6	789.0	742.6	698.7	647.9	604.3
2 nd Condenser							
1 st Condenser Gas Flow /Nm ³ ·h ⁻¹	329.7	312.2	269.8	275.5	257.3	205.1	210.6
2 nd Condenser Gas Flow /Nm ³ ·h ⁻¹	62.2	58.9	50.9	52.0	48.5	38.7	39.7
Simulation Index							
Scenario	87	88	89	90	91	92	93

The inverse relationship between increasing methane concentration in the biogas and decreasing recovery can be described by less CO₂ entering the upgrading unit. Figure 20 shows the behaviour of the units implemented for the CO₂ recovery. Additionally, the methane recovery reaches a high value for all unit configurations as the first condenser operates at -27.5 °C, hindering the condensation of the methane and enabling a significant amount to be converted to biomethane in Carborex.

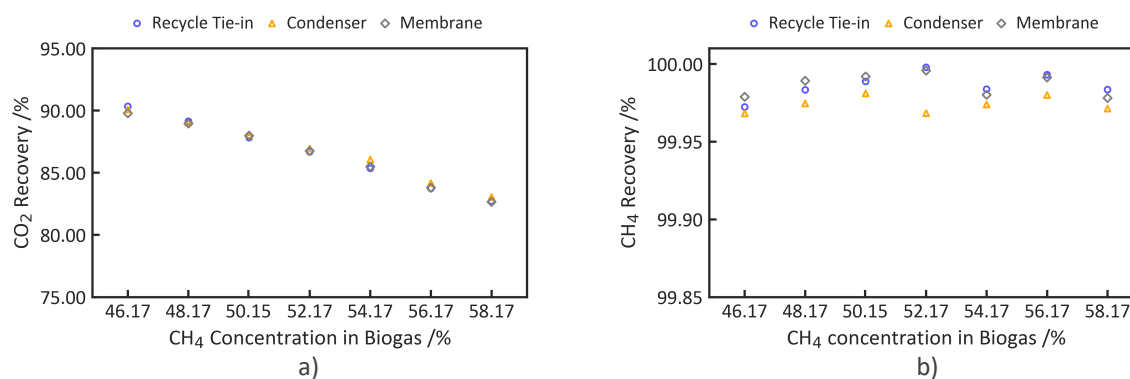


Figure 20. a) CO₂ Recovery and b) CH₄ recovery for the biogas composition study in 2-stage model and 90 % of methane in biomethane

The power consumption for the methane variation in the biogas remained constant for the membrane configuration and condenser as the flow being recycled was stable resulting in a constant feed stream in stage 1. Thus, the power consumption decreased for the recycle tie-in configuration due to the lower recycle flow, as seen in Figure 21.

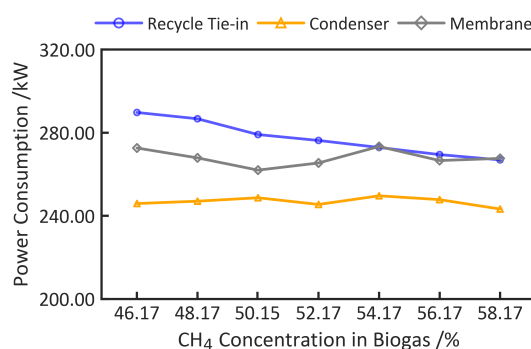


Figure 21. Power consumption for the biogas composition study in 2-stage model and 90 % of methane in biomethane

For the simulation considering 97 % of methane in the biomethane stream and operating at 16.5 bara, the purity quality and the CO₂ flow to the client presented the same behaviour as 90 % of methane in the biogas flow under 10.5 bara. Therefore, the liquid CO₂ flow was slightly higher when operating for the 97 % of methane in the biomethane stream, as illustrated in Figure D.1.

The individual output for each unit configuration of the simulation under 97 % of methane and high pressure can be seen in Table D.1, Table D.2 and Table D.3, for the membrane, recycle tie-in and the second condenser configuration, respectively.

As expected, the simulation with 97 % methane in the biomethane stream produced a smaller amount of biomethane while obtaining a higher flow rate of liquid CO₂. By operating at 16.5 bara, the number of membranes decreased when compared to the simulation with 90 % methane in the biomethane stream at 10.5 bara. Moreover, by producing a lower flow of biomethane, consequently more tail gas is being generated and entering the liquefaction unit, which implies an increase in the recycling.

The membrane configuration followed by the recycle tie-in configuration presented higher values for the recycle flow leading to the urge for optimization. The same modification within the system for the simulation under 90% of methane in the biogas flow is proposed as scenario 97 has the same operating condition as 39, wherein the second condenser temperature should be decreased to -35.0 °C. Therefore, no scenarios are suitable for further studies for both configurations.

For the condenser, since the recycle flow is already near the limit, leading to all scenarios to be set as optimal. Thus, changing the temperature from -42.5 °C to -40.0 °C is not suggested for scenarios 112, 113, and 114.

The CO₂ recovery and CH₄ recovery presented the same behaviour as for the 90 % of methane in the biogas flow and is presented in Figure D.2. As expected, the lower biomethane stream reflected a lower flow rate of CO₂ and CH₄ sent to the grid, allowing higher recovery of both compounds

The power consumption was higher due to the operating pressure, as seen in Figure D.3. The membrane and recycle tie-in configuration showed the same behaviour. Thus, a small error in the methane concentration in the biomethane stream caused some deviation in the 52.17 % data. The second condenser showed an unexpected increase in power consumption, urging more investigation into these results. Therefore, the membrane and recycle tie-in showed the most accurate performance.

Therefore, as only the second condenser achieve the desired target, regardless the methane concentration, which requires great investment, no optimal scenarios were found but modification within the system is required.

4.1.3 CH₄ composition in the tail-gas

The study of the variation of the methane concentration entering the liquefaction unit was proposed to simulate the recovery of the purge under different Carborex® MS parameters configurations. This sensitivity study focused on the methane concentration of 97 % on the biomethane stream at 10.5 bara.

When running the control parameter, the purity levels were not achieved with the simulation input standards for most scenarios. To evaporate part of the condensed methane in the liquefaction unit, it was required to provide 1 kW to 2 kW of heat input to the reboiler. The slightly temperature difference of 0.03 °C in the heat input and the output stream before the reboiler enhanced the purity by a minimum of 0.2 % and 0.1 % for the lower and higher methane concentration in the tail gas, respectively.

As shown in Figure 22, the purity on the membrane configuration for methane concentration of 3 % and 4 % in tail gas was lower than 99.90 % as the input add in the reboiler of 1 kW was not sufficient to condensed a significant part of methane. The purity can be achieved with the input heat of 2 kW. Therefore, the liquid CO₂ flow rate remained constant regardless of the methane concentration in the tail gas.

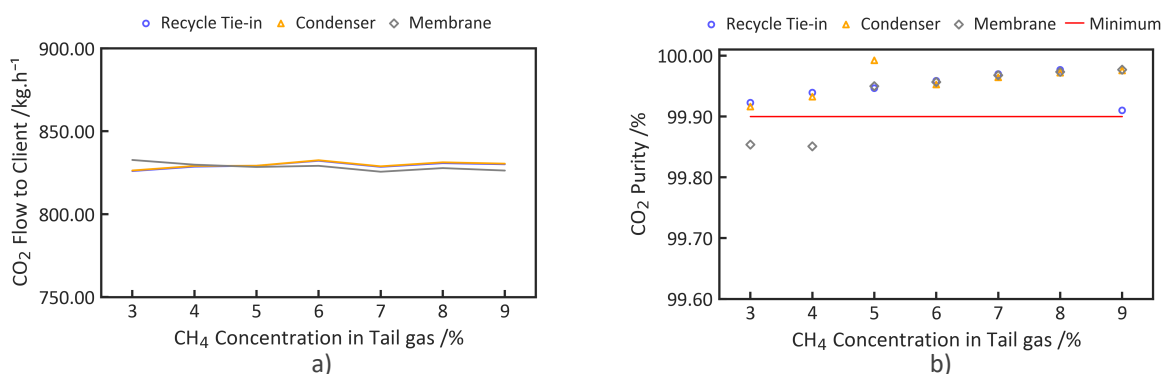


Figure 22. a) Liquid CO₂ and b) CO₂ purity for the tail gas composition study in 2-stage model and 97 % of methane in biomethane

The number of modules, biomethane flow, tail gas and liquid CO₂ flow rate was very similar to all configuration, present in Table 12.

Table 12. Membrane, recycle tie-in and condenser simulation data for the tail gas composition study in 2-stage model and 97 % of methane in biomethane.

Parameters	CH ₄ Concentration in Tail-gas /%						
	3.0	4.0	5.0	6.0	7.0	8.0	9.0
Pressure	Low						
Biomethane /Nm ³ ·h ⁻¹	575.0 - 580.0	577.0 - 578.0	577.0 - 578.0	575.0 - 578.0	577.0 - 580.0	576.0 - 579.0	576.0 - 580.0
Tail-gas /Nm ³ ·h ⁻¹	438.0 - 460.0	440.0 - 480.0	448.0 - 482.0	450.0 - 500.0	450.0 - 520.0	460.0 - 540.0	460.0 - 550.0
Stage 1 Modules /unit	3	4	4	5	5	6	6
Stage 2 Modules /unit	13 - 14	12 - 13	11 - 12	12 - 13	9 - 10	10 - 11	9 - 10
Liquid CO ₂ /kg·h ⁻¹	825.0 - 860.0	828.0 - 830.0	828.0 - 830.0	829.0 - 830.0	827.0 - 828.0	827.0 - 830.0	826.0 - 830.0
Stage X							
Modules /unit	1	1	1	1	2	2	2
Pressure /bara	1.2	2.8	1.2	2.2	1.1	1.7	1.0
Permeate Flow /Nm ³ ·h ⁻¹	32.0	28.1	35.6	39.2	55.1	61.3	65.8
Retentate Flow /Nm ³ ·h ⁻¹	14.3	18.0	27.5	33.5	36.0	42.7	48.2
Scenario	115	116	117	118	119	120	121
Recycle Tie-in							
Flow Rate /Nm ³ ·h ⁻¹	37.3	51.7	59.3	75.4	94.9	113.7	124.6
CH ₄ Composition /%	37.7	37.8	37.9	37.9	38.1	38.1	38.2
CO ₂ Composition /%	60.0	60.0	60.0	60.0	60.0	60.0	60.0
Scenario	122	123	124	125	126	127	128
2 nd Condenser							
1 st Condenser Gas Flow /Nm ³ ·h ⁻¹	37.9	52.5	60.9	76.7	96.6	115.7	126.8
2 nd Condenser Gas Flow /Nm ³ ·h ⁻¹	33.4	46.3	53.7	67.6	85.1	102.0	111.7
Scenario	129	130	131	132	133	134	135

The increase of methane concentration in the tail-gas a rise in recycling as more methane is being recycled. Thus, the recycle tie-in configuration showed the highest recycle flow while the membrane had the lower flow rate, leading to a lower deviation in the process.

The scenarios with methane concentration in the tail-gas of 8.0 % and 9.0 % presented values above the limit for the recycle flow, regardless of the configuration chosen, wherein the concentration of 5 % to 7 %

of methane in the tail-gas was acceptable to use membrane configuration. One proposed alternative is to decrease the primary condenser temperature to -42.5 °C and counterbalance the purity by increasing the heat supplied to the reboiler. Therefore, all scenarios besides 115, 116, 120, 121, 126, 127, 128, 134 and 135 were evaluated.

As seen in Figure 23, the CO₂ recovery is balanced at 96.68 % as the concentration of CO₂ sent to the grid remained constant varying from 1.9 % to 2.5 % within the biomethane stream. As expected, the methane recovery increased as more methane was present in the tail-gas.

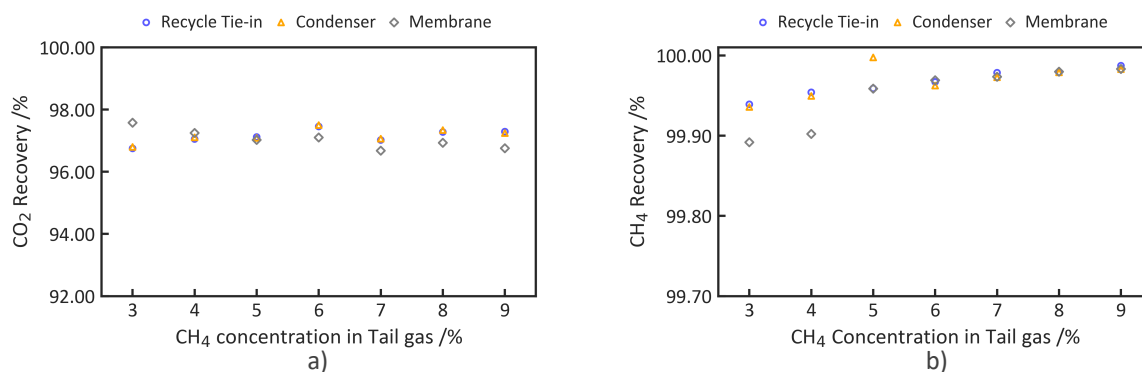


Figure 23. a) CO₂ Recovery and b) CH₄ recovery for the tail gas composition study in 2-stage model and 97 % of methane in biomethane

As the power consumption is mainly dictated by the permeate flow, as the methane concentration increases in the tail-gas resulting in a higher permeate flow from stage 1. This leads to a lower retentate flow rate to the stage 2 which corresponds in a lower permeate flow rate from stage 2 to be recycle. As seen in Figure 24, all unit configurations showed the same behaviour.

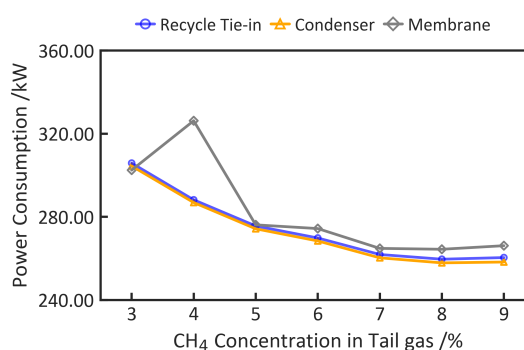


Figure 24. Power consumption for the tail gas composition study in 2-stage model and 97 % of methane in biomethane

Overall, the recycle tie-in configuration was set as the most suitable one for the concentration of 3 % to 7 % of methane in the tail gas as combined lower investment cost with power consumption, as illustrated in Table I.1.

4.2 3-Stage

4.2.1 Temperature Behaviour

As a strategy to achieve a purer biomethane stream and avoid methane losses to the liquefaction unit, the baseline study was set at 90 % methane in the biomethane stream and 0.5 % methane in the tail-gas. An analysis with a higher percentage of methane in the Carborex® MS product, 97 %, and maintaining the methane input concentration to the liquefaction unit, 0.5 %, was performed to analyse the feasibility of the process. Both studies were conducted at 16.5 bara and 10.5 bara. The study conducted at temperatures of -25.0 °C exhibited low process efficiency due to the high temperature, resulting in convergence issues within ChemCAD. As a consequence, it was determined that the evaluation of this study feasibility was not viable.

The purity of all configurations increased as the operating temperature increased, regardless of the operating pressure. Thus, the scenarios operating at -40.0 °C and -37.5 °C presented significant methane impurities urging the necessity of more heat in the reboiler. Therefore, the heat added to the membrane and recycle tie-in configuration was 1.2 kW and 0.9 kW, respectively.

However, the purity remained below 99.90 % for the scenario operating at -40.0 °C wherein a failure occurred on ChemCAD leading to a non-converged simulation. The configuration of the second condenser reached higher purity due to the extremely low operating temperature. The purity behaviour is represented by Figure 25.

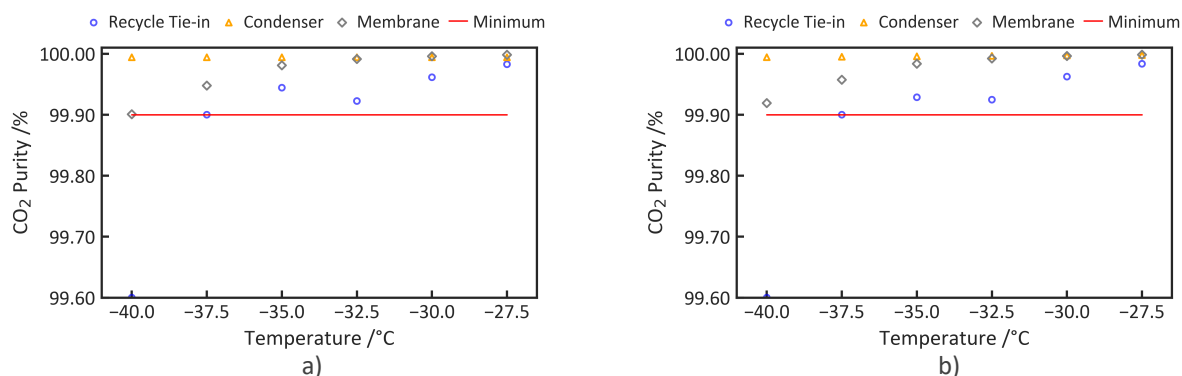


Figure 25. CO₂ purity for temperature behaviour study in 3-stage model and 90 % of methane in biomethane wherein
a) high pressure b) low pressure

The main difference between the simulation of 16.5 bara and 12.5 bara, regardless the methane concentration in the biomethane stream and the unit configuration, is the number of modules required within the Carborex® MS due to the pressure difference within the membranes, as seen in Table 13.

The temperature rising from -40 °C to -27.5 °C leads to a low CO₂ condensation increasing the retentate and permeate flow for the membrane configuration. For operating temperatures ranging from -30.0 °C to

-27.5 °C, the recycled flow exceeds the limit required by DMT, which leaves these scenarios undesirable while scenarios 136, 137, 138, 139, 154, 155 and 156 are suitable for further comparison.

Table 13. Membrane simulation data for temperature behaviour study in a 3-stage model and 90 % of methane in biomethane.

Parameters	Main Condenser Temperature /°C											
	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5
Pressure	High						Low					
Biomethane /Nm ³ .h ⁻¹	621.8	622.0	622.2	622.2	622.2	622.2	621.5	620.6	620.6	620.6	620.6	620.6
Tail-gas /Nm ³ .h ⁻¹	380.1	380.1	380.1	380.1	380.1	380.1	380.5	380.5	380.5	380.5	380.5	380.5
Stage 1 Modules /unit	2	2	2	2	2	2	7	7	7	7	7	7
Stage 2 Modules /unit	5	5	5	5	5	5	9	9	9	9	9	9
Stage 3 Modules /unit	10	10	10	10	10	10	10	10	10	10	10	10
Liquid CO ₂ /kg.h ⁻¹	741.9	742.0	741.9	741.9	742.2	741.9	742.8	742.8	742.7	742.6	742.7	742.7
Stage X												
Module /unit	1	1	1	1	1	1	1	1	1	1	1	1
Pressure /bara	1.8	1.8	1.8	1.8	1.8	1.8	1.5	1.5	1.5	1.5	1.5	1.5
Permeate Flow /Nm ³ .h ⁻¹	23.2	63.0	77.0	91.1	108.0	133.6	18.2	70.5	83.4	96.5	114.0	140.5
Retentate Flow /Nm ³ .h ⁻¹	1.9	2.1	2.3	2.3	2.3	2.3	2.0	2.2	2.3	2.3	2.3	2.3
Simulation Index												
Scenario	136	137	138	139	140	141	154	155	156	157	158	159

The major advantage of the recycle configuration lies in having the same number of modules as the membrane configuration, according to Table 14. The temperature increase, independently of the operating pressure, leads to reduced CO₂ condensation, and consequently, a higher flow rate to be recycled, although the disturbance caused is considered minimum. This makes all scenarios satisfying the DMT criteria.

Table 14. Recycle tie-in simulation data for temperature behaviour study in a 3-stage model and 90 % of methane in biomethane.

Parameters	Main Condenser Temperature /°C											
	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5
Pressure	High						Low					
Biomethane /Nm ³ .h ⁻¹	621.1	623.0	623.6	620.3	621.2	621.7	619.9	622.4	623.7	620.2	621.8	621.4
Tail-gas /Nm ³ .h ⁻¹	380.9	382.4	383.4	387.4	389.5	395.7	381.8	382.2	382.2	388.9	390.3	398.5
Stage 1 Modules /unit	2	2	2	2	2	2	7	7	7	7	7	7
Stage 2 Modules /unit	5	5	5	5	5	5	8	8	8	8	8	8
Stage 3 Modules /unit	10	10	10	10	10	10	11	11	11	11	11	11
Liquid CO ₂ /kg.h ⁻¹	742.1	739.7	738.9	745.4	743.5	742.8	744.4	740.6	738.1	745.6	742.5	743.3
Recycle Tie-in												
Flow Rate /Nm ³ .h ⁻¹	1.9	5.4	6.9	7.7	10.7	17.4	1.8	4.7	6.1	9.1	12.1	20.0
CH ₄ Composition /%	31.6	29.6	25.3	20.2	15.3	10.0	30.7	28.8	24.7	20.1	15.1	9.9
CO ₂ Composition /%	60.1	65.2	70.6	76.2	82.2	88.3	60.1	65.2	70.6	76.2	82.2	88.3
Simulation Index												
Scenario	142	143	144	145	146	147	160	161	162	163	164	165

The condenser configuration condenses a large volume of CO₂. Thus, all scenarios are acceptable for further evaluation. This information can be seen in Table 15.

Table 15. Condenser simulation data for temperature behaviour study in a 3-stage model and 90 % of methane in biomethane.

Parameters	Main Condenser Temperature /°C											
	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5
Pressure	High						Low					
Biomethane /Nm ³ .h ⁻¹	620.9	620.9	620.9	620.9	620.9	620.8	622.8	622.8	622.8	622.8	622.8	622.8
Tail-gas /Nm ³ .h ⁻¹	384.4	384.3	384.3	384.3	384.3	384.3	382.1	382.1	382.1	382.1	382.1	382.1
Stage 1 Modules /unit	2	2	2	2	2	2	7	7	7	7	7	7
Stage 2 Modules /unit	5	5	5	5	5	5	8	8	8	8	8	8
Stage 3 Modules /unit	11	11	11	11	11	11	11	11	11	11	11	11
Liquid CO ₂ /kg.h ⁻¹	744.7	744.5	744.4	744.5	744.3	744.5	740.6	740.8	740.7	740.8	740.8	740.5
2 nd Condenser												
1 st Condenser Gas Flow /Nm ³ .h ⁻¹	5.8	6.8	8.3	10.6	15.2	27.3	5.5	5.5	5.5	5.5	5.5	5.5
2 nd Condenser Gas Flow /Nm ³ .h ⁻¹	5.1	5.2	5.2	5.2	5.2	5.2	4.8	4.8	4.8	4.8	4.9	4.9
Simulation Index												
Scenario	148	149	150	151	152	153	166	167	168	169	170	171

As presented in Figure 26, the CO₂ recovery remained constant with minor variations throughout the temperature increase for the simulation considering 90 % of methane in the biomethane stream. As followed, the CH₄ recovery was evaluated whereas the recovery behaviour remained constant for all configurations and both operating pressure besides the recycle tie-in scenario operating under -40.0 °C due to the glitch on ChemCAD. The CH₄ recovery can be seen in Figure 27.

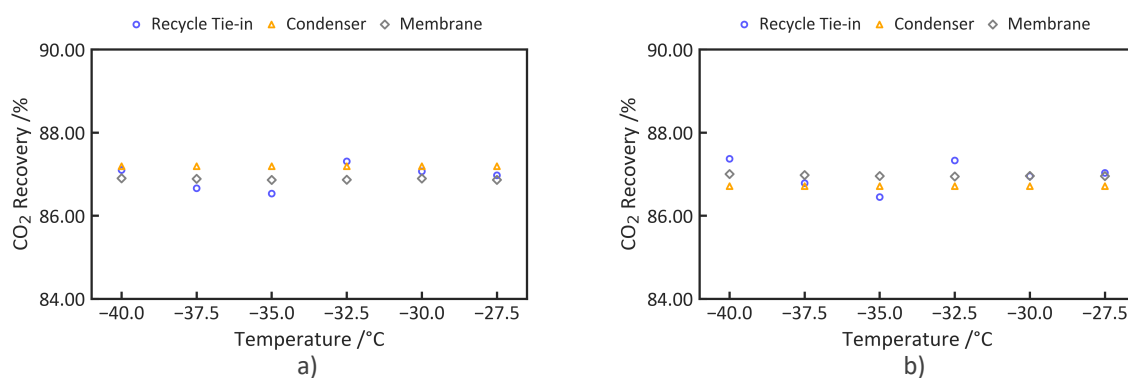


Figure 26. CO₂ recovery for temperature behaviour study in 3-stage model and 90 % of methane in the biomethane wherein a) high pressure b) low pressure

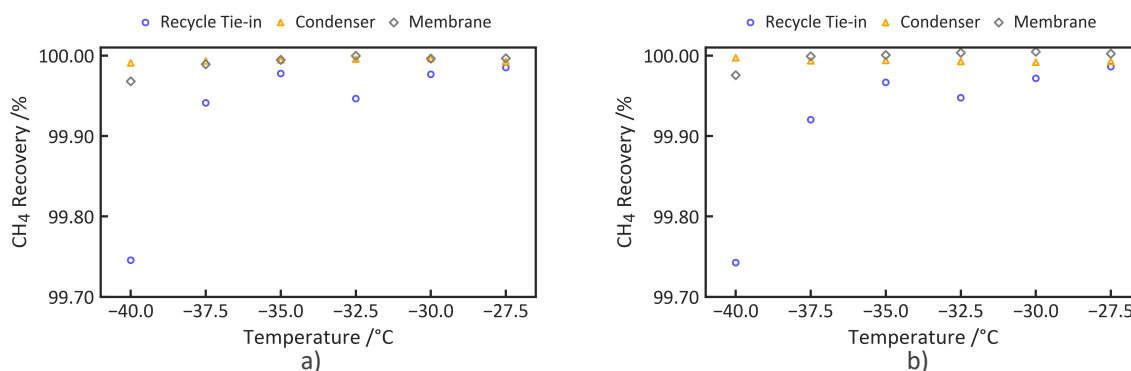


Figure 27. CH₄ recovery for temperature behaviour study in a 3-stage model and 90 % of methane in the biomethane wherein a) high pressure b) low pressure

As the power consumption is directly related to the amount of flow entering the compressors, the behaviour was very similar to 2-stage model. As polishing the tail-gas by adding one more stage results in a higher flow being recycled such as the permeate flow from the stage 2 and the retentate flow from the stage 3, illustrated in Figure 28.

For the membrane and recycle tie-in configuration, the power consumption increased alongside the operating temperature, while the second condenser remained constant. The small deviation in the recycle tie-in configuration is due to the small error in the simulation for the methane concentration in the biomethane stream.

The configurations under high pressure consumed from 7.83 % to 9.97 % more power usage than the lower pressure.

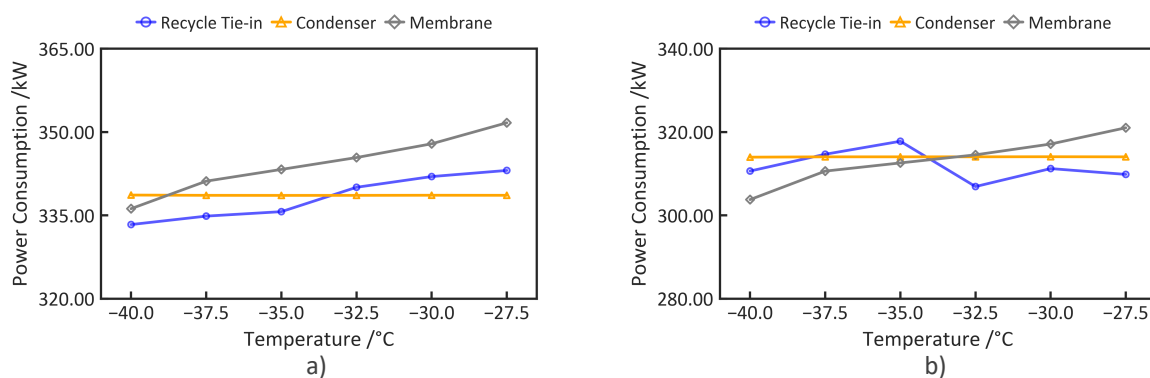


Figure 28. Power consumption for temperature behaviour study in a 3-stage model and 90 % of methane in the biomethane wherein a) high pressure b) low pressure

After detailed analysis regarding the power consumption, the optimum scenarios were set as 136 and 143, as seen in Table G.3.

The study under 97 % of methane in the biomethane stream presented a similar purity pattern as observed in Figure E.1. The composition and flow rate of the tail-gas remains essentially unchanged. Thus, the membrane configuration required a heat input of 1.5 kW in the reboiler, whereas the recycle tie-in configuration only required 0.9 kW.

The same observation of decreasing the operating pressure resulting in higher membranes module is also seen when the concentration increases from 90 % of methane in the biomethane to 97 % of methane in the biomethane stream.

For the membrane configuration, the recycle flow was below the limit proposed by DMT leading to all scenarios being feasible besides scenario 172, as seen in Table E.1. A minor glitch occurred when simulation scenario 172, which leads to a higher permeate flow rate, further investigation is suggested.

In the recycle tie-in configuration, raising the temperature, regardless of the pressure, results in decreased CO₂ condensation and, consequently, a higher flow rate for recycling. However, the resulting disturbance is considered minimal. This ensures that all scenarios meet the DMT criteria, as seen in Table E.2.

As the second condenser efficiently condenses a significant volume of CO₂, the condenser configuration demonstrates the most stable parameters throughout the temperature increase. Consequently, all scenarios are deemed suitable for evaluation. This information can be seen in Table E.3

The CO₂ recovery was higher for the study of 97 % of methane in the biomethane stream since the tail-gas is higher allowing more CO₂ to be converted into liquid CO₂. Thus, the concentration of CO₂ present in the biomethane stream varies from 2.1 % to 2.4 % exiting from 12.12 Nm³·h⁻¹ to 14.05 Nm³·h⁻¹, regardless of the configuration and pressure setup, and can be seen in Figure E.2.

Thus, the increase in methane concentration in the biomethane stream did not impact methane recovery significantly, as the rise in concentration was offset by a decrease in the flow rate of biomethane. The methane recovery behaviour is shown in Figure E.3.

The power consumption presented the same behaviour, thus slightly higher values were observed when the methane concentration in the biogas increased from 90 % to 97 %. As seen in Figure E.4, the tail-gas increased resulting in a higher recycled flow rate and thus higher permeate and retentate flow rates on the membrane system. As expected, the scenarios under 16.5 bara required more power than 10.5 bara varying from 3.76 % to 10.65 %, considering all the unit configurations.

Thus, the optimum scenarios were established in 179 for the recycle tie-in configuration and 192 for the membrane configuration as it combined lower power consumption to affordable investment. The analysis is demonstrated in Table G.4.

4.2.2 CH₄ composition in biogas flow

This sensitivity study focused on the scenario of the methane concentration of 90 % in the biomethane stream and 0.5 % in the tail gas operating at 10.5 bara. Thus, an additional setup of methane concentration of 97 % in the biomethane stream and 0.5 % in the tail gas under 16.5 bara was analysed.

As illustrated in Figure 29, the purity reached values higher than 99.98 % due to the operating temperature of -27.5 °C on the main condenser. The liquid CO₂ and the purity showed the same behaviour for all three unit. Thereby, the decrease in the concentration of CO₂ within the biogas feed directly affects the production of liquid CO₂ in the CarboCap.

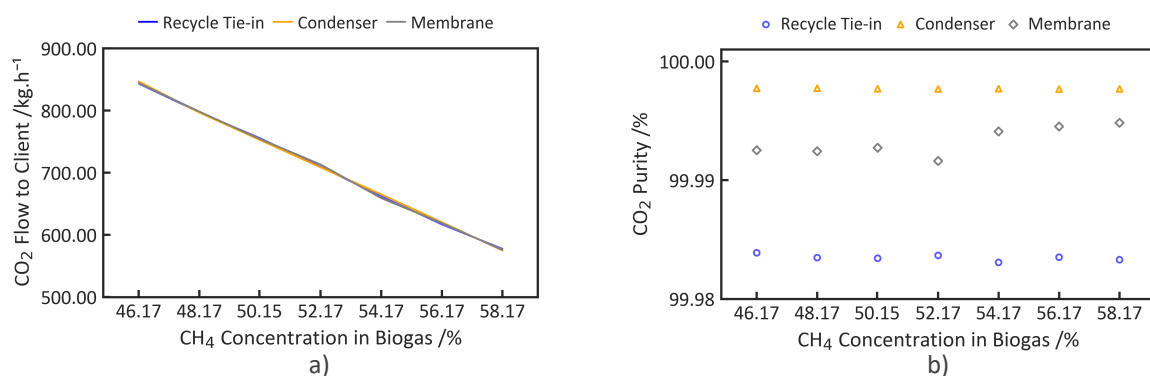


Figure 29. a) Liquid CO₂ and b) CO₂ purity for the biogas composition study in 3-stage model and 90 % of methane in biomethane

As presented in Table 16, the biomethane flow rate, number of modules and the liquid CO₂ flow rate was the same for all configurations. Therefore, all scenarios accomplished satisfactory results for the recycle flow.

Table 16. Membrane, recycle tie-in and condenser simulation data for the biogas composition study in 3-stage model and 90 % of methane in biomethane.

Parameters	CH ₄ Concentration in Biogas /%						
	46.17	48.17	50.17	52.17	54.17	56.17	58.17
Pressure	Low						
Biomethane /Nm ³ ·h ⁻¹	549.0 - 552.0	574.0 - 576.0	597.0 - 600.0	620.0 - 623.0	645.0 - 648.0	669.0 - 672.0	692.0 - 694.0
Tail-gas /Nm ³ ·h ⁻¹	452.0 - 474.0	427.0 - 447.0	404.0 - 433.0	382.0 - 399.0	353.0 - 370.0	331.0 - 347.0	308.0 - 324.0
Stage 1 Modules /unit	7	7	7	7	7	7	7
Stage 2 Modules /unit	8	8	8	8	8	8	8
Stage 3 Modules /unit	14	14	14	14	14	14	14
Liquid CO ₂ /kg·h ⁻¹	881.0 - 885.0	832.0 - 835.0	786.0 - 790.0	740.0 - 746.0	688.0 - 696.0	644.0 - 649.0	600.0 - 604.0
Stage X							
Modules /unit	1	1	1	1	1	1	1
Pressure /bara	3	3	3	3	3	3	3
Permeate Flow /Nm ³ ·h ⁻¹	56.2	54.7	54.2	44.2	54.9	55	54.5
Retentate Flow /Nm ³ ·h ⁻¹	2.7	2.8	2.7	2.4	2.1	2	2
Scenario	208	209	210	211	212	213	214
Recycle Tie-in							
Flow Rate /Nm ³ ·h ⁻¹	24.6	22.1	21	21.3	17.6	18.1	16.3
CH ₄ Composition /%	9.8	9.9	10	10.1	10.1	10.1	10.1
CO ₂ Composition /%	88.3	88.3	88.3	88.3	88.3	88.3	88.3
Scenario	215	216	217	218	219	220	221
2 nd Condenser							
1 st Condenser Gas Flow /Nm ³ ·h ⁻¹	33.5	29.9	29.6	28.4	25.3	24.5	21.9
2 nd Condenser Gas Flow /Nm ³ ·h ⁻¹	6.4	5.7	5.6	5.4	4.8	4.7	4.2
Scenario	222	223	224	225	226	227	228

For the membrane configuration, the permeate flow and the retentate flow remained within the limit desired by DMT of the inlet flow rate wherein the scenario of 52.17 % of methane in the biogas feed showed a higher deviation of 44.2 Nm³·h⁻¹ on the permeate side.

The recycle tie-in configuration presented lower values of recycled flow compared to the membrane, where the maximum flow was 24.6 Nm³·h⁻¹, which avoids more significant disturbances in the system.

The second condenser configuration achieved the lowest recycle values as it operates at -42.5 °C which allows the recovery of a large amount of non-condensed CO₂ from the first condenser. Table 16 reveals that the flow rate varied from 6.4 Nm³·h⁻¹ to 4.2 Nm³·h⁻¹ with increasing methane concentration since there is less CO₂ in the liquefaction feed stream. Thus, the second condenser provides the best results in avoiding of disturbances and hydrogen build-up.

The CO₂ recovery varies according to the methane input composition of the biogas. The decrease in the recovery is interpreted once the CO₂ composition decreases with the increase of the methane composition. This variance is visualized in Figure 30.

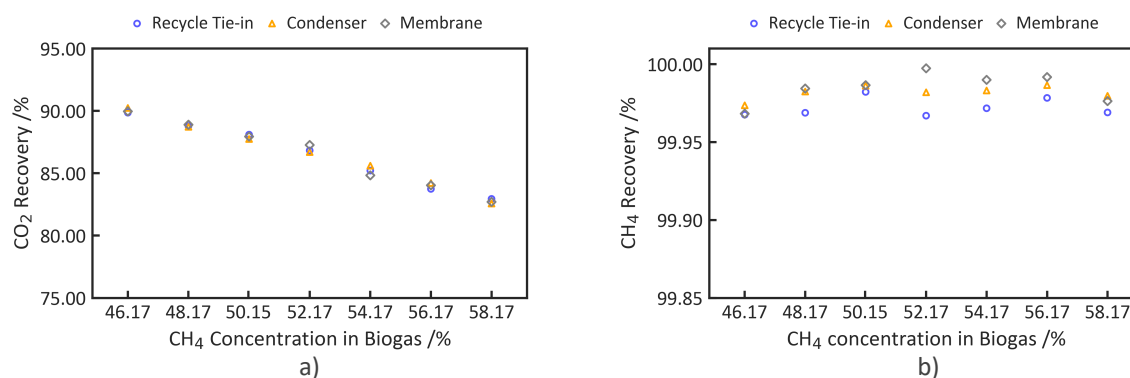


Figure 30. a) CO₂ Recovery and b) CH₄ recovery for the biogas composition study in 3-stage model and 90 % of methane in biomethane

The recovery of methane achieved high values for all unit configurations once the main condenser was operating at -27.5 °C, preventing methane condensation throughout the process. The membrane unit achieved the best CH₄ recovery due to the position of its tie-in directly into the biomethane stream instead of the compressor unit in Carborex.

The power consumption for the methane variation in the biogas increased alongside the methane concentration for all three configurations. As the methane concentration in the biogas increases, there is a corresponding increase in the retentate and the permeate flow on the membrane system in Carborex® MS due to the recycle loop in the membrane system. As seen in Figure 31 and Figure 21, the results for 3-stage were higher than the 2-stage as more modules were required for methane concentration and higher CO₂ concentration entering on the tail-gas demanded more efficient separation.

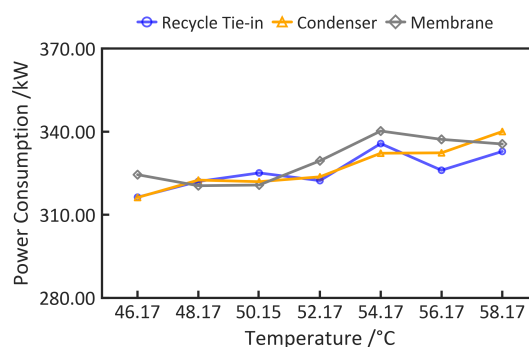


Figure 31. Power consumption for the biogas composition study in 3-stage model and 90 % of methane in biomethane.

For the study considering 97 % of methane in the biomethane stream under 16.5 bara, the purity remained very similar while the flow of condensed CO₂ was higher when compared with 90 % of methane in the biomethane stream due to a higher tail-gas entering the liquefaction unit. The purity and liquid CO₂ flow can be seen in Figure F.1.

As presented in Table F.1, the biomethane flow rate, number of modules and the liquid CO₂ flow remained similar for all unit configurations. Thus, the recycle flow was slightly higher than the simulation under 90 % of methane in the biomethane flow due to the higher tail-gas entering the CarboCap. All scenarios were set to evaluation.

The CO₂ recovery and CH₄ recovery presented the same variation as for the 90 % methane concentration in the biomethane stream, in which the CO₂ concentration decreased as the methane concentration in the biogas increased, presented in Figure F.2.

Therefore, once the rise in methane concentration balances out the reduction in biomethane flow rate, the methane recovery attains comparable values to the 90 % methane simulation in the biomethane stream.

For the simulation considering 97 % of methane in the biomethane stream and operating at 16.5 bara, the power consumption was higher due to the operating pressure. All three unit showed the same constant behaviour as seen in Figure F.3.

Overall, regardless the methane concentration in biomethane stream, the recycle tie-in showed the most suitable results as combined lower power consumption and interesting investment cost when compared to the membrane configuration. The results are illustrated in Table H.1 for 90% of methane in the biomethane and in Table H.2 for 97% of methane in the biomethane.

4.2.3 CH₄ composition in the tail-gas

The evaluation of the variation of the methane concentration in the tail gas unit was proposed to simulate the recovery of the purge under different Carborex® MS parameters configurations. This sensitivity study focused on the methane concentration of 97% on the biomethane stream at 10.5 bara.

As presented in Figure 32, the liquid CO₂ flow and the purity obtained was similar for all unit configuration once the design of the parameters within the Carborex® MS matched near-identical.

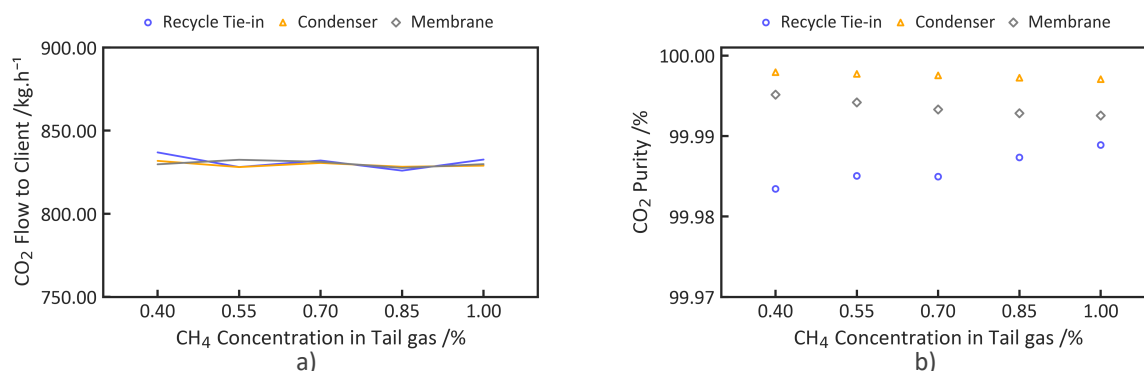


Figure 32. a) Liquid CO₂ and b) CO₂ purity for the tail gas composition study in 3-stage model and 97 % of methane in biomethane

The biomethane and liquid CO₂ flow rate was slightly higher for the membrane configuration while the second condenser achieved the lowest value. As seen in Table 17, the recycle flow for all configurations was below the limit DMT proposed, wherein the second condenser achieved the lowest results. For that, all the scenarios are settled to be evaluated for the feasibility of the process.

Table 17. Membrane, recycle tie-in and condenser simulation data for the tail gas composition study in 3-stage model and 97 % of methane in biomethane.

Parameters	CH ₄ Concentration in Tail-gas /%				
	0.40	0.55	0.70	0.85	1.00
Pressure	Low				
Biomethane /Nm ³ .h ⁻¹	576.0 – 578.0	576.0 – 579.0	576.0 – 579.0	578.0 – 579.0	576.0 – 578.0
Tail-gas /Nm ³ .h ⁻¹	429.0 – 443.0	426.0 – 448.0	426.0 – 447.0	425.0 – 462.0	427.0 – 474.0
Stage 1 Modules /unit	7	8	8	8	7
Stage 2 Modules /unit	13	12	12	11	12
Stage 3 Modules /unit	9	9	9	9	10
Liquid CO ₂ /kg.h ⁻¹	829.0 – 837.0	828.0 – 832.0	830.0 – 832.0	825.0 – 828.0	828.0 – 832.0
Stage X					
Modules /unit	1	1	1	1	1
Pressure /bara	1.4	1.36	1.3	1.3	1.2
Permeate Flow /Nm ³ .h ⁻¹	67.6	64.7	63.0	63.2	64.4
Retentate Flow /Nm ³ .h ⁻¹	1.9	2.7	3.4	4.1	4.7
Scenario	250	251	252	253	254
Recycle Tie-in					
Flow Rate /Nm ³ .h ⁻¹	17.2	26.2	25.2	40.6	50.7
CH ₄ Composition /%	8.9	9.3	9.2	9.6	9.6
CO ₂ Composition /%	88.3	88.3	88.3	88.3	88.3
Scenario	255	256	257	258	259
2 nd Condenser					
1 st Condenser Gas Flow /Nm ³ .h ⁻¹	28.4	34.8	42.4	53.3	61.2
2 nd Condenser Gas Flow /Nm ³ .h ⁻¹	5.0	7.0	8.0	10.0	12.0
Scenario	260	261	262	263	264

As illustrated in Figure 33, the minimum CO₂ recovery is 96.70 % where the rest exits in biomethane stream. The CO₂ concentration in the biomethane stream varies from 1.9 % to 2.4 % where this value represents from 10.9 Nm³·h⁻¹ to 13.9 Nm³·h⁻¹, taking into consideration all units. As expected, the methane recovery increased as more methane was present in the tail-gas thus, as higher the concentration, the higher the recovery.

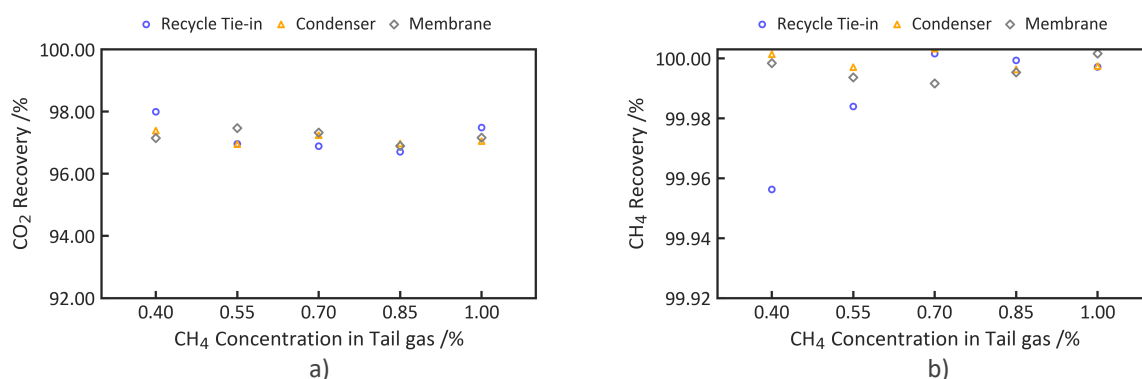


Figure 33. a) CO₂ Recovery and b) CH₄ recovery for the tail gas composition study in 3-stage model and 97 % of methane in biomethane

As methane concentration increases in the tail-gas, the retentate flow in stage 2 increases and the permeate flow in stage 3 decreases, mainly influencing power consumption. This impact in a lower recycle flow on the membrane system leading to a lower power consumption on the compressors. As seen in Figure 34, all unit configurations showed the same behaviour.

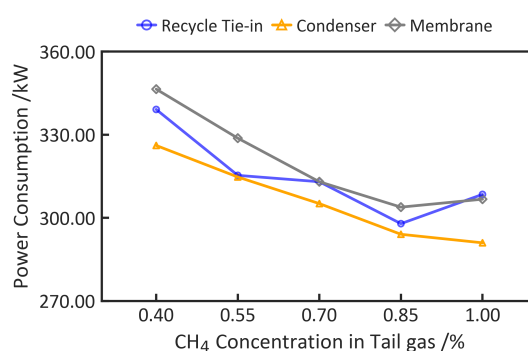


Figure 34. Power consumption for the tail gas composition study in 3-stage model and 97 % of methane in biomethane

Thus, the recycle tie-in configuration proved to be the optimal choice for achieving satisfactory results when compared to the membrane configuration when evaluating power consumption and investment cost. Therefore, the recycle tie-in configuration is set as an optimal unit to be selected in this case. The comparison can be seen in Table I.2.

5 Conclusion

This study aimed to obtain the most suitable configuration to recovery and recycle the purge flow in order to design a closed-loop system. For that, three main designs were reviewed such as the additional of a membrane stage, a condenser or simply a recycle tie-in system. In addition, several operational parameters were tested to better understand the boundaries to implement in an integrated biogas upgrading (for both the 2-stage and 3-stage model) and CO₂ liquefaction process. In parallel, it was possible to set operational boundaries to the CO₂ liquefaction as a separate plant to maximize the liquid CO₂ production.

Three main criteria were established to evaluate the results. Firstly, the CO₂ purity in the liquid CO₂ flow to client exiting the liquefaction unit must be equal or above 99.90 % to attend the requirements imposed by the food industry. Then, the limit imposed by DMT on the recycle flow rate was 9.5 % of the biogas upgrading plant inlet, representing 95 Nm³·h⁻¹. Lastly, the strategy of the membrane configuration and the recycle tie-in configuration was set as preferred over the condenser configuration as it requires more financial cost due to the cooling fluid.

For the case of stable biogas composition of 52.17 % methane, operating at 16.5 bara and 10.5 bara in a 2-stage layout, it was evaluated the main condenser temperature for a methane concentration in the biomethane of 90 % and 97 %. The optimal scenario was adding a membrane or a simple recycle tie-in with the main condenser operating at -35.0 °C and at low pressure. In addition, the operational temperature boundaries for the main condenser are set as -32.5 °C when using the stage X strategy or recycle tie-in configuration. The methane concentration in the biomethane stream did not influence in this optimal decision.

The 3-stage configuration was performed for the same conditions as above of biogas composition of 52.17 % of methane under high and low pressure where the main condenser temperature was studied. Two optimal scenarios were established for the 90 % of methane in the biomethane stream which are the addition of the membrane at -40.0 °C or the recycle tie-in strategy at -37.5 °C under high pressure. The methane concentration of 97 % on the biomethane stream obtained the most suitable results when adding a membrane at -35.0 °C at low pressure or a recycle tie-in at -37.5 °C and high pressure.

The best unit was evaluated to recover the purge case using a 2-stage model wherein the biogas varied from 46.17 % to 58.17 % of methane concentration. The methane concentration of 90 % in the biomethane stream under 10.5 bara and methane concentration of 97 % in the biomethane stream under 16.5 bara were evaluated using the main condenser temperature of -27.5 °C. For the simulation of 90 % of methane in the biomethane stream, only the condenser configuration reached the target of the recycle flow. Therefore, it is required optimization in the membrane configuration to be optimal by decreasing

the main condenser temperature to -32.5 °C for methane concentration in the biogas from 52.17 % to 58.17 % while from 46.17 % to 50.17 % of methane concentration in the biogas feed the temperature should decrease to -35.0 °C. Thus, for the methane concentration of 97 % in the biomethane stream, the same optimization on the condenser temperature was proposed. For methane concentration from 52.17 % to 58.17 % in the biogas, the condenser temperature should be adjusted to -35.0 °C while for methane concentration from 46.17 % to 50.17 % in the biogas the temperature should be -37.5 °C.

Thus, the 3-stage model leads to the recycle flow below the limit regardless the biogas composition. For both methane concentration of 90 % and 97 % in the biomethane stream, the recycle tie-in showed the most suitable results as matched lower recycle flow rate with lower power consumption as compared to other unit configurations.

The study of the variation of the methane concentration in the tail-gas from 3 % to 9 % for the 2-stage model consisted in a 97 % of methane in the biomethane stream at 10.5 bara while the condenser temperature remained -40.0 °C. The membrane configuration and recycle tie-in configuration required up to 2 kW of heat in the reboiler due to the number of impurities in the liquid CO₂ flow to be set as an optimal configuration to recover the purge for the concentration of 3 % to 7 % of methane in the tail gas. For higher concentration of methane in the tail gas it is recommended to run at lower temperatures such as -41.0 °C.

Another study on the variation of the methane concentration from 0.4 % to 1.0 % in the tail gas was performed on a 3-stage model. The most suitable unit considered on this case was the recycle tie-in configuration once it reached low recycle flow rates and the power consumption was similar to other units.

6 Assessment of the work done

6.1 Objectives Achieved

- Overview of the previous projects of the CO₂ liquefaction unit and the techniques to condensate CO₂.
- Performed a sensitivity study to recover the purge stream by adding a membrane, a second condenser and a recycle tie-in system for 2-stage and 3-stage layouts.
- Set operational boundaries in accordance with the evaluation regarding the variation in the parameters within the biogas upgrading plant and in the liquefaction unit.
- Obtained the most suitable scenario to be designed as a closed loop regarding specific inlet conditions for 2-stage and 3-stage layouts.
- Implemented suggestion in the parameters to the scenarios not feasible due to high impurities or high recycle flow.

6.2 Other Work Carried Out

- Performed a literature review regarding H₂ membranes separation and hydrogen build-up in pipelines.
- Brainstormed with other companies such as BASF and Air Products to evaluate the feasibility of implementing their H₂ membrane in the DMT process.

6.3 Final Assessment

The work performed during this internship demonstrates that it is possible to recover the purge stream from the CO₂ liquefaction unit. Therefore, the 3-stage layout provided more satisfactory results when compared to 2-stage as the 2-stage layout required modification within the process system. In addition, the recycle tie-in configuration obtained interesting results followed by the membrane and the second condenser configuration.

In addition, further studies on this subject should focus on adding a hydrogen membrane to treat the purge stream before it is recycled once the lack of a purge leads to accumulation of hydrogen within the system. Thus, to the feasible scenarios it is recommended to perform an energy balance. Additional study should focus on increasing the size of the main condenser and compare the results with the simulation using two condensers on the liquefaction unit.

7 References

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Annex A - CO₂ Phase Diagram

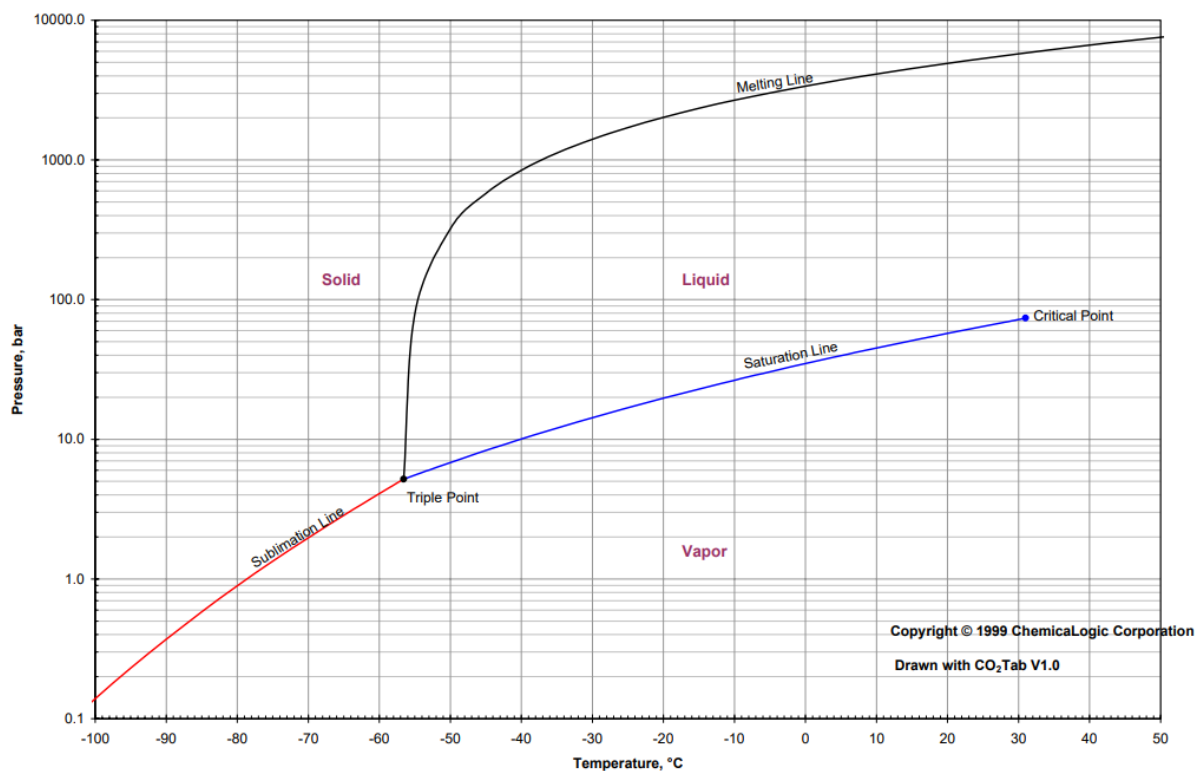


Figure A.1. CO₂ phase diagram showing the temperature and pressure conditions for the different states of carbon dioxide

Appendix A - Simulation Process Flow Diagram

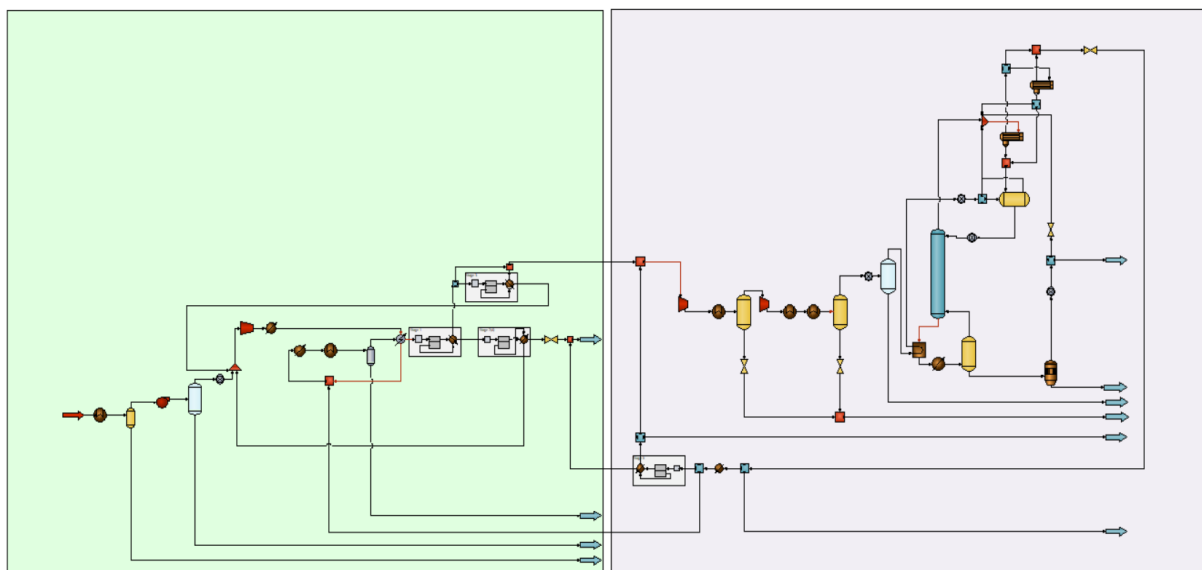


Figure A.1. ChemCAD process flow diagram

Appendix B - Flow Chart Diagram

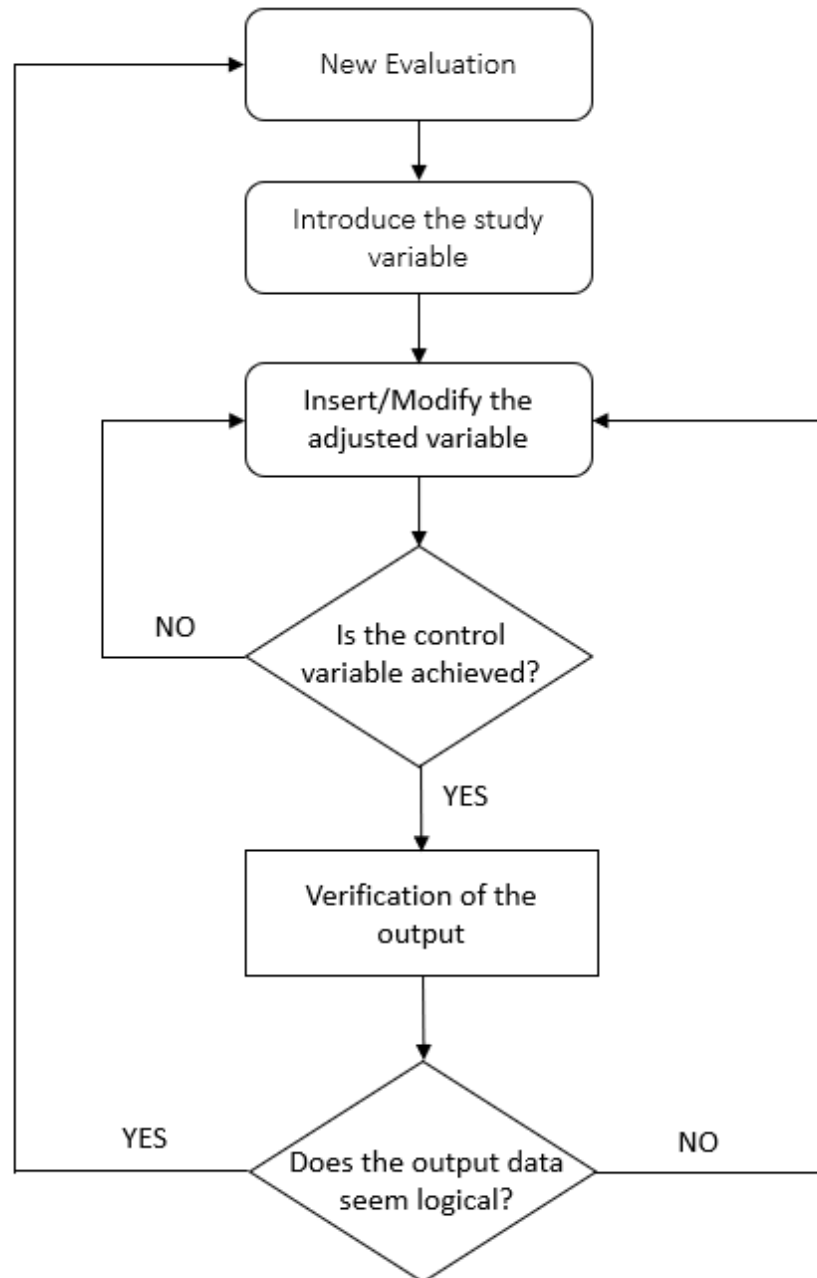


Figure B.1. Simulation procedures flowchart

Appendix C - Results for Temperature Behavior of a 2-stage Model with 97 % of Methane in the Biomethane Stream

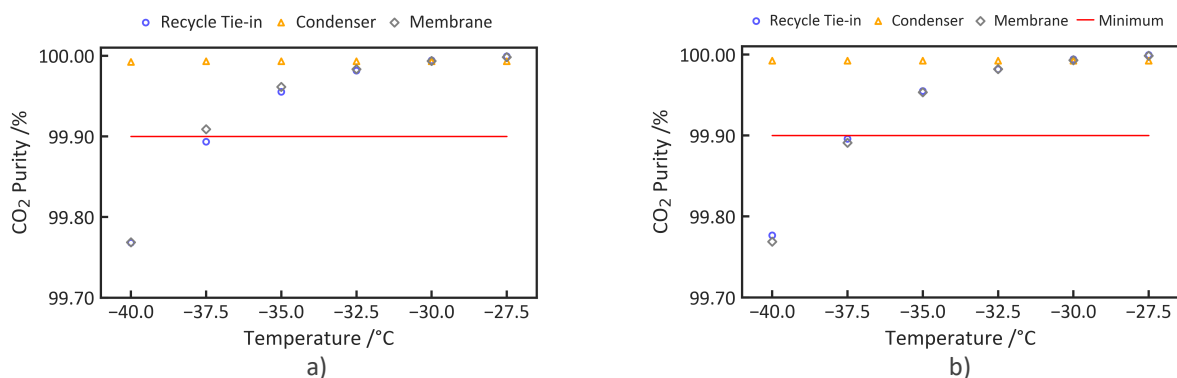


Figure C.1. CO₂ Purity for temperature behaviour study in 2-stage model and 97 % of methane in biomethane wherein
a) high pressure b) low pressure)

Table C.1. Membrane simulation data for temperature behaviour study in 2-stage model and 97 % of methane in biomethane

Parameters	Main Condenser Temperature /°C											
	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5
Pressure	High						Low					
Biomethane /Nm ³ .h ⁻¹	576.5	577.3	577.9	578.6	576.7	575.3	576.6	577.9	575.4	577.5	577.4	576.8
Tail-gas /Nm ³ .h ⁻¹	457.4	448.5	448.5	448.5	452.2	452.2	448.6	448.6	449.9	448.3	448.2	448.3
Stage 1 /unit	3	3	3	3	3	3	4	4	4	4	4	4
Stage 2 /unit	9	6	6	6	7	7	12	12	12	12	12	12
Liquid CO ₂ /kg.h ⁻¹	830.5	829.5	828.5	827.2	832.8	826.5	829.6	828.3	827.4	831.6	829.9	830.9
Stage X												
Module /unit	1	4	4	4	4	4	1	1	2	2	2	3
Pressure /bara	4	4.5	4.5	4.5	4.5	4.5	1.2	1.2	1.15	1.25	1.25	1.25
Permeate Flow /Nm ³ .h ⁻¹	28.7	57.1	71.7	93.5	129.6	208.0	37.1	45.9	66.8	85.5	123.8	212.7
Retentate Flow /Nm ³ .h ⁻¹	33.9	25.8	26.4	27.1	27.9	27.5	25.2	26.5	25.3	25.8	25.7	25.0
Simulation Index												
Scenario	37	38	39	40	41	42	55	56	57	58	59	60

Table C.2. Recycle tie-in simulation data for temperature behaviour study in 2-stage model and 97 % of methane in biomethane

Parameters	Main Condenser Temperature /°C											
	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5
Pressure	High						Low					
Biomethane /Nm ³ .h ⁻¹	577.8	578.3	578.6	578.6	576.8	576.0	577.6	575.8	576.5	577.4	578.4	576.6
Tail-gas /Nm ³ .h ⁻¹	484.3	495.6	510.4	534.8	594.0	778.9	487.4	499.4	512.2	536.8	587.5	791.8
Stage 1 /unit	3	3	3	3	3	4	5	5	5	5	5	7
Stage 2 /unit	9	9	9	9	9	8	12	13	13	13	13	13
Liquid CO ₂ /kg.h ⁻¹	827.8	828.1	827.4	827.2	831.1	834.4	828.5	832.2	831.4	829.5	827.7	831.3
Recycle Tie-in												
Flow Rate /Nm ³ .h ⁻¹	62.1	73.8	89.0	113.3	171.0	354.2	65.0	75.1	88.6	114.3	166.0	368.3
CH ₄ Composition /%	37.9	33.0	27.9	22.5	16.9	11.1	37.8	32.9	27.8	22.5	16.9	11.1
CO ₂ Composition /%	60.0	65.1	70.5	76.2	82.1	88.3	60.0	65.1	70.5	76.2	82.1	88.3
Simulation Index												
Scenario	43	44	45	46	47	48	61	62	63	64	65	66

Table C.3. Condenser simulation data for temperature behaviour study in 2-stage model and 97 % of methane in biomethane

Parameters	Main Condenser Temperature /°C											
	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5
Pressure	High						Low					
Biomethane /Nm ³ .h ⁻¹	576.4	576.4	576.4	576.4	576.4	576.4	577.0	577.0	577.0	577.0	577.0	577.0
Tail-gas /Nm ³ .h ⁻¹	481.3	481.3	481.3	481.3	481.3	481.3	482.1	482.1	482.1	482.1	482.1	482.1
Stage 1 /unit	3	3	3	3	3	3	5	5	5	5	5	5
Stage 2 /unit	10	10	10	10	10	10	12	12	12	12	12	12
Liquid CO ₂ /kg.h ⁻¹	832.0	831.5	831.8	832.1	831.9	831.9	830.8	830.3	830.4	831.0	830.7	830.7
2 nd Condenser												
1 st Condenser Gas Flow /Nm ³ .h ⁻¹	65.5	76.4	92.6	119.0	169.7	169.7	67.1	78.2	94.8	121.9	173.8	313.1
2 nd Condenser Gas Flow /Nm ³ .h ⁻¹	57.7	57.7	57.8	57.8	57.8	57.8	59.2	59.1	59.1	59.2	59.1	59.1
Simulation Index												
Scenario	49	50	51	52	53	54	67	68	69	70	71	72

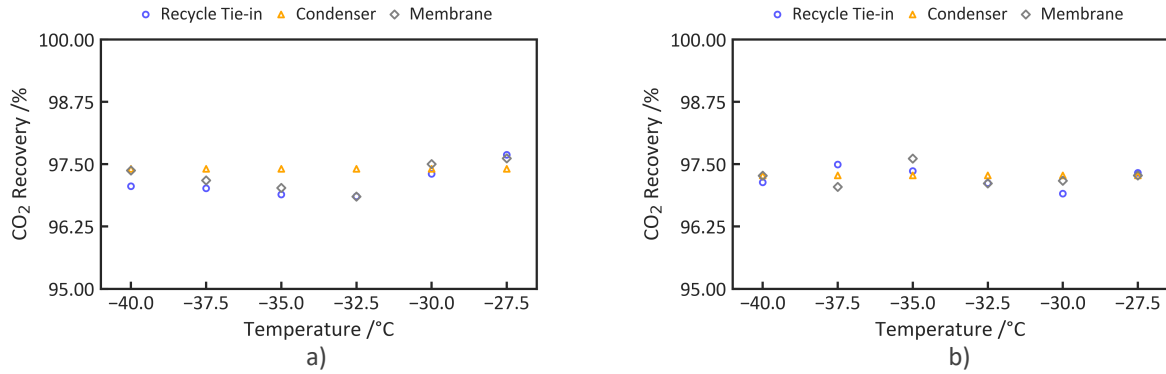


Figure C.2.CO₂ recovery for temperature behaviour study in 2-stage model and 97 % of methane in the biomethane wherein a) high pressure b) low pressure

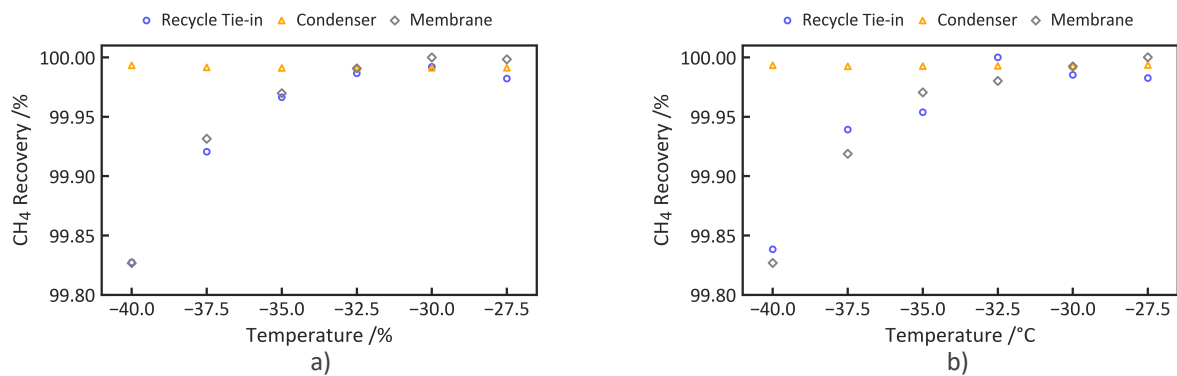


Figure C.3. CH₄ recovery for temperature behaviour study in 2-stage model and 97 % of methane in the biomethane wherein a) high pressure b) low pressure

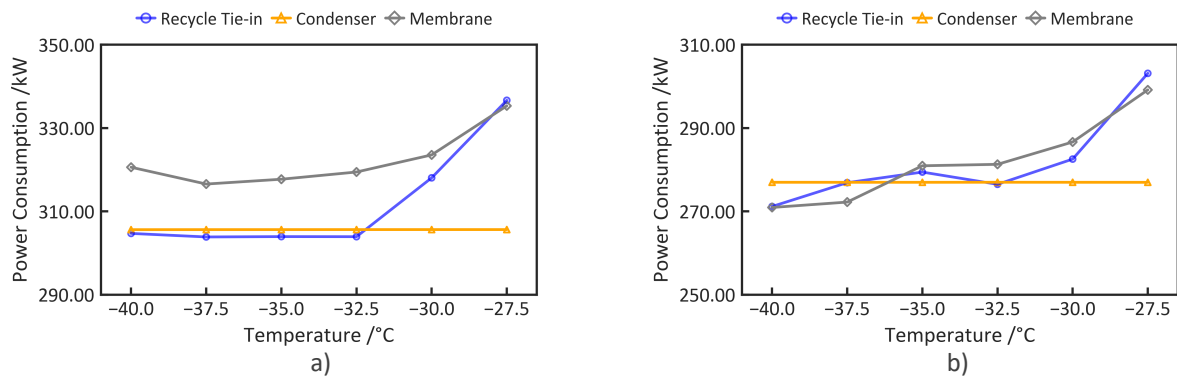


Figure C.4.Power consumption for temperature behavior study in 2-stage model and 97 % of methane in the biomethane wherein a) high pressure b) low pressure

Appendix D - Results for the Methane Variation in the Biogas of a 2-stage Model with 97 % of Methane in the Biomethane Stream

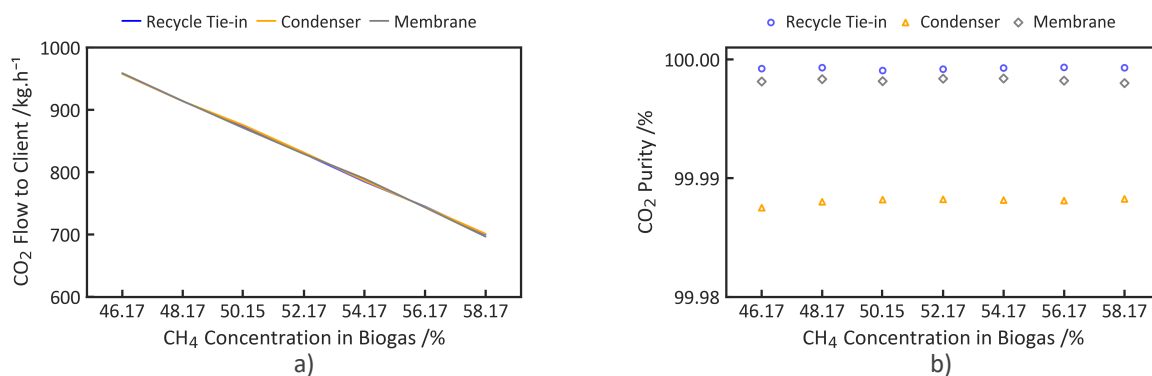


Figure D.1. a) Liquid CO₂ and b) CO₂ purity for the biogas composition study in 2-stage model and 97 % of methane in biomethane.

Table D.1. Membrane simulation data for biogas composition study in a 2-stage model and 97 % of methane in biomethane.

Parameters	CH ₄ Concentration in Biogas /%						
	46.17	48.17	50.17	52.17	54.17	56.17	58.17
Pressure	High						
Biomethane /Nm ³ ·h ⁻¹	511.7	534.3	556.4	576.1	598.1	621.9	645.1
Tail-gas /Nm ³ ·h ⁻¹	518.8	496.9	474.2	452.6	433.3	398.6	377.2
Stage 1 /unit	3	3	3	3	3	2	2
Stage 2 /unit	6	6	7	7	8	6	6
Liquid CO ₂ /kg·h ⁻¹	958.8	914.2	871.0	829.3	789.8	743.5	696.7
Stage X							
Module /unit	3	3	3	3	3	2	1
Pressure /bara	3.0	3.0	4.0	4.0	4.5	1.1	1.3
Permeate Flow /Nm ³ ·h ⁻¹	233.4	236.1	211.7	220.2	203.1	188.0	164.1
Retentate Flow /Nm ³ ·h ⁻¹	30.4	31.2	30.6	28.7	31.4	19.9	22.3
Simulation Index							
Scenario	94	95	96	97	98	99	100

Table D.2. Recycle tie-in simulation data for biogas composition study in a 2-stage model and 97 % of methane in biomethane.

Parameters	CH ₄ Concentration in Biogas /%						
	46.17	48.17	50.17	52.17	54.17	56.17	58.17
Pressure	High						
Biomethane /Nm ³ ·h ⁻¹	512.1	534.2	555.2	577.7	600.4	620.7	643.5
Tail-gas /Nm ³ ·h ⁻¹	890.8	871.1	781.6	762.0	742.5	713.5	665.1
Stage 1 /unit	5	5	4	4	4	4	4
Stage 2 /unit	6	6	7	7	7	7	7
Liquid CO ₂ /kg·h ⁻¹	957.8	913.8	873.2	829.7	784.9	745.0	700.0
Recycle Tie-in							
Flow Rate /Nm ³ ·h ⁻¹	402.9	406.0	336.7	339.8	342.8	334.2	308.6
CH ₄ Composition /%	11.1	11.1	11.1	11.1	11.1	11.1	11.2
CO ₂ Composition /%	88.3	88.3	88.3	88.3	88.3	88.3	88.3
Simulation Index							
Scenario	101	102	103	104	105	106	107

Table D.3. Condenser simulation data for biogas composition study in a 2-stage model and 97 % of methane in biomethane.

Parameters	CH ₄ Concentration in Biogas /%						
	46.17	48.17	50.17	52.17	54.17	56.17	58.17
Pressure	High						
Biomethane /Nm ³ ·h ⁻¹	511.8	534.0	553.9	576.4	599.1	621.1	642.6
Tail-gas /Nm ³ ·h ⁻¹	550.4	529.0	508.5	483.2	456.9	431.9	408.0
Stage 1 /unit	3	3	3	3	3	3	3
Stage 2 /unit	6	6	6	7	7	7	7
Liquid CO ₂ /kg·h ⁻¹	957.7	913.9	875.5	831.6	786.7	744.1	701.3
2 nd Condenser							
1 st Condenser Gas Flow /Nm ³ ·h ⁻¹	331.4	336.4	330.7	315.5	296.4	280.7	268.1
2 nd Condenser Gas Flow /Nm ³ ·h ⁻¹	62.6	63.6	62.5	59.6	55.9	53.0	50.6
Simulation Index							
Scenario	108	109	110	111	112	113	114

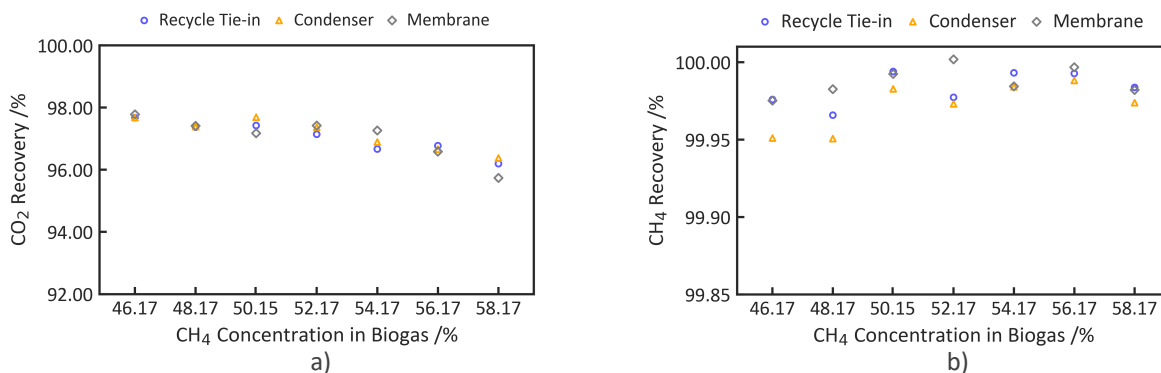


Figure D.2. a) CO₂ Recovery and b) CH₄ recovery for the biogas composition study in 2-stage model and 97 % of methane in biomethane.

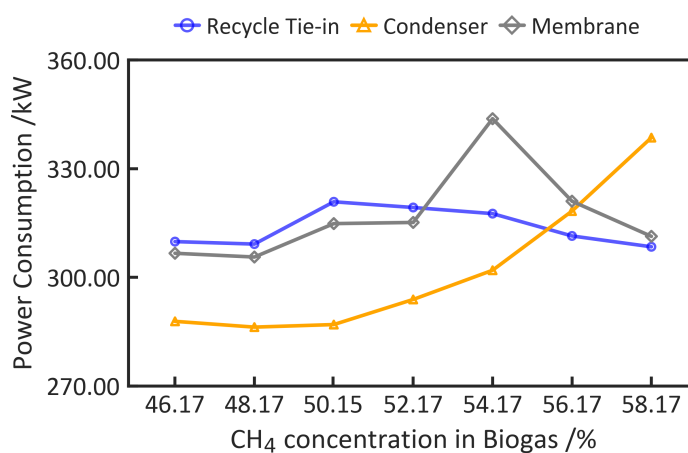


Figure D.3. Power consumption for the biogas composition study in 2-stage model and 97 % of methane in biomethane.

Appendix E - Results for Temperature Behavior of a 3-stage Model with 97 % of Methane in the Biomethane Stream

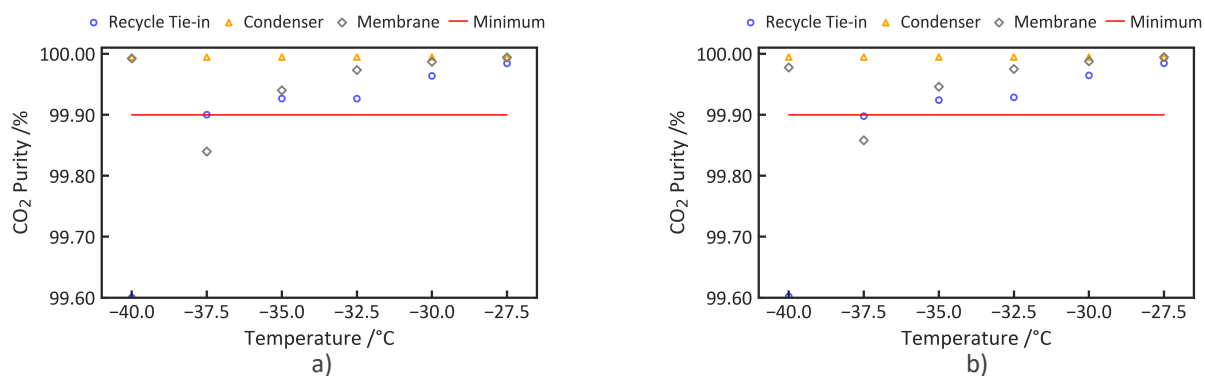


Figure E.1. CO₂ Purity for temperature behaviour study in 3-stage model and 97 % of methane in biomethane wherein
a) high pressure b) low pressure.

Table E.1. Membrane simulation data for temperature behaviour study in a 3-stage model and 97 % of methane in biomethane.

Parameters	Main Condenser Temperature /°C											
	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5
Pressure	High						Low					
Biomethane /Nm ³ .h ⁻¹	578.2	578.2	578.2	578.2	578.2	578.2	577.7	577.2	577.6	577.7	577.8	577.8
Tail-gas /Nm ³ .h ⁻¹	424.2	424.2	424.2	424.2	424.2	424.2	424.7	424.7	424.7	424.8	424.8	424.8
Stage 1 Modules /unit	3	3	3	3	3	3	7	7	7	7	7	7
Stage 2 Modules /unit	7	7	7	7	7	7	12	12	12	12	12	12
Stage 3 Modules /unit	12	12	12	12	12	12	9	9	9	9	9	9
Liquid CO ₂ /kg.h ⁻¹	828.3	828.8	828.5	828.4	828.3	828.0	829.0	829.4	829.1	829.1	828.8	828.9
Stage X												
Module /unit	1	1	1	1	1	1	1	1	1	1	1	1
Pressure /bara	1.7	1.7	1.7	1.7	1.7	1.7	1.4	1.4	1.4	1.4	1.4	1.4
Permeate Flow /Nm ³ .h ⁻¹	105.5	20.6	30.9	38.5	47.0	60.8	54.2	25.2	34.7	41.6	50.5	64.7
Retentate Flow /Nm ³ .h ⁻¹	2.4	1.7	2.2	2.3	2.4	2.4	2.5	2.0	2.4	2.5	2.5	2.6
Simulation Index												
Scenario	172	173	174	175	176	177	190	191	192	193	194	195

Table E.2. Recycle tie-in simulation data for temperature behaviour study in a 3-stage model and 97 % of methane in biomethane

Parameters	Main Condenser Temperature /°C											
	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5
Pressure	High						Low					
Biomethane /Nm ³ ·h ⁻¹	576.3	577.3	577.8	578.4	578.6	578.3	577.2	578.5	578.2	577.6	578.1	578.3
Tail-gas /Nm ³ ·h ⁻¹	426.1	428.8	430.3	430.5	434.4	444.4	424.9	427.1	426.8	432.4	435.6	443.5
Stage 1 Modules /unit	3	3	3	3	3	3	7	7	7	7	7	7
Stage 2 Modules /unit	7	7	7	7	7	7	12	12	12	12	12	12
Stage 3 Modules /unit	12	12	12	12	12	12	10	10	10	10	10	10
Liquid CO ₂ /kg·h ⁻¹	829.9	829.2	828.6	827.3	827.4	827.9	828.2	826.9	827.9	829.1	828.3	828.0
Recycle Tie-in												
Flow Rate /Nm ³ ·h ⁻¹	2.3	6.2	8.2	8.9	13.0	22.7	2.2	5.7	5.1	10.0	13.6	21.7
CH ₄ Composition /%	29.4	27.5	23.5	18.9	14.3	9.4	28.5	26.6	34.7	18.4	13.9	9.2
CO ₂ Composition /%	60.1	65.2	70.6	76.2	82.2	88.3	60.1	65.2	55.2	76.2	82.2	88.3
Simulation Index												
Scenario	178	179	180	181	182	183	196	197	198	199	200	201

Table E.3. Condenser simulation data for temperature behaviour study in a 3-stage model and 97 % of methane in biomethane.

Parameters	Main Condenser Temperature /°C											
	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5	-40.0	-37.5	-35.0	-32.5	-30.0	-27.5
Pressure	High						Low					
Biomethane /Nm ³ ·h ⁻¹	578.3	578.3	578.3	578.3	578.3	578.3	577.1	577.1	577.1	577.1	577.1	577.1
Tail-gas /Nm ³ ·h ⁻¹	427.6	427.6	427.6	427.6	427.6	427.6	428.9	428.9	428.9	428.9	428.9	428.9
Stage 1 Modules /unit	3	3	3	3	3	3	7	7	7	7	7	7
Stage 2 Modules /unit	7	7	7	7	7	7	12	12	12	12	12	12
Liquid CO ₂ /kg·h ⁻¹	12	12	12	12	12	12	11	11	11	11	11	11
2 nd Condenser												
1 st Condenser Gas Flow /Nm ³ ·h ⁻¹	6.6	7.7	9.3	12.0	17.0	30.5	6.8	8.0	9.7	12.4	17.7	31.7
2 nd Condenser Gas Flow /Nm ³ ·h ⁻¹	5.8	5.8	5.8	5.8	5.8	5.8	6.0	6.0	6.0	6.1	6.1	6.1
Simulation Index												
Scenario	184	185	186	187	188	189	202	203	204	205	206	207

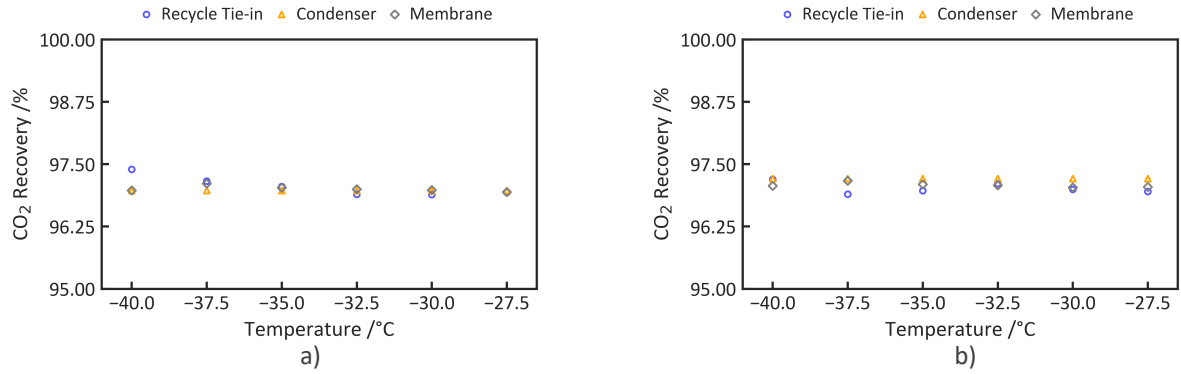


Figure E.2. CO₂ recovery for temperature behaviour study in 3-stage model and 97 % of methane in the biomethane wherein
a) high pressure b) low pressure

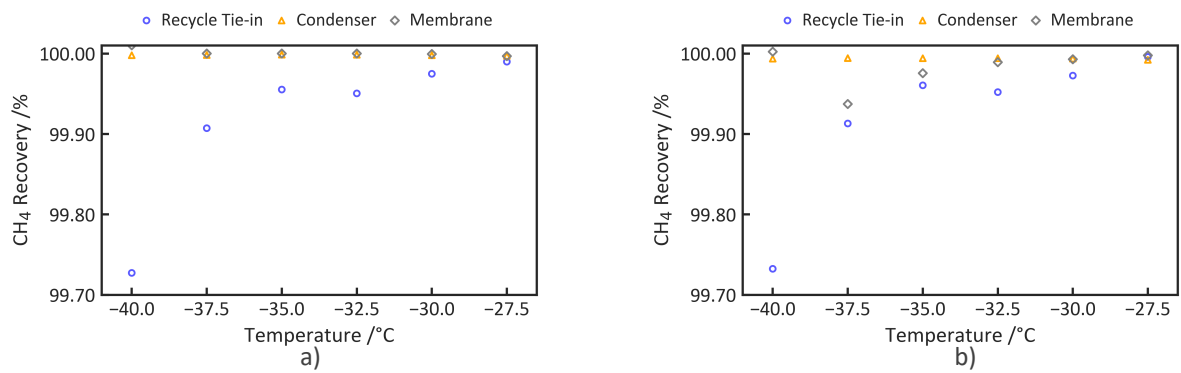


Figure E.3. CH₄ recovery for temperature behaviour study in a 3-stage model and 97 % of methane in the biomethane wherein
a) high pressure b) low pressure

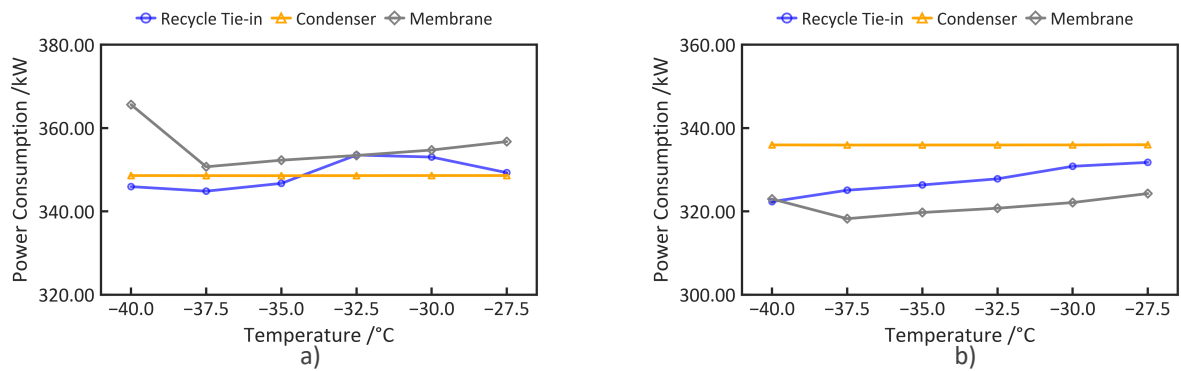


Figure E.4. Power consumption for temperature behaviour study in a 3-stage model and 97 % of methane in the biomethane wherein a) high pressure b) low pressure

Appendix F - Results for the Methane Variation in the Biogas of a 3-stage Model with 97 % of Methane in the Biomethane Stream

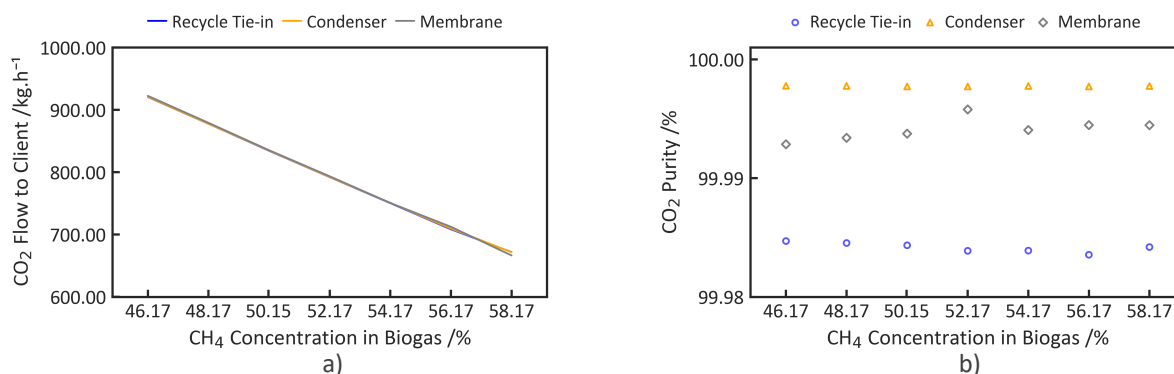


Figure F.1. a) Liquid CO₂ and b) CO₂ purity for the biogas composition study in 3-stage model and 97 % of methane in biomethane

Table F.1. Membrane, recycle tie-in and condenser simulation data for the biogas composition study in 3-stage model and 97 % of methane in biomethane.

Parameters	CH ₄ Concentration in Biogas /%						
	46.17	48.17	50.17	52.17	54.17	56.17	58.17
Pressure	Low						
Biomethane /Nm ³ .h ⁻¹	509.0 - 511.0	532.0 - 533.0	555.0 - 556.0	577.0 - 579.0	600.0 - 601.0	620.0 - 623.0	642.0 - 646.0
Tail-gas /Nm ³ .h ⁻¹	493.8 - 518.0	470.0 - 493.0	447.0 - 469.0	424.0 - 443.0	401.0 - 420.0	381.0 - 396.0	356.0 - 379.0
Stage 1 Modules /unit	3	3	3	3	3	3	3
Stage 2 Modules /unit	7	7	7	7	7	7	7
Stage 3 Modules /unit	12	12	12	12	12	12	12
Liquid CO ₂ /kg.h ⁻¹	961.0 - 964.0	917.0 - 919.0	871.0 - 873.0	827.0 - 832.0	784.0 - 785.0	740.0 - 745.0	696.0 - 703.0
Stage X							
Modules /unit	1	7	7	1	7	1	1
Pressure /bara	3	3	3	3	3	3	3
Permeate Flow /Nm ³ .h ⁻¹	62.3	62	61.4	83.4	59.6	59.7	58
Retentate Flow /Nm ³ .h ⁻¹	3.0	2.7	2.4	2.6	2.3	2.2	2.2
Scenario	229	230	231	232	233	234	235
Recycle Tie-in							
Flow Rate /Nm ³ .h ⁻¹	27.3	25.9	24.4	21.2	20.8	18.5	20.6
CH ₄ Composition /%	9.1	9.2	9.3	9.4	9.5	9.6	9.7
CO ₂ Composition /%	88.3	88.3	88.3	88.3	88.3	88.3	88.3
Scenario	236	237	238	239	240	241	242
2 nd Condenser							
1 st Condenser Gas Flow /Nm ³ .h ⁻¹	38.6	36.2	35.8	33.1	29.6	28.5	26.3
2 nd Condenser Gas Flow /Nm ³ .h ⁻¹	7.4	6.9	6.8	6.3	5.6	5.4	5.0
Scenario	243	244	245	246	247	248	249

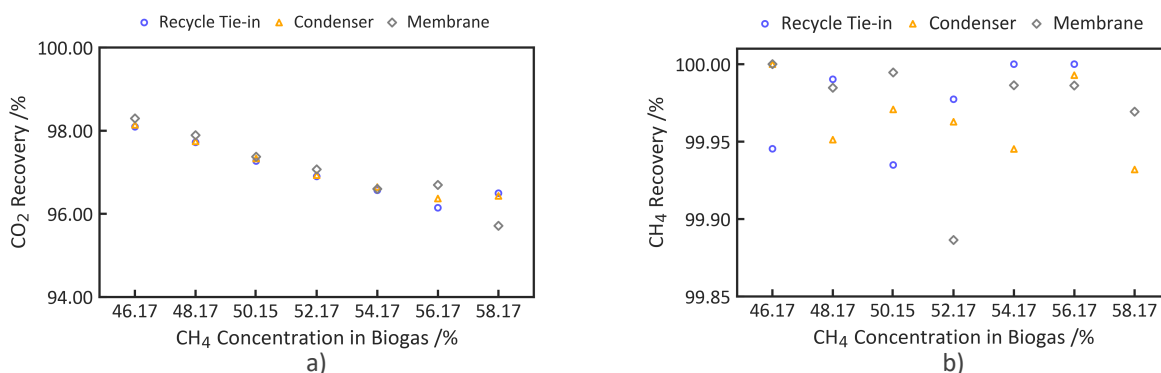


Figure F.2. a) CO₂ Recovery and b) CH₄ recovery for the biogas composition study in 3-stage model and 97 % of methane in biomethane

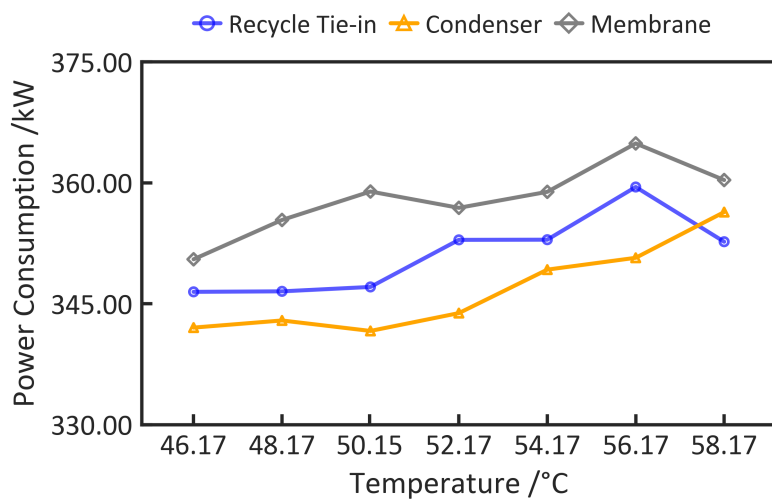


Figure F.3. Power consumption for the biogas composition study in 3-stage model and 97 % of methane in biomethane

Appendix G - Condenser Temperature Boundaries for 2-stage and 3-stage Analysis

Table G.1. Main condenser temperature boundaries analyze to 2-stage model and 90 % of methane in biomethane.

Scenario	Configuration Unit	Flow Rate /Nm ³ .h ⁻¹	CO ₂ Recovery /%	CH ₄ Recovery /%	Liquid CO ₂ /kg.h ⁻¹	Biomethane Flow /Nm ³ .h ⁻¹	Power Consumption /kW	Unit cost
27	Recycle Tie-in	76.89	87.15	99.95	742.53	621.04	247.25	\$
21	Membrane	75.25	86.74	100.00	739.79	623.18	251.89	\$
22	Membrane	92.25	86.74	99.99	739.88	623.11	254.77	\$
3	Membrane	71.44	86.72	99.97	740.52	622.82	276.52	\$
4	Membrane	87.90	86.94	99.98	742.46	621.95	282.79	\$
9	Recycle Tie-in	78.64	99.97	86.53	738.93	623.62	286.32	\$

Table G.2. Main condenser temperature boundaries analyze to 2-stage model and 97 % of methane in biomethane.

Scenario	Configuration Unit	Flow Rate /Nm ³ .h ⁻¹	CO ₂ Recovery /%	CH ₄ Recovery /%	Liquid CO ₂ /kg.h ⁻¹	Biomethane Flow /Nm ³ .h ⁻¹	Power Consumption /kW	Unit cost
63	Recycle Tie-in	88.62	97.36	99.99	831.38	576.46	279.42	\$\$\$
57	Membrane	92.18	97.61	99.95	827.39	575.42	280.93	\$\$
45	Recycle Tie-in	89.02	96.89	99.97	827.37	578.56	303.93	\$\$
38	Membrane	82.87	97.17	99.99	829.54	577.28	316.54	\$

Table G.3. Main condenser temperature boundaries analyze to 3-stage model and 90 % of methane in biomethane.

Scenario	Configuration Unit	Flow Rate /Nm ³ .h ⁻¹	CO ₂ Recovery /%	CH ₄ Recovery /%	Liquid CO ₂ /kg.h ⁻¹	Biomethane Flow /Nm ³ .h ⁻¹	Power Consumption /kW	Unit cost
161	Recycle Tie-in	4.70	86.78	99.92	740.63	622.39	314.66	\$\$\$\$
143	Recycle Tie-in	5.39	86.66	99.94	739.72	623.03	334.85	\$\$
162	Recycle Tie-in	6.14	86.45	99.97	738.08	623.7	317.77	\$\$\$\$
144	Recycle Tie-in	6.95	86.53	99.98	738.87	623.6	335.66	\$\$
145	Recycle Tie-in	7.69	87.31	99.95	745.38	620.29	340.04	\$\$
163	Recycle Tie-in	9.07	87.33	99.95	745.58	620.23	306.9	\$\$\$\$
146	Recycle Tie-in	10.68	87.07	99.98	743.52	621.23	341.98	\$\$
164	Recycle Tie-in	12.12	86.95	99.97	742.53	621.77	311.22	\$\$\$\$
147	Recycle Tie-in	17.41	86.97	99.99	742.8	621.74	343.08	\$\$
165	Recycle Tie-in	19.96	87.03	99.99	743.29	621.43	309.82	\$\$\$\$
154	Membrane	20.19	87.37	99.74	742.83	621.45	303.77	\$\$\$\$
136	Membrane	25.12	86.9	99.97	741.89	621.79	336.19	\$\$\$
137	Membrane	65.17	86.89	99.99	741.99	622.05	341.15	\$\$\$
155	Membrane	72.65	86.98	100.00	742.80	621.62	310.61	\$\$\$\$
138	Membrane	79.25	86.86	99.99	741.87	622.15	343.26	\$\$\$
156	Membrane	85.68	86.95	100.00	742.67	621.70	312.58	\$\$\$\$
139	Membrane	93.43	86.86	100.00	741.94	622.23	345.40	\$\$\$

Table G.4. Main condenser temperature boundaries analyze to 3-stage model and 97 % of methane in biomethane.

Scenario	Configuration Unit	Flow Rate /Nm ³ ·h ⁻¹	CO ₂ Recovery /%	CH ₄ Recovery /%	Liquid CO ₂ /kg·h ⁻¹	Biomethane Flow /Nm ³ ·h ⁻¹	Power Consumption /kW	Unit cost
192	Membrane	37.06	97.09	99.98	829.13	577.61	319.72	\$\$\$\$
193	Membrane	44.06	97.07	99.99	829.07	577.74	320.74	\$\$\$\$
194	Membrane	53.04	97.03	99.99	828.76	577.78	322.11	\$\$\$\$
190	Membrane	56.73	97.06	100	828.8	577.73	322.95	\$\$\$\$
195	Membrane	67.3	97.04	100	828.87	577.83	324.26	\$\$\$\$
197	Recycle Tie-in	5.65	96.9	99.91	826.94	578.46	325.06	\$\$\$\$
198	Recycle Tie-in	5.06	96.97	99.96	827.87	578.22	326.33	\$\$\$\$
199	Recycle Tie-in	9.99	97.11	99.95	829.1	577.57	327.8	\$\$\$\$
200	Recycle Tie-in	13.63	96.99	99.97	828.29	578.05	330.8	\$\$\$\$
201	Recycle Tie-in	21.75	96.95	100	828.03	578.31	331.75	\$\$\$\$
179	Recycle Tie-in	6.24	97.16	97.11	829.16	577.33	344.83	\$\$\$
180	Recycle Tie-in	8.16	97.05	97.03	828.59	577.81	346.71	\$\$\$
183	Recycle Tie-in	22.69	96.93	96.94	827.88	578.35	349.28	\$\$\$\$
174	Membrane	33.12	97.03	100.00	828.53	578.19	352.27	\$\$\$
182	Recycle Tie-in	13.02	96.89	96.98	827.4	578.56	353.02	\$\$\$
175	Membrane	40.81	97.00	100.00	828.39	578.19	353.41	\$\$\$
181	Recycle Tie-in	8.91	96.89	97	827.26	578.44	353.5	\$\$\$

Appendix H - Unit Selection for the Variation of Methane Concentration in the Biogas Flow Analysis

Table H.1. Unit selection analysis for biogas composition to a 3-stage model and 90 % of methane in biomethane.

Methane Composition /%	Scenario	Configuration Unit	Flow Rate /Nm ³ ·h ⁻¹	CO ₂ Recovery /%	CH ₄ Recovery /%	Liquid CO ₂ /kg·h ⁻¹	Biomethane Flow /Nm ³ ·h ⁻¹	Power Consumption /kW	Investment cost
46.17	215	Recycle Tie-in	24.60	89.85	99.97	881.03	551.22	316.33	\$\$\$\$
	208	Membrane	58.90	89.96	99.97	882.11	550.57	324.45	\$\$\$\$
	222	Condenser	6.40	90.23	99.97	884.81	549.27	316.21	\$\$\$\$
48.17	216	Recycle Tie-in	22.12	88.77	99.97	833.03	575.72	322.01	\$\$\$\$
	209	Membrane	57.54	88.89	99.98	834.15	574.65	320.47	\$\$\$\$
	223	Condenser	5.70	88.72	99.98	832.57	575.93	322.50	\$\$\$\$
50.17	217	Recycle Tie-in	21.03	88.09	99.98	789.51	597.80	325.09	\$\$\$\$
	210	Membrane	56.97	87.94	99.99	788.17	598.57	320.72	\$\$\$\$
	224	Condenser	5.60	87.74	99.99	786.43	599.68	321.93	\$\$\$\$
52.17	218	Recycle Tie-in	21.25	86.82	99.97	741.53	622.23	322.30	\$\$\$\$
	211	Membrane	46.60	87.26	100.00	745.33	620.55	329.46	\$\$\$\$
	225	Condenser	5.40	86.69	99.98	740.50	622.72	323.68	\$\$\$\$
54.17	219	Recycle Tie-in	17.62	85.21	99.97	691.87	647.53	335.67	\$\$\$\$
	212	Membrane	56.96	84.83	99.99	688.79	647.92	340.21	\$\$\$\$
	226	Condenser	4.80	85.60	99.98	695.09	645.86	332.20	\$\$\$\$
56.17	220	Recycle Tie-in	18.05	83.74	99.98	644.63	671.65	326.04	\$\$\$\$
	213	Membrane	56.95	84.03	99.99	646.90	669.72	337.19	\$\$\$\$
	227	Condenser	4.70	84.21	99.99	648.30	669.95	332.34	\$\$\$\$
58.17	221	Recycle Tie-in	16.34	82.94	99.97	603.51	692.54	332.84	\$\$\$\$
	214	Membrane	56.49	82.70	99.98	601.80	693.46	335.53	\$\$\$\$
	228	Condenser	4.20	82.57	99.98	600.84	693.85	340.03	\$\$\$\$

Table H.2. Unit selection analysis for biogas composition to a 3-stage model and 97 % of methane in biomethane.

Methane Composition /%	Scenario	Configuration Unit	Flow Rate /Nm ³ ·h ⁻¹	CO ₂ Recovery /%	CH ₄ Recovery /%	Liquid CO ₂ /kg·h ⁻¹	Biomethane Flow /Nm ³ ·h ⁻¹	Power Consumption /kW	Investment cost
46.17	236	Recycle Tie-in	27.31	98.09	99.95	961.82	510.12	346.47	\$\$\$
	229	Membrane	65.38	98.29	100.00	963.84	509.85	350.51	\$\$\$
	243	Condenser	7.40	98.14	100.00	962.35	509.90	342.03	\$\$\$\$
48.17	237	Recycle Tie-in	25.87	97.72	99.99	916.96	533.01	346.53	\$\$\$
	230	Membrane	64.70	97.89	99.98	918.63	532.12	355.39	\$\$\$\$
	244	Condenser	6.90	97.74	99.95	917.26	532.80	343.92	\$\$\$\$
50.17	238	Recycle Tie-in	24.42	97.27	99.93	871.75	555.98	347.08	\$\$\$
	231	Membrane	63.83	97.37	99.99	872.73	555.28	358.91	\$\$\$\$
	245	Condenser	6.80	97.33	99.97	872.36	555.60	341.62	\$\$\$\$
52.17	239	Recycle Tie-in	21.21	96.90	99.98	827.59	578.39	352.92	\$\$\$
	232	Membrane	86.05	97.07	99.89	831.11	577.74	356.89	\$\$\$
	246	Condenser	6.30	96.93	99.96	827.92	578.30	343.83	\$\$\$\$
54.17	240	Recycle Tie-in	20.78	96.57	100.00	784.05	600.69	352.94	\$\$\$
	233	Membrane	61.99	96.60	99.99	784.36	600.45	358.88	\$\$\$\$
	247	Condenser	5.60	96.64	99.95	784.73	600.37	349.23	\$\$\$\$
56.17	241	Recycle Tie-in	18.47	96.14	100.00	740.10	622.98	359.47	\$\$\$
	234	Membrane	61.84	96.69	99.99	744.38	620.93	364.88	\$\$\$
	248	Condenser	5.40	96.37	99.99	741.88	622.19	350.96	\$\$\$\$
58.17	242	Recycle Tie-in	20.57	96.49	99.78	702.13	642.32	352.69	\$\$\$
	235	Membrane	60.27	95.71	99.97	696.48	645.16	360.34	\$\$\$
	249	Condenser	5.00	96.43	99.93	701.72	642.62	356.36	\$\$\$\$

Appendix I - Unit Selection for the Variation of the Methane Concentration in the Tail Gas Analysis for 2-stage and 3-stage

Table I.1. Unit selection analysis for tail gas composition to a 2-stage model.

Methane Composition /%	Scenario	Configuration Unit	Flow Rate /Nm ³ ·h ⁻¹	CO ₂ Recovery /%	CH ₄ Recovery /%	Liquid CO ₂ /kg·h ⁻¹	Biomethane Flow /Nm ³ ·h ⁻¹	Power Consumption /kW	Investment cost
3	129	Condenser	33.40	99.94	96.80	832.70	578.90	304.41	\$\$\$
	122	Recycle Tie-in	37.26	96.75	99.94	826.00	579.11	305.83	\$\$
	115	Membrane	46.30	97.58	99.89	826.36	575.58	302.45	\$\$\$
4	116	Membrane	46.19	97.25	99.90	829.08	576.90	326.21	\$\$\$
	130	Condenser	46.30	99.95	97.11	829.86	577.59	286.85	\$\$\$
	123	Recycle Tie-in	51.66	97.05	99.95	828.66	577.83	288.16	\$\$
5	131	Condenser	53.70	100.00	97.09	828.47	577.62	274.22	\$\$\$
	124	Recycle Tie-in	59.29	97.12	99.96	829.25	577.55	275.59	\$\$
	117	Membrane	63.16	97.02	99.96	829.23	577.92	276.12	\$\$
6	132	Condenser	67.60	99.96	97.50	829.17	575.84	268.37	\$\$\$
	118	Membrane	72.65	97.10	99.97	832.55	577.58	274.33	\$\$\$
	125	Recycle Tie-in	75.41	97.46	99.97	832.21	576.05	269.81	\$\$
7	133	Condenser	85.10	99.97	97.06	825.60	577.78	260.25	\$\$\$
	119	Membrane	91.08	96.68	99.97	828.88	579.51	264.80	\$\$

Table I.2. Unit selection analysis for tail gas composition to a 3-stage model.

Methane Composition /%	Scenario	Configuration Unit	Flow Rate /Nm ³ ·h ⁻¹	CO ₂ Recovery /%	CH ₄ Recovery /%	Liquid CO ₂ /kg·h ⁻¹	Biomethane Flow /Nm ³ ·h ⁻¹	Power Consumption /kW	Investment cost
0.4	255	Recycle tie-in	17.25	97.99	99.96	836.92	577.28	339.09	\$\$\$\$
	250	Membrane	69.57	97.15	100.00	829.76	577.23	346.42	\$\$\$\$
	260	Condenser	5.00	97.39	100.00	831.83	576.21	326.09	\$\$\$\$
0.55	256	Recycle tie-in	26.24	96.96	99.98	828.11	578.21	315.31	\$\$\$\$
	251	Membrane	67.41	97.47	99.99	832.49	576.09	328.73	\$\$\$\$
	261	Condenser	7.00	96.95	100.00	828.09	578.24	314.72	\$\$\$\$
0.7	257	Recycle tie-in	25.25	96.89	100.00	832.05	578.48	313.00	\$\$\$\$
	252	Membrane	66.38	97.32	99.99	831.26	576.67	313.00	\$\$\$\$
	262	Condenser	8.00	97.24	100.00	830.57	577.08	305.12	\$\$\$\$
0.8	258	Recycle tie-in	40.65	96.70	100.00	825.95	578.51	297.88	\$\$\$\$
	253	Membrane	67.30	96.89	100.00	827.59	578.61	303.84	\$\$\$\$
	263	Condenser	10.00	96.97	100.00	828.29	578.27	294.04	\$\$\$\$
1	259	Recycle tie-in	50.68	97.48	100.00	832.62	576.04	308.44	\$\$\$\$
	254	Membrane	69.15	97.16	100.00	829.85	577.48	306.71	\$\$\$\$
	264	Condenser	12.00	97.05	100.00	828.94	577.76	290.97	\$\$\$\$