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LIQUEFACTION OF CO₂ FROM A BIOGAS UPGRADING PLANT FOR FOOD-GRADE APPLICATIONS

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***Liquefaction of CO₂ from a Biogas Upgrading
Plant for Food-grade Applications***

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held in

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Abstract

A multi-stage membrane upgrading unit (Carborex®MS) aims to remove the bulk of CO₂ from the raw biogas while producing biomethane. Instead of releasing the CO₂ to the atmosphere, the tail gas can be further purified and liquefied to create an extra revenue stream.

A “Bolt-on” liquefaction unit to a 3-stage membrane upgrading system was studied in the first part of the dissertation. The study showed how the raw biogas composition will affect the total system performance. The results indicated that for low CO₂ and CH₄ concentrations, increasing inerts will decrease both CH₄ and CO₂ concentration in the biomethane stream and increase the CH₄ content in the liquid CO₂. For 0.40 % N₂ and 0.10 % O₂, the raw biogas should have 45.00 to 50.28 % of CH₄ and 43.00 to 48.28 % of CO₂ for a proper operation.

The main goal of the project was to investigate the integration of the liquefaction system within the upgrading system, having several tie-in options for the outlet gas stream from the condenser. The integration can impact the membrane design due to the flow rate and composition of recycle stream, that is being redirected to the Carborex®MS after the Pressure Temperature Swing Adsorption (PTSA) regeneration. To reach the specification of the biomethane and CO₂ purity, as well as to ensure the required outlet gas flow rate to regenerate the PTSA, the condenser temperature for the 3-stage configurations should be adjusted within the range of -25.50 to -23.50 °C. The integration of the LCO₂ within the 3-stage membrane upgrading system increased the production of CO₂ in around 7 % in comparison with the Bolt-on, however it also increased the compressors flow rate by 6 to 14 %.

Afterwards, the Bolt-on and integrated configuration were modeled for the 2-stage design, which presented several challenges to achieve the required product quality while also while also keeping the operation of the system within acceptable ranges of flow rates. Besides the design optimization of the Carborex®MS done for the integrated configurations, some design options were studied in the liquefaction design for the Bolt-on configuration. In terms of operating costs, the 2-stage integrated configurations revealed an increase of the compressor flow rate of 26 to 38 % compared to the 3-stage Bolt-on configuration.

The two changes proposed for the liquefaction unit involved either adding a heat exchanger after the reboiler or a second condenser. These alternatives will require a lower condenser temperature (around -33 °C. Although the alternative with the extra heating has a superior heating duty, it will increase the liquid CO₂ production by a 14 %.

Keywords (theme):

Food-grade CO₂ / CO₂ liquefaction / Biogas upgrading /
Simulation and Modelling / CHEMCAD

Resumo

O sistema de purificação por membranas Carborex®MS tem como objetivo a produção de biometano através da remoção do CO₂ da corrente de biogás. De forma a eliminar as emissões globais líquidas, seria benéfico dar um passo adiante e utilizar este CO₂ em vez de o emitir para a atmosfera.

A adição de um sistema “Bolt-on” de liquefação de CO₂ a uma configuração com 3 estágios de membranas da Carborex®MS foi explorada na primeira parte da dissertação. Os resultados indicaram que, para baixas concentrações de CH₄ e de CO₂, aumentar a quantidades de inertes irá reduzir a concentração destas espécies nas correntes de biometano e de CO₂ líquido. De modo a operar corretamente, para uma concentração de 0.40 % N₂ e de 0.10 % O₂ no biogás, o mesmo deverá apresentar 45.00 a 50.28 % de CH₄ e 43.00 a 48.28 % de CO₂.

O objetivo principal do projeto consistiu na investigação da possibilidade de integração do sistema de liquefação com o sistema de purificação. Esta integração pode ter impacto no *design* das membranas devido a composição e ao caudal da corrente de reciclo, que ira ser redirecionada para a Carborex®MS após a regeneração do PTSA. De modo a atingir os requisitos do biometano e do CO₂ líquido e assegurar, em simultâneo, o caudal necessário à regeneração da unidade *Pressure Temperature Swing Adsorption* (PTSA), a temperatura do condensador para as configurações de 3 estágios deve ser ajustada a um intervalo de -25.50 a -23.50°C. Adicionalmente, a integração aumentou a produção de CO₂ líquido em 7 % em comparação com a versão *Bolt-on* no entanto, aumentou também o caudal que atravessa os compressores entre 6 a 14%.

De seguida, as configurações *Bolt-on* e integradas foram simuladas para a formato de 2 estágios da Carbores®MS. Estas configurações apresentaram algumas dificuldades na obtenção de produto com a qualidade necessária e em operar com caudais em intervalos admissíveis em simultâneo. Além das alterações no *design* das membranas da Carborex®MS realizado para as configurações integradas, algumas sugestões foram feitas no modelo da unidade de liquefação para a configuração *Bolt-on*. As configurações integradas no formato com 2 estágios apresentaram um aumento de 26 a 38 % nos caudais que atravessam os compressores em comparação com a configuração *Bolt-on*.

As duas sugestões propostas para a unidade de liquefação envolveram a adição de um permutador de calor ou de um segundo condensador. Estas alternativas carecem de uma temperatura no condensador mais baixa (cerca de -33 °C), o que significa precisam de um maior arrefecimento do que a configuração Bolt-on no formato de 3 estágios. Apesar da alternativa com o permutador de calor exigir um maior aquecimento revela um aumento na produção de CO₂ líquido de 14 %.

Palavras-chave:

CO₂ qualidade alimentar / Liquefação CO₂ / Purificação de biogás / Simulação e Modelação / CHEMCAD

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

Sign and date

Daniela Alves Gonçalves

03/08/2022

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Notation and Glossary

B	Channel base	m
C_G	Proportional factor	
d	Diameter	m
d_{eq}	Equivalent diameter	m
D	Diffusivity	$m^2 s^{-1}$
E	Activation energy	$J mol^{-1}$
h	Crimp height	m
k	Gas-side mass transfer coefficient	ms^{-1}
P	Permeability	$mol m^{-1} s^{-1} Pa^{-1}$
P_0	Pre-exponential factor	
Re	Reynolds number	
N	Flux	$Kg m^{-2} s^{-1}$
Q	Permeance	$mol m^{-2} s^{-1} Pa^{-1}$
S_i	Sorption	$kg s^{-1} m^{-2} Pa^{-1}$
S	Channel side	m
Sc	Schmidt number	
T	Temperature	°C

Greek Letters

α	Selectivity	
δ	Membrane thickness	m
Δp	Partial pressure difference	bar
μ	Viscosity	$N s m^{-2}$
ρ	Molar density	$mol m^{-3}$
u_e	Effective velocities	ms^{-1}

Indexes

i, j	Index or counter
L	Liquid
G	Gas

List of Acronyms

AD	Anaerobic Digestion
CEPS	Centre for European Policy Studies
CNG	Compressed Natural Gas
CSEP	Component Separator
DMT	Dirkse Milieu Technologie
EIGA	European Industrial Gases Association
IPCC	International Plant Protection Convention
LNG	Liquefied Natural Gas
MAP	Modified Atmospheric Packaging
MEA	Monoethanolamine
PFD	Process flow diagrams
PR	Peng-Robinson
PTSA	Pressure Temperature Swing Adsorption
RK	Redlich Kwong
SRK	Soave-Redlich-Kwong
VLE	Vapor Liquid Equilibrium
VOC	Volatile Organic Carbons

1 Introduction

1.1 Framing and presentation of the work

Despite recent climate change and related calamities having attracted worldwide attention and brought about efforts to reduce greenhouse gases, the global energy-related carbon dioxide emissions rose by 6% in 2021 to 36.3 billion tonnes, their highest ever level, as the world economy rebounded strongly from the Covid-19 crisis. This data emphasizes the significance of CO₂ reduction technology in the current environmental situation, where CO₂ is thought to be the primary cause of global warming [1].

According to a Centre for European Policy Studies (CEPS) analysis from March 2022, it is anticipated that negative emissions will be crucial to meet the Paris Agreement temperature goals as well as the EU's goal of 2050 climate neutrality and net-negative emissions after that [2].

Carbon dioxide and methane, the two primary components of biogas, are separated via the membrane upgrading system Carborex®MS. Due to the high CO₂ content of the biogas, the biogas upgrading process will generate a second stream that is predominantly made up of CO₂, which will typically be released into the atmosphere through a chimney. Because the biogas source is considered third-generation waste or has a sustainable origin, this CO₂ emission may be deemed CO₂ neutral. To achieve net-zero global emissions, however, going a step farther and turning this CO₂ into a useful application would be especially beneficial.

In this project, a CO₂ liquefaction unit will be simulated and modelled to turn the CO₂-rich stream that was previously regarded as a waste stream and released into the atmosphere into a valuable product in and of itself. This unit can therefore be implemented within the biogas upgrading plant (Carborex®MS) in different configurations.

1.2 Presentation of the company

As a leading company in the biogas upgrading industry, DMT has been helping customers for 35 years to turn waste into biomethane, including customers in the agricultural sector (e.g., farmers), wastewater treatment facilities, commercial industries (e.g., food and beverage), and waste facilities.

In 1987, Rob Dirkse founded DMT as Dirkse Milieu Technologie to provide sustainable technological solutions. After achieving international market success, the company was renamed DMT. Its past technologies included groundwater purification, sequence batch reactors, and odor reduction. Later, the business changed its focus to biogas upgrading and desulphurization, developing the Carborex®MS, a unique multistage membrane process for CH₄ purification, and the Sulfurex®, which combines chemical and biological scrubbing technologies. In 2021, DMT was acquired by Broadview Energy Solutions BV.

DMT Environmental Technology headquarters are in Joure, with more than 100 employees, agents, and partners spread throughout Europe, North America, and Asia. DMT holding includes DMT Clear Gas Solutions, which has been operating since 2015 and covers the North American market. Figure 1.1 shows DMT biogas conditioning and upgrading references as of 2021.

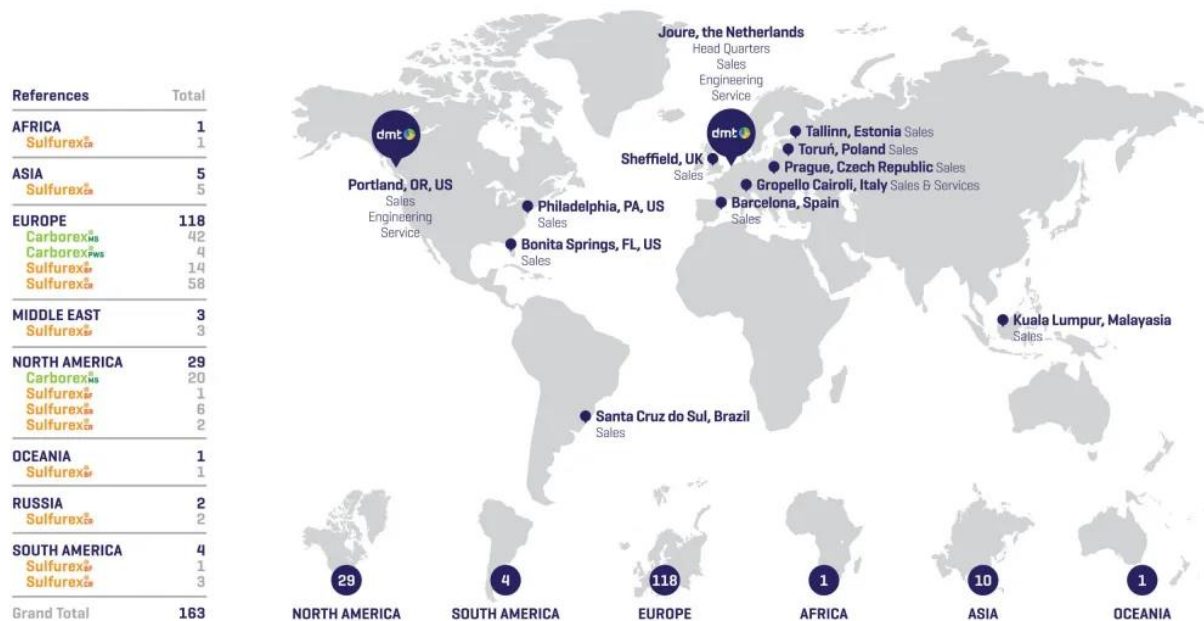


Figure 1.1 - Company biogas conditioning and upgrading location and actuating areas of 2021.

1.3 Contribution of the author to the work

This work was carried out in the framework of DMT's goal to bring to the market a Bolt-on CO₂ liquefaction system design that can be applied downstream of a biogas upgrading unit. Part of the analysis of this work included membrane modelling, which was carried out with the assistance of DMT, as they provided guidance on the required adjustments on each case scenario. The focus of the analysis was on the liquefaction system.

Both the Bolt-on and an integration of the liquefaction system to a multistage membrane system (3-stage and 2-stage) were studied, using CHEMCAD as modelling tool. In the first part of this project, a Bolt-on liquefaction unit was simulated with a 3-stage membrane upgrading unit, and a sensitivity study was performed varying the raw biogas composition.

To extend the research, the integration of the liquefaction unit was studied by means of recycling the outlet gas of the condenser to different points of the Carborex®MS. This was studied for both 3-stage membrane system and 2-stage membrane system, since DMT commercializes both designs depending on the market.

The research conducted during the five-month internship period within DMT Environmental Technology was in conjunction with DMT engineering team of the design of a Bolt-on CO₂ liquefaction system. The results can be used as a base for an integrated system design and the development of a zero-emission solution.

1.4 Organization of the dissertation

This dissertation report is organized into six chapters. Chapter 1 provides the framework, the project presentation, and main objectives.

In the first part of the second chapter, an overview of the Carborex®MS operating conditions is given, followed by an introduction to some relevant definitions and concepts regarding the membranes used in the biogas upgrading plant. Secondly, a brief description of the liquefaction unit step was done, serving as a basis for the decisions and considerations that will be taken into account in the unit modeling and simulation. This section also includes the quality specifications and main applications of food-grade CO₂.

The third chapter explains how the results were obtained, starting with an introduction to the software employed in the simulation, CHEMCAD, followed by the thermodynamic model selection and correlations applied in the simulation. The presentation of the different configurations to be considered in the report and methodologies used in the project is also done in this chapter.

The results and discussion of the simulations for both Bolt-on and integrated configurations are presented in Chapter 4. The results of the sensitivity study of the raw biogas composition are presented and discussed for the 3-stage Bolt-on. This chapter also includes the results of the remaining 3-stage and 2-stage configurations as well as the optimized and suggested designs.

Chapter 5 addresses the main conclusions and goals archived during the project. Finally, Chapter 6 provides a final review of the work done and suggestions for future projects on the topic.

2 Context and state of the art

2.1 Carborex®MS

Biogas will play a pivotal role in the future renewable energy market as it is considered a clean and environmentally friendly fuel, unlike non-renewable resources such as fossil fuels. The main components in biogas are methane (CH₄) and carbon dioxide (CO₂). In addition, some trace components such as ammonia (NH₃), hydrogen sulfide (H₂S), siloxanes, volatile organic carbons (VOCs), oxygen (O₂), and nitrogen (N₂) are also present in biogas [3].

Biogas must be upgraded to specific conditions according to the final application to be used as fuel or distributed into the natural gas grid. The biogas upgrading process consists mainly of removing carbon dioxide and other contaminants to increase the calorific value of the gas and achieve the end-product quality specifications [4]. Figure 2.1 shows the main steps and byproducts of DMT Environmental Technology's Carborex® MS biogas upgrading process.

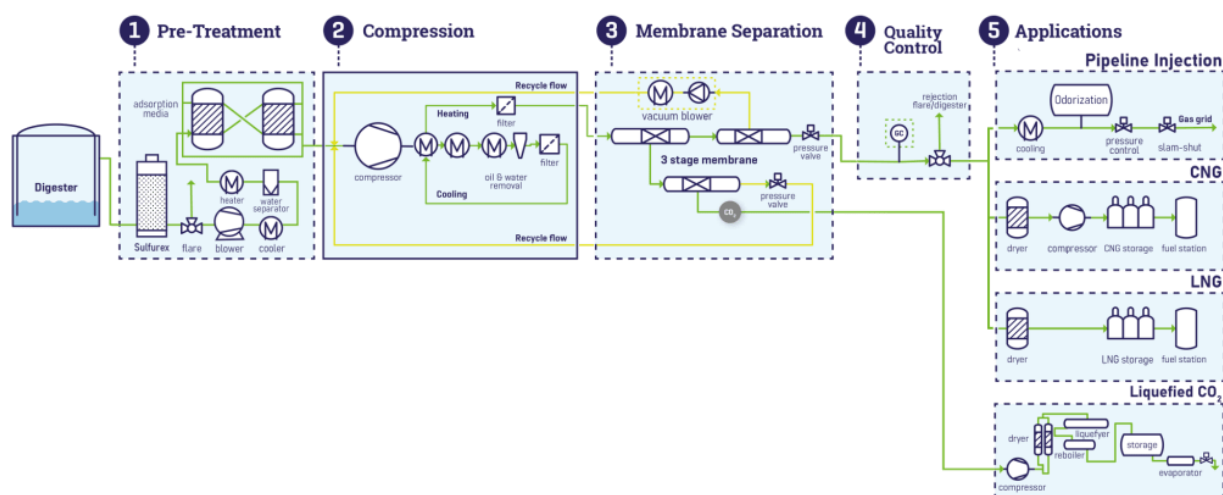


Figure 2.1 - Schematic representation of the Carborex® MS process, adapted from [5].

The system begins with the biogas pre-treatment that includes a dehydration step, followed by an activated carbon filter to remove any contaminants present in the raw biogas to prevent damage to the upgrading equipment, such as compressors and membranes. Sulfurex, an additional product of DMT, is also shown in the schematic representation (Figure 2.1). This unit focuses on removing hydrogen sulphide, preventing corrosion problems and SO_x emissions.

After the pre-treatment and before entering the membrane separation system, the cleaned biogas is compressed to achieve the optimum conditions. The resulting compressed gas will have a pressure between 10-20 bar and a temperature of 25-30°C.

The current membrane design combines three stages of membranes to produce biomethane. Two streams will result from the membrane unit, one primarily composed of CO₂ (tail or off-gas) and the other mainly of CH₄ (product gas), regulated to fit the desired specifications.

In the first membrane separation stage, the raw gas will be split into two streams: retentate with 60-80 % of CH₄ and 20-40 % of CO₂ at high pressure, and permeate with 60-80 % CO₂ and 20-40 % CH₄ at lower pressure.

The retentate from the first stage will be polished to a biomethane stream in the second stage. The retentate of this stage is the product gas, with quality that varies from 88 % to above 99 % CH₄, depending on the application, while the permeate is recycled back to the system feed to recover the CH₄ that passed through the membrane.

Since the permeate stream of the first stage still contains a considerable amount of methane, this product is recovered with a means of a third membrane stage to achieve a typical value of 0.5 %. This stage is used more frequently in European projects, as they require reduced methane emissions in the atmosphere. For this project, the methane slip is defined as the proportion of methane lost to emissions, or the stack, to the methane in the feed, as shown in Equation 2.1.

$$\text{Methane Slip (\%)} = \frac{\text{Methane molar flow rate lost}}{\text{Methane molar flow rate in the feed}} \times 100 \quad (2.1)$$

The retentate stream is recycled back to the system, while the permeate is typically vented to the atmosphere. Within this project, the CO₂-rich stream will be sent to a CO₂ liquefaction unit for further treatment downstream of the Carborex®MS.

CO₂ liquefaction is already an established and commercialized process in industries like fossil fuel power plants, refineries, and hydrogen production plants [6]. However, the standard procedure is to use monoethanolamine (MEA), a cold, chemical absorbent that recovers CO₂ from the inlet gas and releases it by adding heat [7]. In the biogas upgrading sector, Pentair Haffmans (Netherlands) offers a technology that combines a multi-stage membrane separation process with a CO₂ liquefaction unit [8].

2.1.1 Membrane Separation

The biogas upgrading unit core is the membrane separation system, separating methane and CO₂ using membranes. The molecular interactions of these two gaseous species with the membrane material are used to separate them, enabling one to permeate freely while the other is retained.

The key property of the membranes is their ability to control the permeation rate of a chemical species through the membrane. Two models are used to describe the mechanism of permeation: the sorption-diffusion model and the pore-flow model. For this project, the solution-diffusion model is considered, which assumes that the permeants sorbs in the membrane material and then diffuse through it according

to the concentration gradient. The permeants are separated because of the differences in the sorptions of the molecules in the membrane and the differences in the rates at which the same molecules diffuse through the membrane [9].

The flux through the membrane for a particular species is determined by both sorption and diffusivity, as well as the driving force of a concentration/partial pressure difference between either side of the membrane. Equation 2.2 can be used to determine the flux across the membrane, N_i , where S_i represents the sorption, D_i the diffusivity of the material, Δp_i the partial pressure difference on either side of the membrane and δ the membrane thickness [10].

$$N_i = D_i \cdot S_i \cdot \frac{\Delta p_i}{\delta} \quad (2.2)$$

The two inherent material properties of diffusivity and sorption are often combined into one factor, the permeability (coefficient), as seen in Equation 2.3 [9], [10].

$$P_i = D_i \cdot S_i \quad (2.3)$$

However, permeability only reflects membrane properties. Permeance, Q_i , is then essential in a gas permeation membrane technical use since it indicates material properties by taking membrane thickness into account and can be calculated using Equation 2.4 [10].

$$Q_i = \frac{P_i}{\delta} \quad (2.4)$$

The membrane permeance is also dependent on temperature as permeability increases with temperature. The effect of temperature, T , on permeance can be represented by an Arrhenius-type equation as shown in Equation 2.5, where P_{i_0} is the pre-exponential factor independent of temperature, E_i the activation energy for permeation, and R the ideal gas constant [11], [12].

$$P_i(T) = P_{i_0} \cdot e^{-\frac{E_i}{R \cdot T}} \quad (2.5)$$

The selectivity, α , of a membrane is the ratio of the permeabilities for two different gas species i and j , and it characterizes the separation performance of the membrane, as can be seen in Equation 2.6. For multicomponent gas mixtures, selectivity is often reported concerning the slowest permeating gas species [9], [10].

$$\alpha_{i,j} = \frac{P_i}{P_j} \quad (2.6)$$

The Evonik membranes were employed for the simulation done in this project. Evonik offers a variety of membrane types and models, most of which are composed of polyamide [13]. For this material, some information was gathered and presented in Table 2.1 to have a reference for the properties of the membranes used.

Table 2.1- Single gas permeation data of EVONIK P84 based hollow fiber membrane [13].

Polymer	d _{inner} (μm)	d _{outer} (μm)	Gas	Pressure (bar)	Permeance (GPU)	Selectivity
P84 type 70	250	412	CO ₂	5	6.03	72
			CH ₄		0.084	
			CO ₂	40	8.99	88
			CH ₄		0.101	

2.2 CO₂ Purification Process

Green CO₂ produced from biogas is a more sustainable product than traditional CO₂ sourced from fossil fuels as it contributes to global net-zero emissions through the capture and utilization of this stream [14].

Negative emissions are currently receiving increased attention since they will be essential to satisfy the Paris Agreement temperature goals, as well as the EU's 2050 climate neutrality goal and future net-negative emissions targets. The International Panel on Climate Change's (IPCC) Assessment Report (AR6) also confirmed that CO₂ removal is being used as a global mitigation strategy limiting global warming to 1.5 °C. Thus, the trend in the EU is clearly shifting in favor of zero to negative emission pathways [15].

With the addition of the liquefaction unit, the off-gas previously vented into the atmosphere is now considered a co-product. The liquefaction unit's basic principle is to cool down the stream, turning CO₂ into a liquid state while methane remains in a gaseous state. In this way, these two gases can be separated from each other. However, this straightforward transition occurs only at higher pressure because at atmospheric pressure CO₂ will desublimates, transitioning from a gaseous to a solid state. Annex A presents the temperature-pressure diagram of CO₂.

The integration of the liquefaction system in the Carborex®MS might improve methane recovery in the upgrading unit, eventually replacing the third membrane stage by recycling the remaining methane upstream and lowering methane emissions to the atmosphere.

Although several configurations of CO₂ liquefaction units can be presented, the underlying process stays the same. The essential steps of the CO₂ liquefaction unit are shown in Figure 2.2.

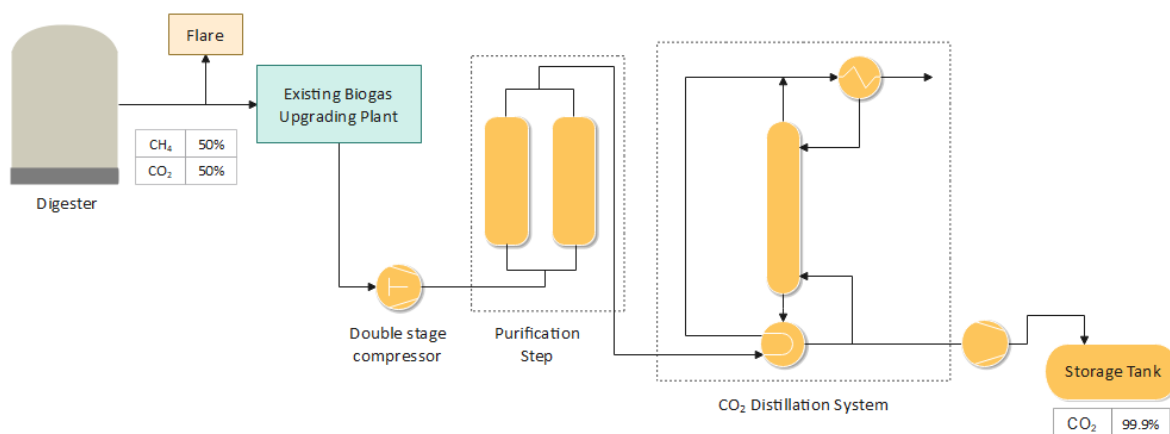


Figure 2.2 - Schematic representation of the CO₂ Liquefaction unit.

2.2.1 Double stage compressor

The tail-gas of the Carborex®MS, i.e., the permeate stream of the third membrane stage, is a relatively dry gas in near-atmospheric pressure and typically consists mainly of CO₂ but also small amounts of CH₄, moisture, H₂S, and some minor trace components.

Because CO₂ desublimates at atmospheric pressure, a double-stage compressor with intercooling raises the stream pressure to 16-25 bar. Two water separators were also installed after each compressor to remove as much water as possible from the stream.

2.2.2 Purification Step

The presence of water in the liquefaction step may lead to the formation of hydrates, equipment corrosion, and frosting hazards that can result in plugging issues in the liquefaction system. For that reason, removing these components and drying the stream as much as possible before the liquefaction step is essential. This polishing step is based on the operating principle of a Pressure Temperature Swing Adsorption (PTSA) unit. This unit consists of two packed columns, meaning that the system can operate continuously because while one column is being used, the other is regenerating, and vice versa.

An adsorption unit offers a wide range of adsorbents that might be employed for the treatment process. An extensive range of adsorbents is available, each with a different affinity for removing the contaminants. As a result, selecting the most appropriate adsorbent is crucial to ensure that the unit successfully removes VOCs and other trace components from the stream before liquefaction.

The operation of a PTSA process involves defining a cycle, that is, a sequence of elementary steps through which the column undergoes based on the process requirements [16]. This cycle can be observed in Figure 2.3, where the adsorption and regeneration of the column are alternated successively.

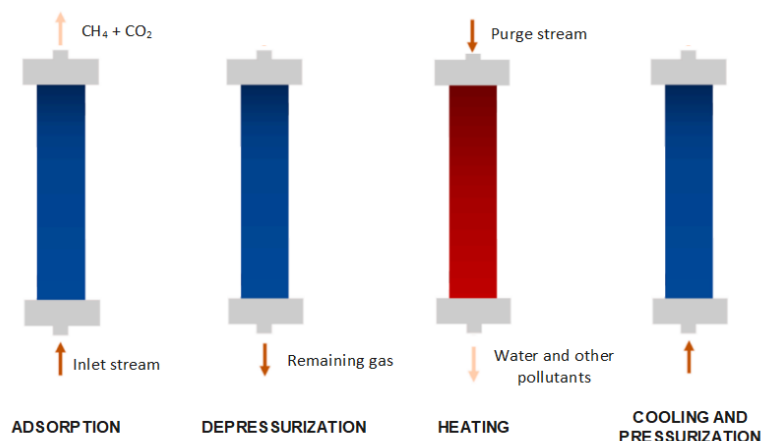


Figure 2.3 – Schematic diagram of the PTSA cycle, adapted from [17].

In the adsorption phase, the gas flows at a constant speed from the bottom up through the adsorbent. The adsorbent selectively adsorbs water and contaminants, whereas the CH₄ and CO₂ flow out through the top of the column. The column is then shifted to the regeneration mode, which combines the regeneration of the desiccant with a heated purge stream, cooling the column after regeneration and restoring the adsorption pressure and temperature.

In the first regeneration step, the system is depressurized via the 4-way valve at the bottom of the adsorption column, where the gas remaining in the bed is discharged. Furthermore, a 4-way valve at the top of the adsorption column leads the regeneration gas, mostly made of CO₂. Higher temperature and lower operating pressure improve the desorption of water and the adsorbed impurities onto the column. For that reason, the CO₂ used for the flush is heated up to enhance the regeneration process. After the flushing procedure, the column's pressure and temperature are restored before starting a new cycle.

2.2.3 CO₂ Distillation System

The CO₂ Distillation System, which is done through low-temperature distillation, is the core of the LCO₂ unit. This stage is based on cryogenic distillation as it will take place at negative temperatures. Cryogenic distillation is a well-established process for air separation, natural gas liquids recovery, ethylene recovery, and propylene recovery, indicating that most of the technology's initial flaws and inherent difficulties have been removed or decreased through past development [18]. Furthermore, because of the benefits of achieving high product purity (99.9 %) and requiring no volatile chemicals, it is widely used in industrial applications [19],[20].

Despite being relatively new, this method can also be employed as a biogas upgrading technology. However, due to the required operating conditions, it consumes a lot of energy. It also has high production costs compared to other commonly used technologies such as pressure swing adsorption (PSA), water scrubbing, or membrane [19].

Holmes and Ryan proposed a conventional cryogenic distillation process for natural gas purification. The detailed separation process is summarized in Figure 2.4.

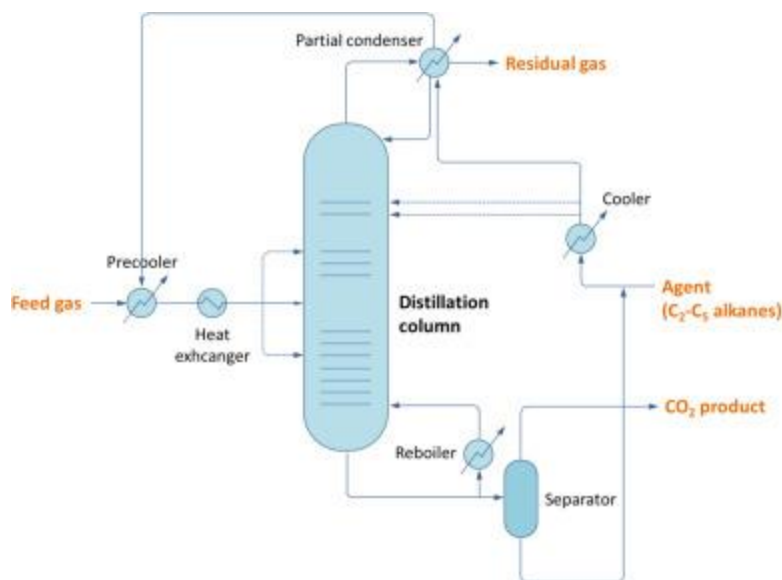


Figure 2.4 - Holmes and Ryan's separation process for natural gas purification, adapted from [21].

The proposed procedure starts with pre-cooling the feed gas before chilling it to a low temperature using a heat exchanger. The cooled feed gas is then sent to the distillation column, containing several vapor-liquid contact devices (trays or packing materials). The stream is primarily separated into top and bottom products. The methane separated at the top is withdrawn via a partial condenser, and the remained CO₂ is condensed and recovered at the bottom of the distillation column. Part of the rich CO₂ stream is recycled to the distillation column by passing through the reboiler to provide vaporization heat. The other part of the CO₂ stream is further separated, and finally, the purified CO₂ product is extracted from the separator [22].

DMT's low-temperature distillation process was developed to produce food-grade CO₂ while considering the upgrading unit stream specific conditions and feed composition. As a result, the methodology developed differs from the one proposed by Holmes and Ryan, with the most notable variation being the feed stream entry into the distillation column. Rather than feeding the stream directly into the distillation column, the DMT process uses the feed to produce vaporization heat by passing it via the reboiler. The stream will then pass through the top of the distillation column, where it will be mixed with the top product before being directed to the partial condenser. Figure 2.5 shows the schematic representation of DMT's purification step.

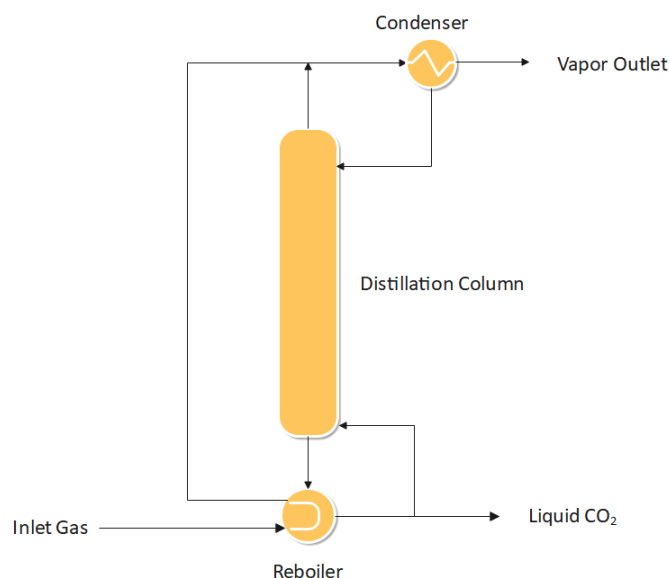


Figure 2.5 – Schematic representation of the CO₂ Distillation System step developed by DMT.

The temperature used in the partial condenser is another noteworthy difference. While the conventional method employs cryogenic temperatures (under -150°C), low-temperature distillation cools the stream to a temperature between -20 and -35°C , condensing the CO₂ present in the stream [23]. Despite presenting a significant amount of methane, the gaseous stream that leaves the condenser primarily comprises CO₂. Nevertheless, recirculating this stream in case of integration will help to reduce methane slip.

The condensed stream will then be fed to the top of the distillation column. Due to the different boiling points of the two components, it is possible to complete the CO₂ purification and obtain the required quality specifications.

2.3 CO₂ Product Specifications

According to Grand View Research, food and beverage emerged as the most prominent application category with a revenue share of over 41 % in 2020, with the worldwide CO₂ market size estimated at 7.06 billion euros. CO₂ is frequently used as a critical component in the food industry modified atmospheric packaging (MAP). The MAP process lowers the oxygen content in food packages, mainly for meat, fruit, and vegetables, which contributes to a slower oxidation rate. Another common way to utilize carbon dioxide in the food industry is to produce carbonated soft drinks and soda water [24].

The second-highest revenue share was the medical application segment, where CO₂ is used in surgeries, such as arthroscopy, laparoscopy, and endoscopy, to stabilize body cavities and enlarge the surgical surface area. It is also used to maintain cryotherapy temperatures of approximately -76°C . Rubber,

firefighting, oil and gas, and horticulture are some other sectors that use a significant amount of liquid CO₂ [24].

Taking into account the global carbon dioxide market, DMT aimed for the production of food-grade CO₂. Upper limits to the potential impurities depend on the end application, meaning that several quality requirements apply to liquid CO₂ in various sectors. Some crucial limits for CO₂ to be used in beverages, considering the European Industrial Gases Association (EIGA) and based on a CO₂ liquefaction process performed at DMT, are:

- minimum of 99,9 % v/v CO₂ purity;
- maximum of 20 ppm v/v of moisture;
- maximum of 30 ppm v/v of oxygen;
- maximum of 50 ppm v/v of total volatile hydrocarbon with no more than 20 ppm v/v non-methane hydrocarbons.

The quality specification according to the European Industrial Gases Association (EIGA) standard 'Carbon Dioxide Food and Beverages Grade, Source Qualification, Quality Standards and Verification' EIGA Doc 70/17 are presented in Annex B.

3 Materials and Methods

The total system (raw biogas, pre-treatment, upgrading, and liquefaction) was modeled. In the first phase, the upgrading unit was designed considering 3-stage membrane configuration, according to the standard European configuration followed by DMT, and later 2-stage configurations were examined for both Bolt-on and integrated systems. Figure 3.1 shows the steps taken to obtain the results, as well as their order.

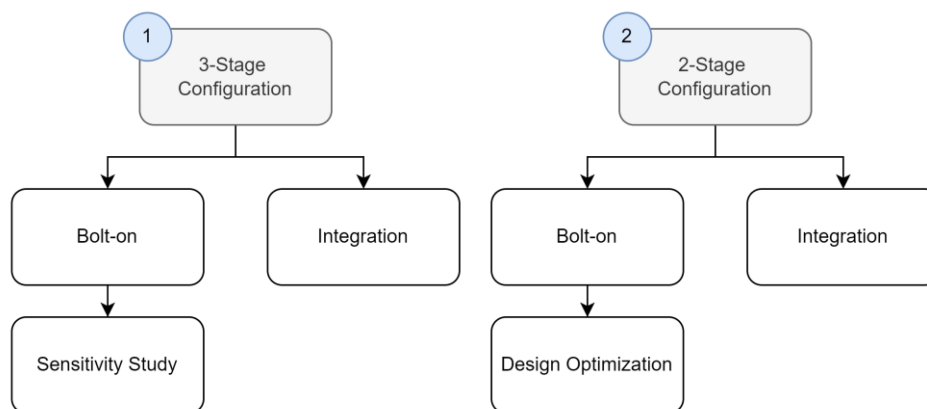


Figure 3.1 – Procedure followed to obtain the results.

3.1 CHEMCAD

The program used for the modeling and simulation of the CO₂ liquefaction unit was CHEMCAD, which DMT owns a license for. CHEMCAD is widely used and can simulate most chemical processes, making it an essential part of the chemical engineering workflow. It allows the user to size systems, determine the process operating conditions, and perform sensitivity studies, similarly to other modeling and simulation software such as Aspen [25].

The focus of this study was mainly on the liquefaction unit. However, the total system was simulated using existing models for the Carborex®MS, which were modified accordingly, to adapt to the needs of each configuration. This allowed investigating the various effects on the total system performance during integration.

3.1.1 Thermodynamic Method Selection

Process modeling requires a suitable thermodynamic model for predicting the enthalpy-H and phase equilibrium-K, thus preventing convergence problems and inaccurate results [26].

Given that the distillation column is the heart of the simulation, selecting the appropriate thermodynamic method is vital to predict the components separation and the boundary stream compositions. The use of cubic equations of state is quite functional for calculating vapor pressures and equilibrium-phase

compositions of mixtures and evaluating corresponding experimental data, as they yield relatively accurate results. Some of the most popular ones are the Redlich Kwong (RK) equation, the Soave-Redlich-Kwong (SRK) equation, and the Peng-Robinson (PR) equation [27]. The last two are considered appropriate for vapor-liquid equilibrium (VLE) calculations [28].

Because SRK was used to model the Carborex[®]MS, this thermodynamic method was chosen for the rest of the simulation to predict both enthalpy-H and phase equilibrium-K.

3.1.2 Component Selection

After selecting the right thermodynamic method, the following step is to add the components that will be present in the process to the simulation.

Biogas is a combustible gas, produced by bacteria through anaerobic digestion (AD) of organic substrates in the absence of oxygen [29]. Agricultural leftovers (straw, catch crops, manure, and so on), energy crops, sewage sludge, segregated domestic trash, and organic industrial waste can all be sourced as a substrate to produce biogas. However, the composition of the resulting biogas will vary depending on the source [30]. Since the CO₂ liquefaction unit will be connected to the Carborex[®]MS's tail gas, its components will be identical to those in the biogas.

Table 3.1 shows the components of the biogas, as well as their concentrations, which will be employed in the simulations made.

Table 3.1 – Biogas inlet composition.

Component	Concentration % (v/v)
CH ₄	48.78
CO ₂	44.50
O ₂	0.40
N ₂	0.10
H ₂ O	6.22

As shown in Table 3.1, the simulation only considered the primary components of raw biogas, implying that no contaminants were assumed.

3.1.3 Simulation Units

After selecting the thermodynamics models and components, the final step in the process design is to choose the operating units and set their parameters. Some of the assumptions made in the simulation of the units are presented in Table 3.2.

Table 3.2 – General assumptions made for the modeling and simulation.

Units	Considerations
Compressor	Efficiency of 80 %
Heat Exchanger	0.1 bar of pressure drop
Multipurpose Flash	Calculations based on the inlet temperature and pressure

The compressor efficiency was selected based on common values to represent the real-type of compressors, accounting for non-ideal effects, such as friction and sudden expansion.

Except for the distillation column condenser and reboiler, which have no pressure drop, all heat exchangers have a pressure drop of 0.1 bar. This value was selected based on field data and previous experience in the simulation of the Carborex[®]MS system.

In contrast to the mentioned units, the PTSA and the distillation column have individual considerations to address. The PTSA was simulated using a Component Separator (CSEP). Since its detailed representation was not in this project scope and no extra contaminants were considered in the stream, the PTSA was assumed to only act as a dewatering step. Although The PTSA system is not regenerating in a continuous mode, the modeling of this unit is useful to Have an indication of how the system will behave and the composition of the stream that leaves the PTSA. The PTSA outlet stream composition is important to predict how this stream will impact the system in case of recycling. It was also considered a pressure drop of 0.2 bar for the unit, a value that DMT engineering team estimated.

The distillation column was designed by the DMT engineering team to operate in continuous mode. As the column's feed stage is at the top of the column with the reflux stream, there are no rectifying stages, so stripping occurs at all stages of the column. The considerations of the column are presented in

Table 3.3.

Table 3.3 – Considerations made for the distillation column.

Column pressure drop (bar)	0.02
Number of segments	6
Reflux feed segment	1
Boil up feed segment	6

The packed column mass transfer option was used for the simulation model. Because this option was selected, CHEMCAD requested further information about the packing and models to be considered, which can be seen in Table 3.4.

Table 3.4 – Information regarding the packing and selected models.

Column diameter (m)	0.21
Packing height (m)	1.52
Liquid flow model	Plug flow
Heat transfer option	Heat transfer

As presented in Table 3.4, plug flow was considered inside the column, as well as the presence of heat transfer (instead of the isothermal mode option). The plug flow model assumes a constant velocity profile in the phase across any cross-section of the column. It represents the ideal case of hydrodynamic behavior from the perspective of separation efficiency in a mass-transfer exchanger [31]. The option of vapor recondensing was also selected. Once again, the column diameter and the packing height were values provided by DMT.

Distillation columns might have internal packing to improve mass and heat transfers between the liquid and vapor phases, as it promotes intimate contact between both phases. The current distillation column has structured packing, which means that the packing is stacked in a regular pattern in the column [32].

For mass transfer calculations, it was chosen the Bravo, Rocha, Fair model for structured packing. Table 3.5 shows the information for the selected packing.

Table 3.5 – Packing information.

Type	Structured
Name	Mellapack
Material	Metal
Size	350Y
Crimp height (mm)	0.90
Channel base (mm)	15.30
Channel side (mm)	11.90
Channel flow angle (degrees)	45

Bravo et al. developed a method for predicting mass transfer coefficients for structured packing taking into consideration the geometry of the packing. The method is one of the most popular correlations and calculates the interfacial areas from the packing geometry [28].

The authors studied distillation processes for which liquid-side mass transfer resistance could be neglected. Consequently, height equivalent to a theoretical plate (HETP) could be approximated to the gas-side resistance of the mass transfer[33].

Based on the two-film theory, it was possible to determine gas and liquid mass transfer coefficients. The gas-side mass transfer coefficient, k_y , was estimated using the proposed by Johnstone and Pigford equation for counter-current evaporation in a wetted-wall column as presented in Equation 3.1 [34].

$$k_y = C_G \cdot Re_G^{0.8} \cdot Sc_G^{1/3} \cdot \left(\frac{D_G}{d_{eq}}\right) \cdot \rho_y \quad (3.1)$$

C_G represents a proportional factor that must be adjusted to a fixed value of 0.0338 to determine the gas-side mass transfer coefficient, ρ_y is the molar gas density and D_G the gas phase diffusivity. Equations 3.2 to 3.4 show the equivalent diameter, d_{eq} , the Schmidt gas number, Sc_G , and the Reynolds gas number, Re_G , for the Bravo, Rocha, Fair model [33].

$$Sc_G = \frac{\mu_G}{\rho_G \cdot D_G} \quad (3.2)$$

$$Re_G = \frac{d_{eq} \cdot \rho_G (u_{Ge} + u_{Le})}{\mu_G} \quad (3.3)$$

The mass gas viscosity is represented by μ_G and the gas and liquid effective velocities through the channel are represented by u_{Ge} and u_{Le} , respectively.

$$d_{eq} = B \cdot h \cdot \left(\frac{1}{B+2 \cdot S} + \frac{1}{2 \cdot S}\right) \quad (3.4)$$

The equivalent diameter is calculated using the channel base, B , crimp height, h , and channel side, S . Because the Mellapak packing values were not updated in the software, they were manually replaced according to Flagiello, D et al. Figure 3.2 illustrate the Mellapak 350Y packing as well as a representation of the structured packing dimensions.

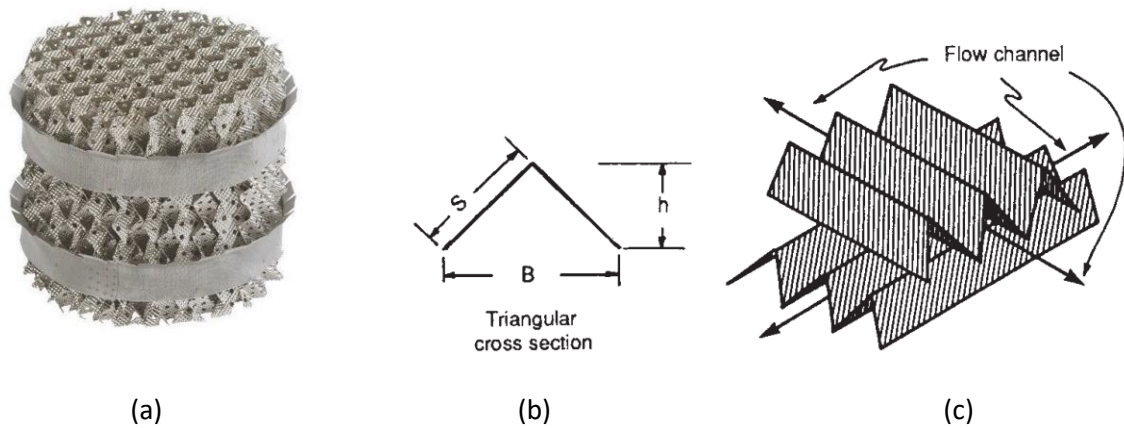


Figure 3.2 - Mellapak 350Y packing. (a) Crimp geometry in structured packings. (b) Flow channel cross-section. (c) Adapted from [28], [35].

Finally, some controllers were employed in the simulation to regulate some specific parameters. The first controller is placed after the PTSA and is used to regulate the water content. This means that the controller will vary the amount of water that will be removed by the PTSA until the water molar fraction in the stream that goes to the distillation column is equal to 8×10^{-7} . This value is indicative to minimum water content, provided by DMT.

Two more controllers were used in purification step. These controllers allow the pressure of the streams of this step to be automatically set to the same pressure as the stream leaving the PTSA, avoiding any potential issues with pressure drop in the distillation column, reboiler, and condenser.

The last controller regulates the condenser temperature or the divider unit according to the configuration in question to set the flow of the stream that will do the PTSA regeneration to 7% of the total LCO₂ inlet.

3.2 Proposed configurations

DMT is offering multistage membrane configurations, that are adjusted depending on the customer's requirements on product quality and emission restrictions. Typically, 3-stage and 2-stage membrane systems with 0.5 and 2.5% methane slip are offered. In the European market, 3-stage is the most common.

DMT standard systems have a well-defined design for specific inlet conditions and desired output, which was used as a base in the models. In this project, the biomethane quality was set to match H-gas grid specifications for a maximum of 2.5% CO₂ and a minimum of 96.5% CH₄ content.

Therefore, pre-determined and standardized 3-stage and 2-stage systems were used for a flow rate of 1280 Nm³/h with the stated inlet composition as a starting point. The standardized 3-stage configuration comprises 24 EVONIK SEPURAN® Green 6" G5X membranes, divided equally between the three stages (8-8-8). As for the 2-stage, the EVONIK SEPURAN® Green of 4" are used. Because these membranes have a lower separation capacity, a total of 39 membranes are employed, 10 in the first stage and 29 in the second one (10-29).

Regarding the operating temperature of Carborex®MS, the 3-stage configuration temperature is set to 25 °C through the heat exchanger prior to the first stage. A 2-stage configuration includes an extra heat exchanger before the product stage (stage 2), allowing for the regulation of the product quality. This also allows lowering the inlet temperature, leading to 20 °C and 40 °C for stages 1 and 2 respectively. The placement of the extra heat exchanger will increase the quality of the upgraded biogas. This is because raising the temperature in the second stage will increase the membrane permeance, which will lead to better product quality. However, if the same behavior occurs in the third stage, it will result in a higher CH₄ slip.

Four different configurations for the 3-stage membrane system were examined, including the Bolt-on case, and three for the 2-stage system. As the configurations are similar for both 3-stage and 2-stage membrane systems, the next paragraphs will only describe on the 3-stage schematic representations. All Process Flow Diagrams (PFDs) can be found in Appendix A.

The possibility of improving methane recovery in the upgrading unit and hence replacing the third membrane stage will be studied by integrating the CO₂ liquefaction unit in the 2-stage configurations.

3.2.1 Bolt-on

The first configuration consists of the Bolt-on model of the liquefaction unit. As shown in Figure 3.3, in this configuration, the vapor outlet of the partial condenser is used to regenerate the PTSA, and it is estimated that its flow should be around 7 % of the feed to ensure proper regeneration. The resulting stream of the regeneration is then vented to the atmosphere.

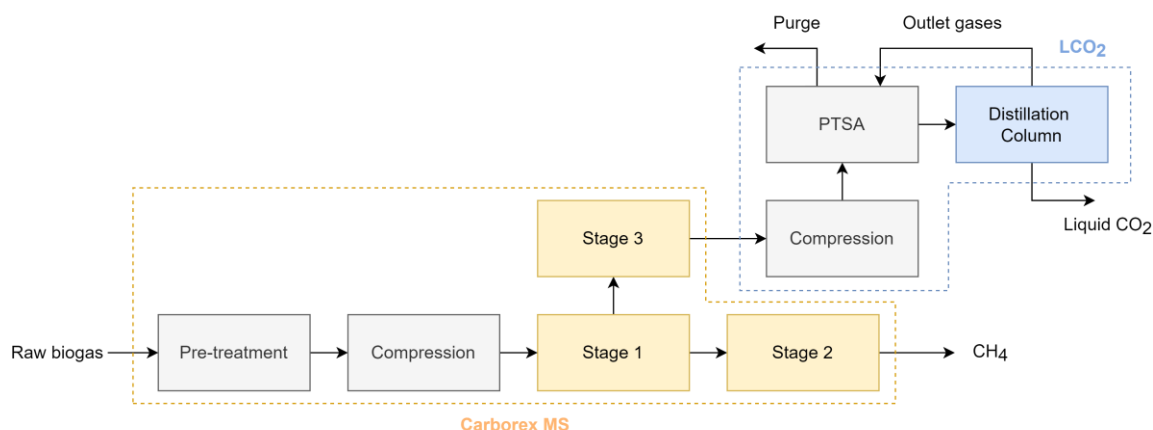


Figure 3.3- Simplified representation of the Bolt-on configuration.

3.2.2 Integration

Integrating the CO₂ liquefaction unit to the Carborex®MS aims to eliminate the methane slip and CO₂ losses while optimizing the system performance and cost. This can be realized by tying the outlet gas stream into various points of the MS. Several configurations were therefore considered. Due to extended pipeline length, the pressure drop was assumed to be circa 1.5 bar for the recycle lines from the liquefaction unit to the Carborex®MS, based on DMT's estimations.

Figure 3.4 shows the first configuration with recycling to the Carborex®MS. This is the most straightforward configuration, as just one recycle leaves the PTSA and is routed to the pre-treatment stage after the dewatering step. Because the PTSA regenerates at low pressure and high temperature, the recycle stream must first pass through a heat exchanger and a valve before entering the PTSA. This way, the recycle stream will pass through the carbon filters, and the contaminants from the PTSA will be eliminated.

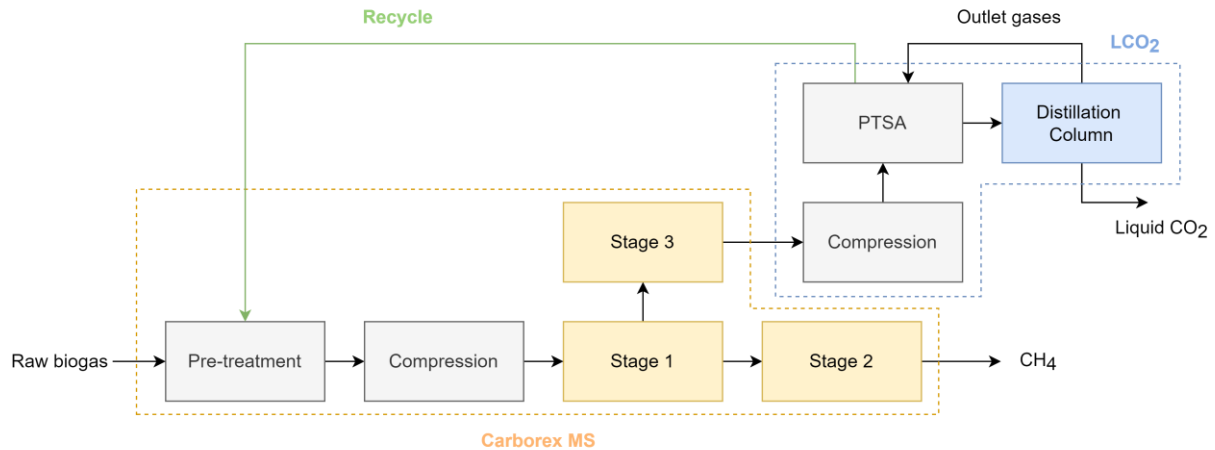


Figure 3.4 – Simplified representation of Configuration 1.

Figure 3.5 shows the second configuration with recycle, which includes two recycle streams going to the Carborex[®]MS. The first recycle involves sending non-condensable gases to the compression phase after the compressor. This location was selected to prevent higher compressor duty and also because removing unwanted compounds is unnecessary as the recycled stream is not used to regenerate the PTSA. However, having the tie-in point after the compressor will limit the maximum operating pressure for the membrane stages.

The second recycle involves using a fraction of the end product (liquid CO₂) for the PTSA regeneration. As in the first configuration, the stream must pass through a heat exchanger and a valve before going to the PTSA. However, since the stream used for PTSA regeneration is essentially made up of CO₂, it is then redirected to the inlet of the CO₂ liquefaction unit instead.

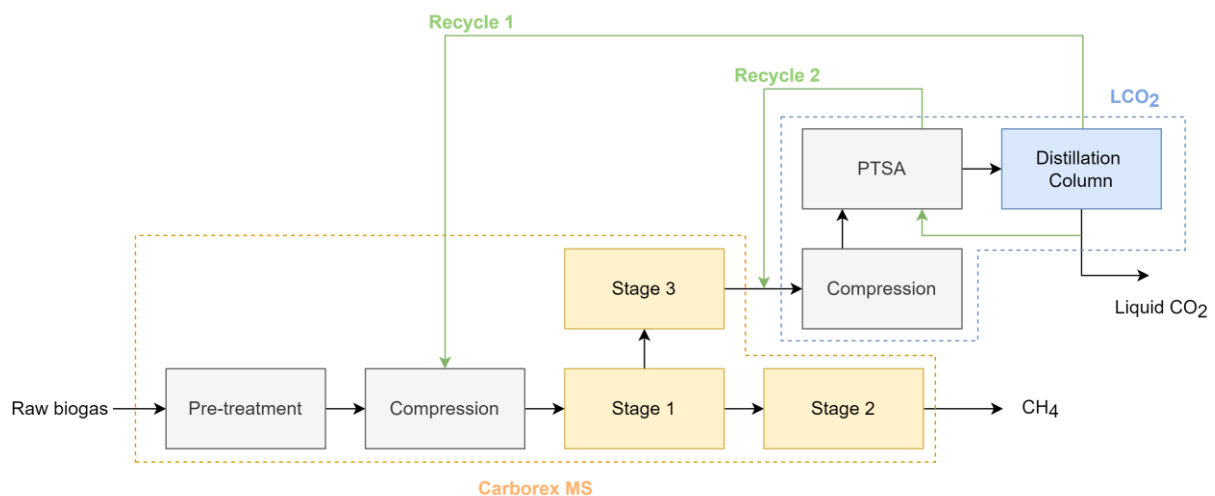


Figure 3.5 – Simplified representation of Configuration 2.

Finally, the third configuration is shown in Figure 3.6. Like the previous configuration, the outlet gas is recycled, but this time to the third stage of the Carborex[®]MS. This alternative is considered more

conservative since the third stage is the stage that least affects the Carborex®MS system. In this way, it may be easier to adjust the operating conditions in the event of product quality issues without disrupting the system.

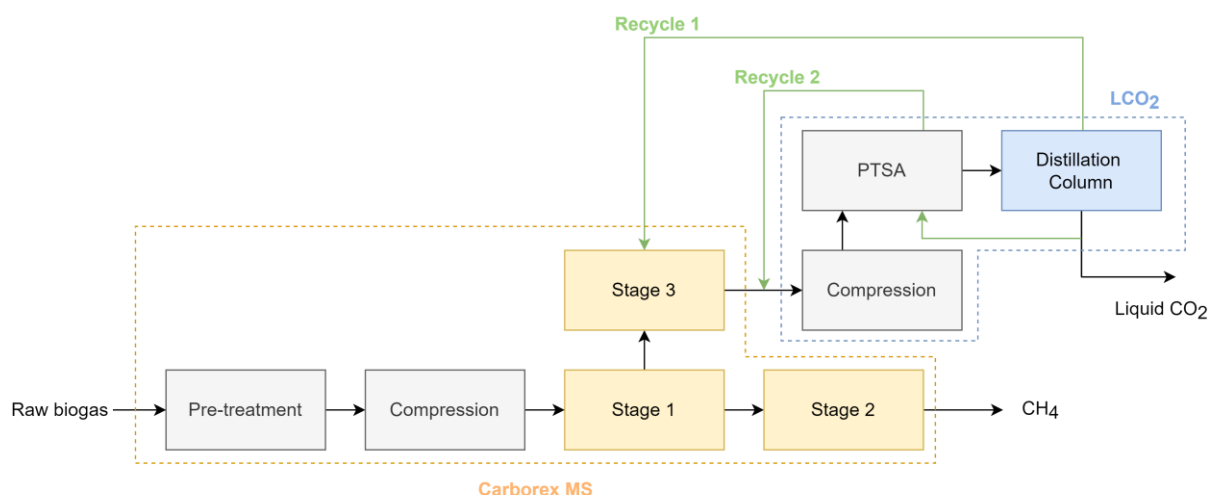


Figure 3.6 – Simplified representation of Configuration 3.

Recycling to the third stage is only possible with a 3-stage membrane configuration. In the case of 2-stage configuration both recycle streams would be redirected to the inlet of the CO₂ liquefaction unit. In this case, accumulation of methane is expected, as the only outlet of the LCO₂ unit, would be the product stream.

3.3 Vapor-Liquid Equilibrium Diagram

One of the critical parameters to adjust in the simulation of the different configurations is the condenser temperature. To establish this temperature, the vapor-liquid equilibrium diagrams of CH₄-CO₂ and O₂-CO₂ were generated and provided by DMT. Figure 3.7 shows a close-up version of the diagram, where it's easier to visualize the curves for the range of temperature and composition that are going to be employed in the following simulations.

The presented results were obtained using CHEMCAD at a pressure of 18.5 bar and employing SRK as the selected thermodynamic method. Because N₂ is present in residual concentrations in the LCO₂ unit, its vapor-liquid equilibrium curves were not considered in the diagram. The complete version of the vapor-liquid equilibrium curves can be seen in Annex C.

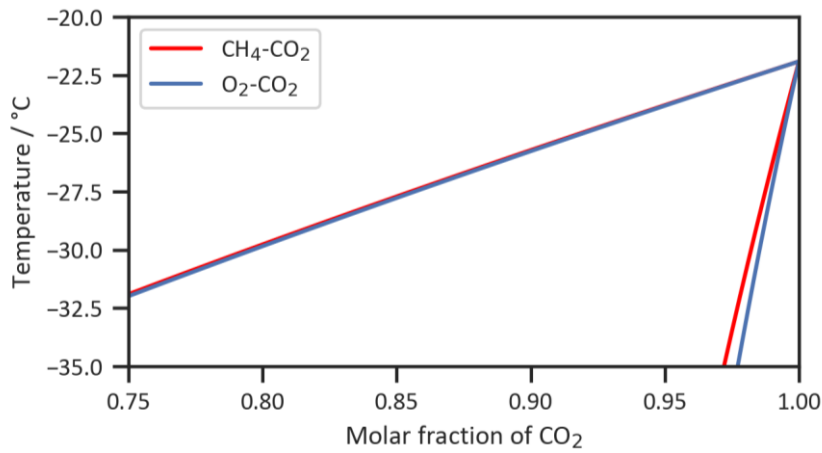


Figure 3.7 -Close-up version of the CH₄-CO₂ and O₂-CO₂ vapor-liquid equilibrium curves.

3.4 Optimization methodology

One of the approaches to optimize the configurations is to adjust the design of the Carborex®MS. This process was made following a specific order of steps, as presented in Figure 3.8. The modifications of Carborex®MS were made under the guidance of DMT engineering team.

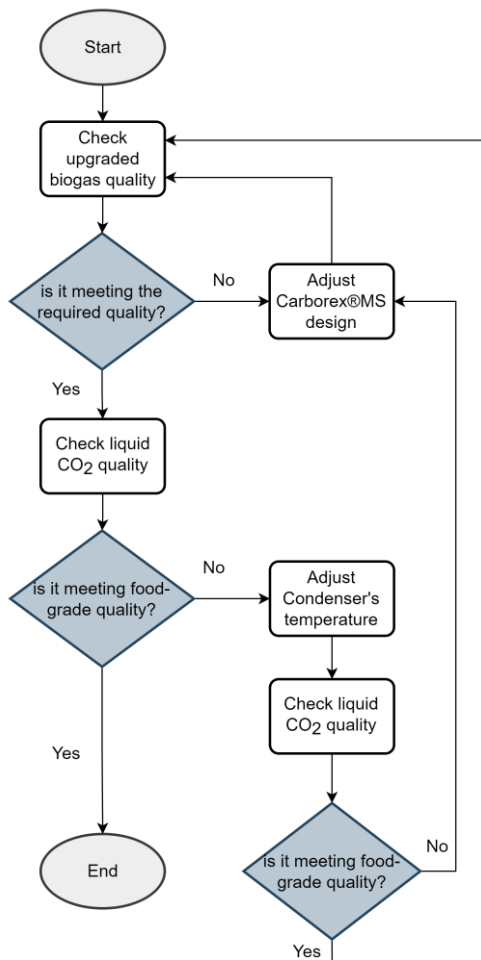


Figure 3.8 – Flux diagram of the optimization process.

4 Results and discussion

The previous chapters are the foundation for the results and discussion that follow in this section. Indeed, this section is divided into two sub-sections: 3-stage and 2-stage.

4.1 3-stage results

This subsection will present the results of the 3-stage configurations. Initially, the analysis is regarding the Bolt-on system, looking into the significant streams and system behavior. The results of a sensitivity study of the raw biogas composition effect are also presented. In the second phase, the integration of the liquefaction system is discussed, and the optimization of the design of one of the configurations is done. The results from these configurations are presented in Appendix C.

4.1.1 Bolt-on

Based on the established design previously discussed, the condenser temperature is the only parameter that can be adjusted in the Bolt-on configuration, and it will change the properties of the liquefaction unit outlet streams. Therefore, a sensitivity study was conducted on these streams' properties (temperature, flow, composition) to select the appropriate condenser temperature.

The sensitivity study was made with the assistance of a controller to ensure that sufficient outlet gas flow rate (minimum of 7 %) will be available for the PTSA regeneration step. Figure 4.1 shows the relationship between condenser temperature and outlet gas flow and how it affects the outlet gas composition, while Figure 4.2 presents the flow rate and composition of the CO₂ product as a function of the gas output/LCO₂ inlet ratio.

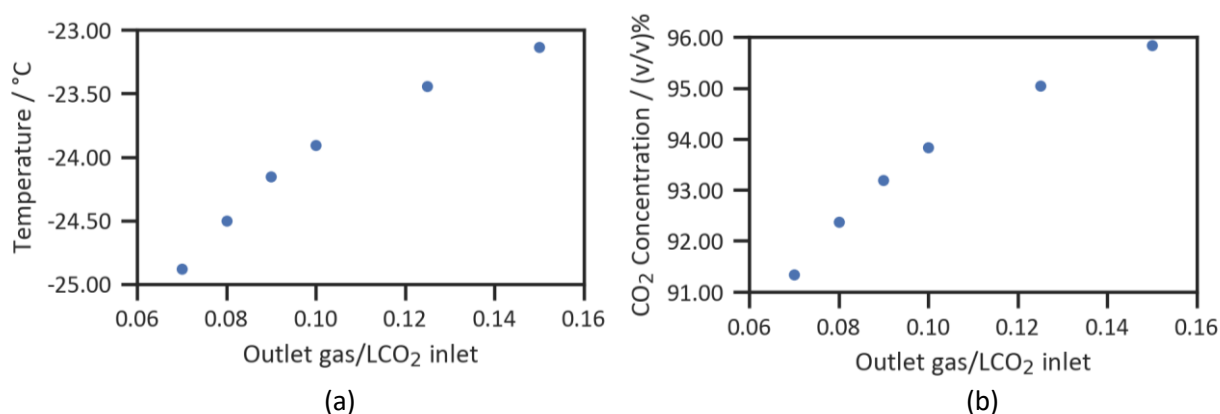


Figure 4.1 – Condenser Temperature (a) and CO₂ concentration (b) in the outlet gas as function of outlet gas/LCO₂ inlet ratio.

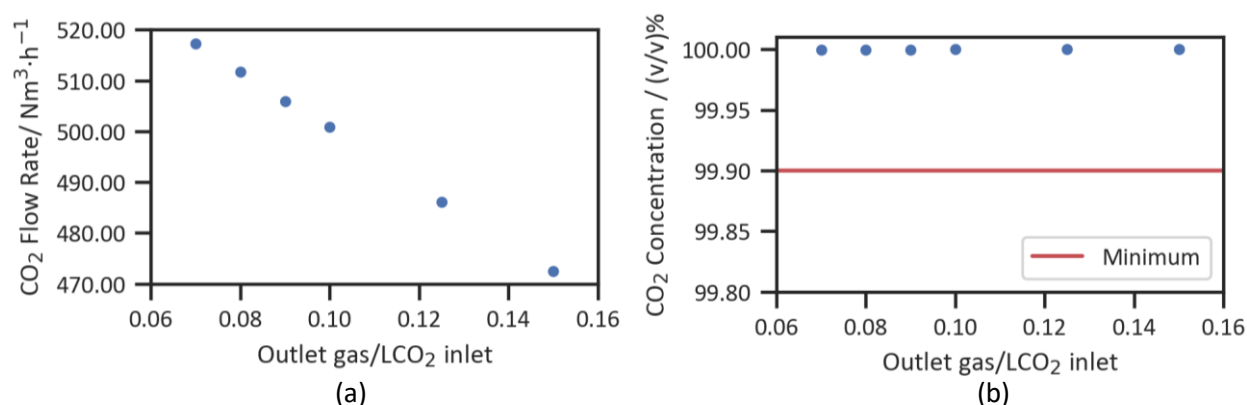


Figure 4.2 – Liquid CO₂ flow rate (a) and CO₂ concentration (b) as function of outlet gas/ LCO₂ inlet ratio.

As seen in Figure 4.1, a larger outlet gas flow rate is associated with a higher temperature in the condenser. Thus, less CO₂ liquefies, leading to a higher CO₂ concentration in the outlet gas. The flow rate and CO₂ concentration in the product stream will naturally be lower as less CO₂ liquefies. As shown in Figure 4.2, although the product quality decrease is insignificant, the product flow rate was reduced by 9%, when increasing the purge to 15%. To achieve maximum production, a 7% outlet gas/LCO₂ ratio was chosen. Table 4.1 and Table 4.2 summarize the main results for the selected conditions.

Table 4.1- Properties and composition of 3-stage Bolt-on's main streams.

Parameters	CH ₄ product	Inlet LCO ₂	Condenser's Inlet	PTSA outlet
Pressure (bar)	16.43	1.05	18.70	1.01
Temperature (°C)	13.33	20.91	-17.12	130.00
Flow Rate (Nm ³ h ⁻¹)	641.70	559.16	608.47	41.58
Composition % (v/v)				
CH ₄	96.80	0.54	1.10	7.24
CO ₂	2.29	99.21	98.73	90.10
N ₂	0.79	0.01	0.01	0.14
O ₂	0.12	0.09	0.16	1.17
H ₂ O	3.40 x 10 ⁻⁶	0.15	7.34 x 10 ⁻⁷	1.35

An upgraded biogas that meets the quality specifications is essential for properly operating the whole system. Suppose the biomethane does not meet the required specifications. In that case, it is rejected by the grid and typically redirected to the digester, leading to a change in the raw biogas composition and consequently endangering the operation of the LCO₂ unit.

From the simulation results, it's visible that the biomethane quality is within the desired specifications. The inlet of the LCO₂ unit has a very low CH₄ concentration, and most of the methane is removed in the outlet gas stream.

Table 4.2 – Liquid CO₂ properties and composition from the 3-stage Bolt-on.

Parameters	Liquid CO ₂
Pressure (bar)	18.72
Temperature (°C)	-21.53
Flow Rate (Nm ³ h ⁻¹)	517.27
Main Composition % (v/v)	
CO ₂	100.00
Trace Composition (ppmv)	
CH ₄	4.54
N ₂	2.96 x 10 ⁻¹²
O ₂	9.15 x 10 ⁻⁴
H ₂ O	0.85

Regarding the liquid CO₂, the CO₂ concentration is above the minimum value of 99.9%, with just a minor amount of trace components. The most significant trace components are CH₄ and water, with concentrations of 4.54 and 0.85 ppm(v), respectively. It's possible to assure this way that all the quality specifications of this stream are met.

The current model assumes specific composition in the inlet. However, in reality, the biogas composition can fluctuate significantly on the methane/carbon dioxide content and in the presence of higher inert or contaminants content. This analysis aims to study the system behavior with a set methane and carbon dioxide content while looking at the effect of inert content in the stream.

The minimum concentration of CH₄ expected in the raw biogas is 45%. For that concentration, a sensitivity study was performed by increasing the inert content from 0.00 to 0.50 % and 2.00 % of O₂ and N₂, respectively. This increase was made simultaneously using a proportion of 1:4 between the two components. Figure 4.3 shows the concentration of CH₄ and CO₂ as a function of the inlet of O₂ and N₂.

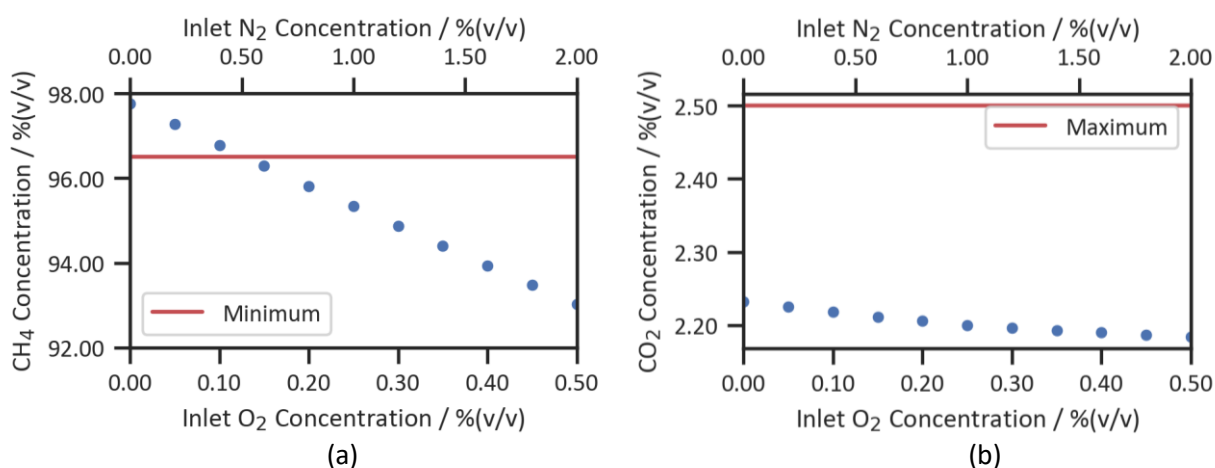


Figure 4.3 – CH₄ (a) and CO₂ (b) concentration in the biomethane as function of the inerts in the inlet for the minimum inlet of CH₄.

It is noticeable that the increase of inerts content severely impacts the product quality. The biomethane does not meet the quality specifications for concentrations higher than 0.10% of O₂ and 0.40% of N₂, even though the CO₂ content is below the maximum allowed value. The decrease in the concentration of CH₄ in the biomethane can be explained by the characteristic's similarity between CH₄ and N₂. As a result, just like CH₄, N₂ will stay on the membrane retentate side. CO₂ has a higher permeability than them; thus, a fraction will permeate, and the remaining CO₂ will remain in the retentate stream. The same study was made on the liquid CO₂, with the results being presented in Figure 4.4 and Figure 4.5.

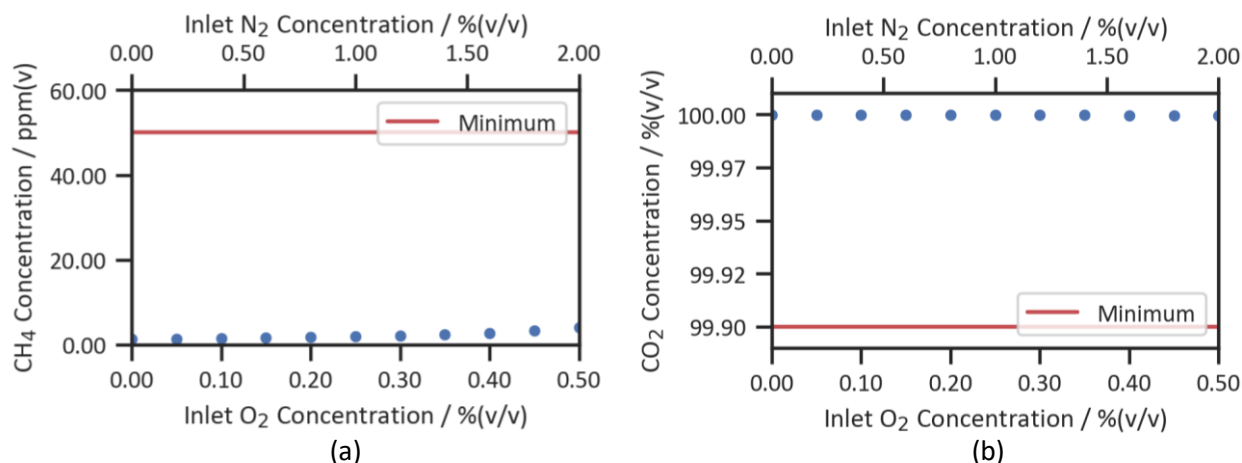


Figure 4.4- CH₄ (a) and CO₂ (b) concentration in the liquid CO₂ as function of the inerts for the minimum inlet of CH₄.

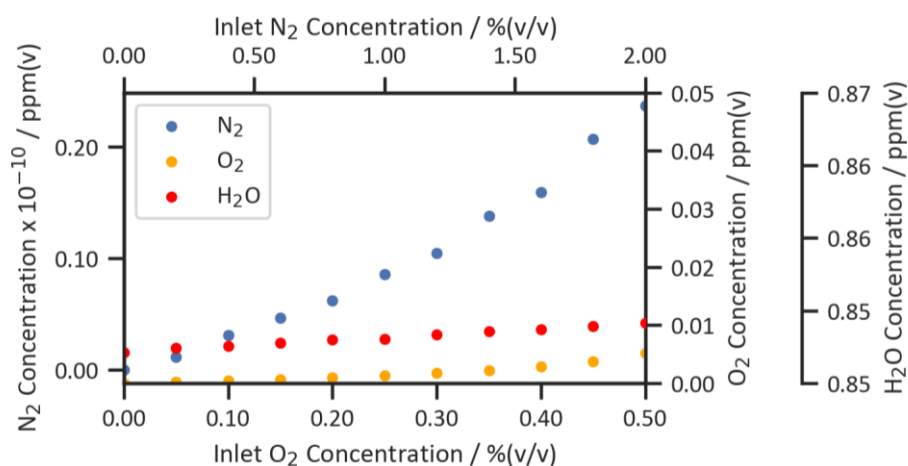


Figure 4.5 – Trace components' concentration in the liquid CO₂ as function of the inerts for the minimum inlet of CH₄.

On the other hand, all the quality requirements for food-grade CO₂ are met in the liquid CO₂ composition, as it is shown in Figure 4.4 and Figure 4.5. Although the CH₄ is increasing with the concentration of inerts, its concentration is still considerably below the 50 ppm(v) limit. All other components are present in the CO₂ in residual amounts. N₂ stays with CH₄ in the biomethane product streams, which explains the very low concentrations in Figure 4.5. A controller limits the water content; therefore, its value was almost

constant during the sensitivity study – any small deviation are most likely due to the tolerance of the controller itself.

After determining the limit composition of the raw biogas for the minimum amount of CH₄, the same procedure was repeated, assuming a minimum percentage of CO₂ in the raw biogas of 40 %. Figure 4.6 shows the variation of its composition with the increase of inerts.

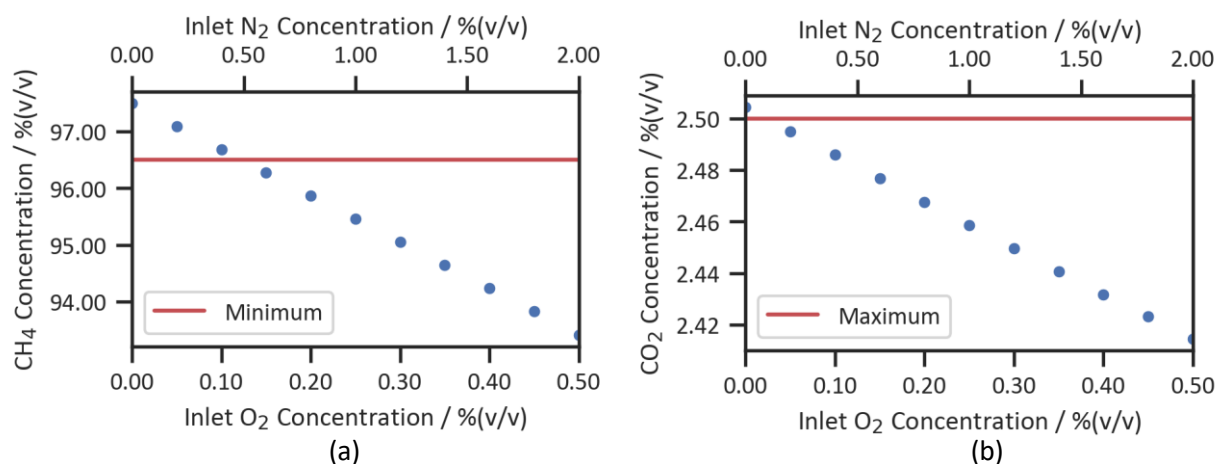


Figure 4.6 – CH₄ (a) and CO₂ (b) concentration in the upgraded biogas as function of the inerts for the minimum inlet of CO₂.

Just like in the minimum inlet of CH₄, the increase of inerts will decrease the concentration of both CH₄ and CO₂ in the biomethane. However, while CO₂ concentration was not an issue in the previous scenario, it is now the primary limiting factor in this stream quality. In this case, to obtain biomethane that meets the quality requirements, the biogas must not contain any inerts, which is highly unlikely. To check the effect of the inerts in the liquid CO₂, the composition of this stream was also monitored. Figure 4.7 presents the concentration of CH₄ and CO₂ in the liquid CO₂.

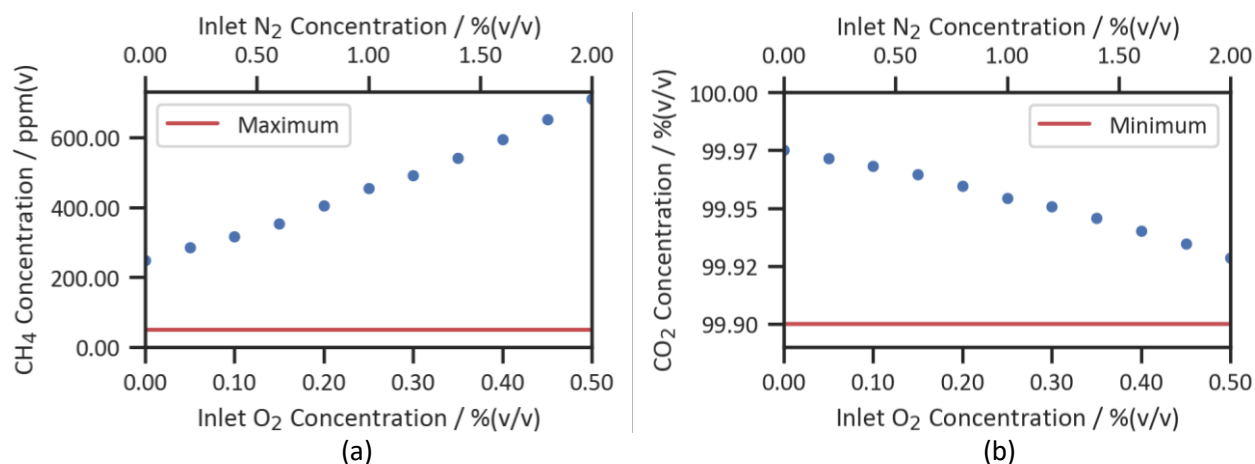


Figure 4.7 – CH₄ (a) and CO₂ (b) concentration in the liquid CO₂ as function of the inerts for the minimum inlet of CO₂.

Regarding the liquid CO₂, the minimum CO₂ molar fraction in the inlet will not allow the quality standards to meet since the CH₄ content is well above the limit. This occurs because the decrease in CO₂ concentration will be balanced by an increase in CH₄ concentration in the raw biogas and the LCO₂ unit.

For a fixed temperature, a lower concentration of CO₂ means that there will be less CO₂ being condensed and thus less liquid product. Therefore, a more considerable outlet gas flow rate will leave the liquefaction unit. However, because the Bolt-on configuration has a controller to set the outlet gas flow rate, the condenser's temperature will drop to control the outlet gas flow, resulting in more CH₄ going to the product stream. The trace components content is presented in Figure 4.8.

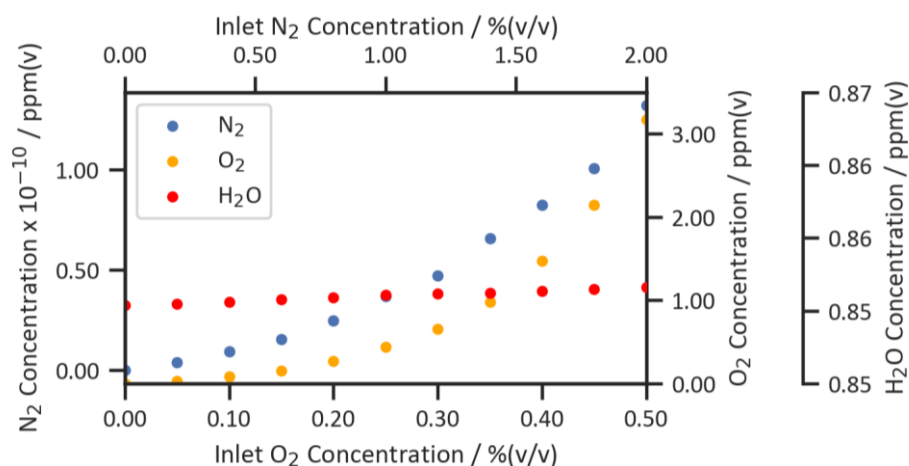


Figure 4.8 – Trace components concentration in the liquid CO₂ as function of the inerts for the minimum inlet of CH₄.

As in the prior scenario, increasing the inerts in the raw gas composition will also increase inerts in the liquid CO₂. When comparing Figures 4.5 and 4.8, it is clear that the inerts content in the second scenario is higher. Because O₂ and CH₄ have similar boiling temperatures, as shown in Figure 3.6 and Annex C, this behavior is likewise linked to a drop in condenser temperature.

From the results, it is clear that the system is susceptible to the amount of inerts in the raw biogas, especially when there is a low concentration of CO₂, which is by itself a negative aspect for the LCO₂ performance. Since the CH₄ content seemed to be the limiting factor in the liquid CO₂ quality, its value was monitored while increasing the CO₂ inlet concentration. For that study, the inlet of inerts was fixed to 0.10 and 0.40% of O₂ and N₂ as it is a typical value. The outcome is shown in Figure 4.9.

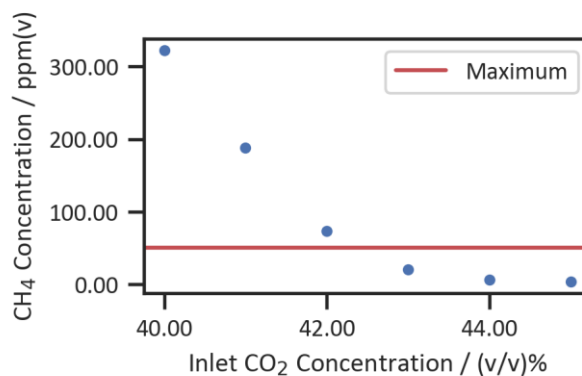


Figure 4.9 – CH₄ concentration in the liquid CO₂ as function of the CO₂ content in the raw biogas.

Figure 4.9 shows that the lower limit of CO₂ concentration in the inlet of the raw biogas is 43.00%, for which the CH₄ content in the CO₂ liquid product is within specifications. The remaining results regarding the sensitivity study are presented in Appendix B.

Based on the previous results and considering the effect of the inerts in the inlet of the raw biogas, it was possible to set a limit composition for a proper operation of the system. This limit composition is shown in Table 4.3 and was determined for 0.40% of N₂ and 0.10% O₂.

Table 4.3 – Raw biogas limit compositions for 0.40% of N₂ and 0.10% O₂.

Component	Composition%(v/v)
CH ₄	45.00 - 50.28
CO ₂	43.00 - 48.28

4.1.2 Integration

Just like in the Bolt-on configuration, the only parameter that can be adjusted in Configuration 1 is the temperature of the condenser. The change of the condenser temperature is done once again by adjusting the outlet gas/LCO₂ inlet ratio in the condenser. However, in the integration case, the change in this parameter will also affect the Carborex®MS and the biomethane quality. To better understand the consequences of the recycle flow rate, a sensitivity study was made to monitor the biomethane quality. Figure 4.10 shows the CH₄ and CO₂ concentrations alongside the outlet gas/LCO₂ inlet ratio.

Looking at the figure, it's evident that the larger the recycling flow, the greater the impact on the upgraded biogas quality. Considering this, the only viable choice for Configuration 1 is a recycle flow rate equal or lower to 7% of the LCO₂ inlet flow rate.

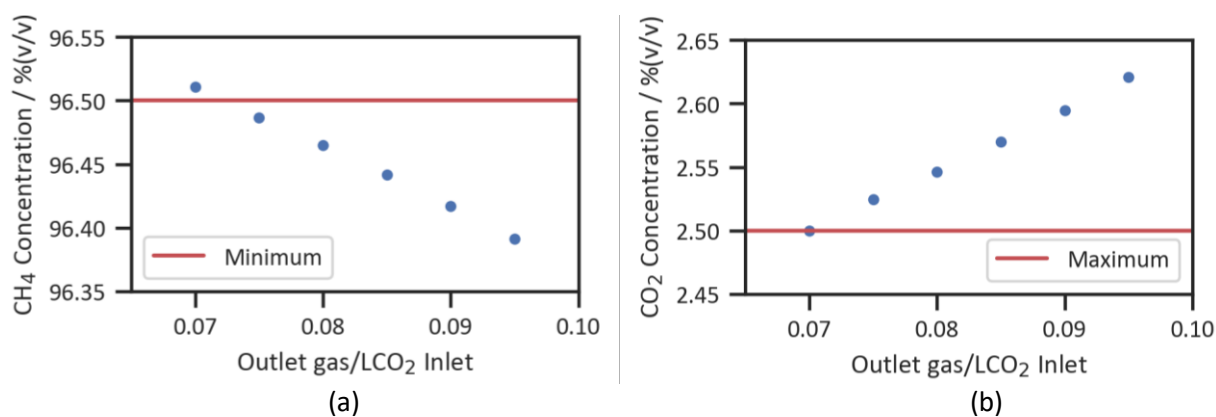


Figure 4.10 - CH₄ (a) and CO₂ (b) concentration in the biomethane for Configuration 1 as a function of the outlet gas/LCO₂ inlet ratio.

In contrast to the preceding configurations, Configuration 2 has two recycles to the Carborex®MS. The first is outlet gas from the condenser, which will reconnect after the compressor, and the second will regenerate the PTSA by reusing a portion of the liquid CO₂. After the PTSA regeneration, the stream will then be routed to the inlet of the LCO₂ unit.

Since the outlet gas of the condenser is no longer being used to regenerate the PTSA, its temperature is no longer adjusted by a controller. This controller is placed instead in the second recycle since it is this stream that will be used for the regeneration. To minimize the product loss of CO₂, the controller fixed the second recycle flow rate to 7 % of the LCO₂ inlet.

A sensitivity analysis of the product streams quality was conducted to evaluate the temperature of the condenser, which will affect the composition and flow rate of the first recycle. The composition of the condenser inlet stream and the vapor-liquid equilibrium diagram were considered when determining the temperature range for this study.

Figure 4.11 and Figure 4.12 show the CH₄ and CO₂ composition in the product streams as a function of the condenser temperature. As visible in these figures, the biomethane will not meet the quality specification for this configuration. This occurs because, as the condenser temperature drops, the biomethane quality improves but the liquid CO₂ quality decreases. This behavior can be explained by the fact that the outlet gas stream, which has a high concentration of CO₂, is being recycled before the membrane stages, has a bigger flow rate. Although CO₂ permeance is higher than CH₄, a fraction of it will end up in the upgraded biogas. As expected, decreasing the condenser temperature will also reduce the liquid CO₂ quality, limiting the condenser temperature to a minimum of -25.50 °C, as illustrated in Figure 4.12.

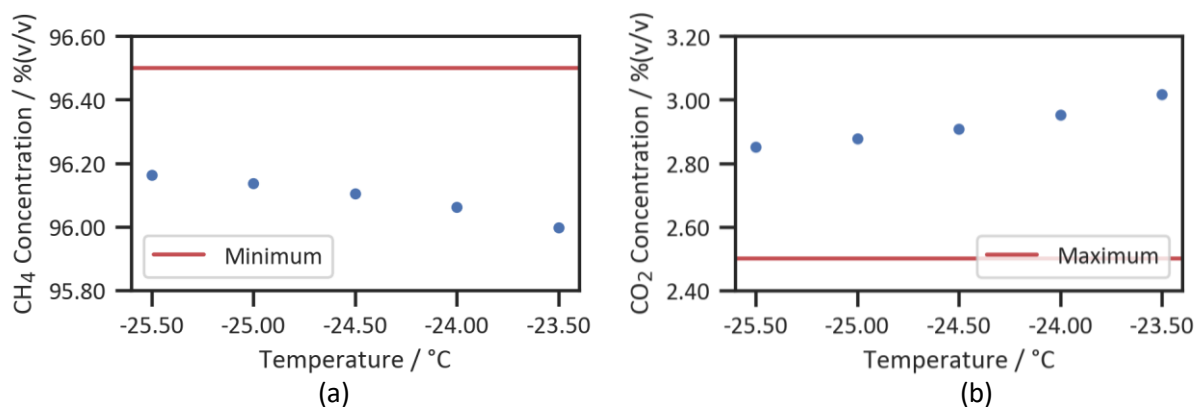


Figure 4.11 - CH₄ (a) and CO₂ (b) composition in the biomethane for Configuration 2 as function of the condenser temperature.

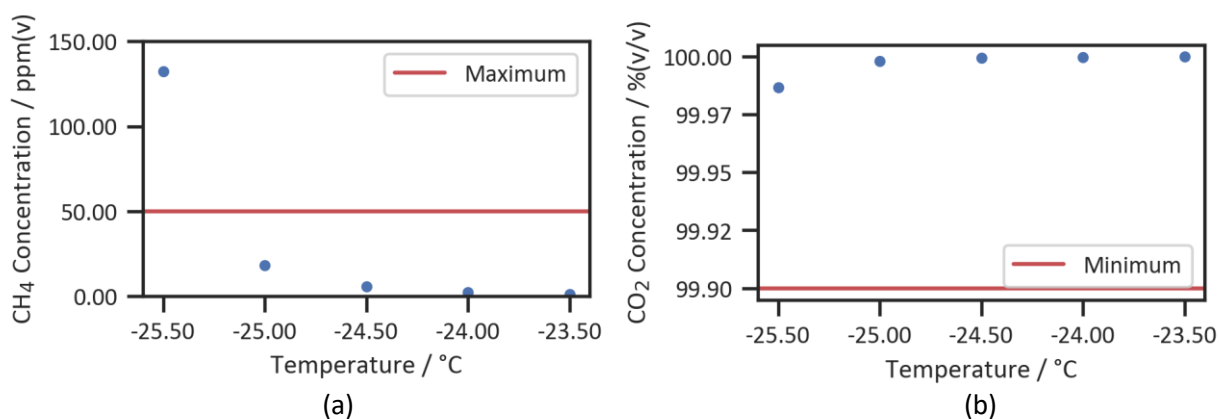


Figure 4.12 - CH₄ (a) and CO₂ (b) composition in the liquid CO₂ for Configuration 2 as a function of the condenser temperature.

Since no other parameters in the LCO₂ unit may be adjusted, one alternative is to optimize the Carborex®MS design. In this sense, the heat exchanger placed before the first membrane stage had its temperature raised to 30 °C. For the new design, a new sensitivity study was made for the condenser temperature to define the optimal operating temperature of the system. Figure 4.13 and Figure 4.14 present the CH₄ and CO₂ composition in the product streams of the optimized Carborex®MS.

As visible in Figure 4.13, the increase in the condenser temperature will cause a drop in the upgraded biogas quality. In this sense, for a proper operation of the Carborex®MS, the condenser temperature should be lower than -23.00 °C. As expected, for lower temperatures, the liquid CO₂ quality will drop. While the CO₂ concentration is not an issue, the CH₄ content is above the limit for temperatures below -25.00 °C. Based on the limitation of the two product streams, it is possible to establish that in Configuration 2, the condenser should operate between -25.00 and -23.50 °C. A simulation was done for both of these temperatures, and the results are presented in Appendix C.

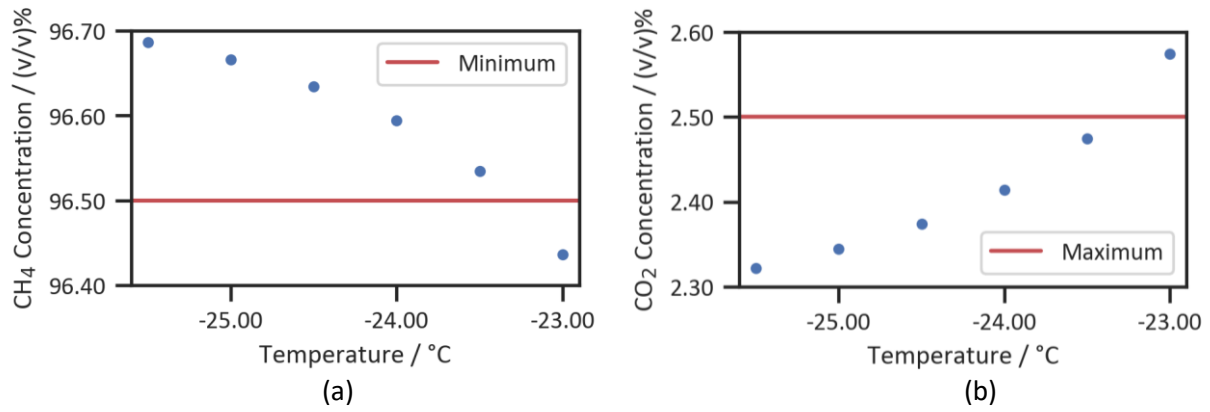


Figure 4.13 - CH₄ (a) and CO₂ (b) composition in the biomethane for the optimized Configuration 2 as function of the condenser temperature.

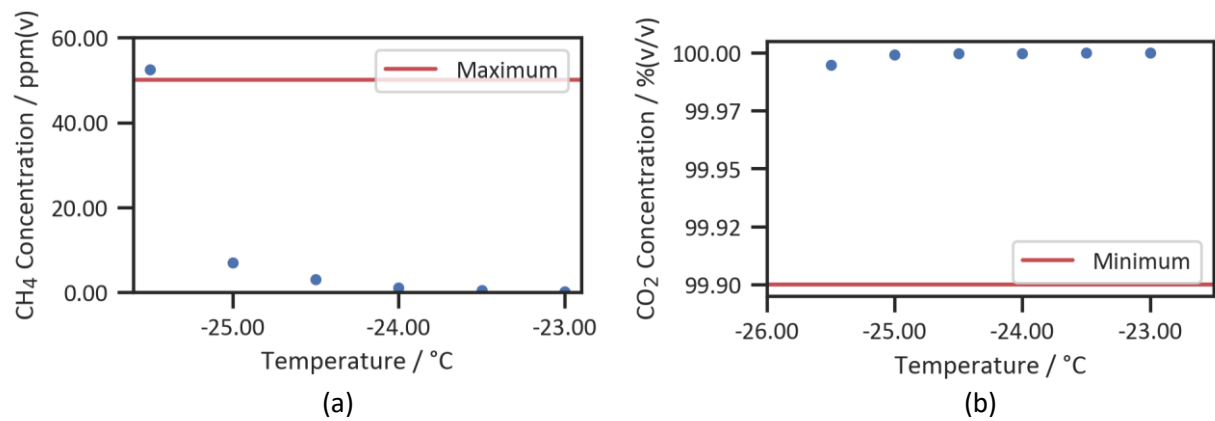


Figure 4.14 - CH₄ (a) and CO₂ (b) composition in the liquid CO₂ for Configuration 2 as a function of the condenser temperature.

Finally, because the recycles in Configuration 3 are comparable to those in Configuration 2, the previous procedure was also followed. Figure 4.15 and Figure 4.16 show the CH₄ and CO₂ content in both product streams as a function of the condenser temperature.

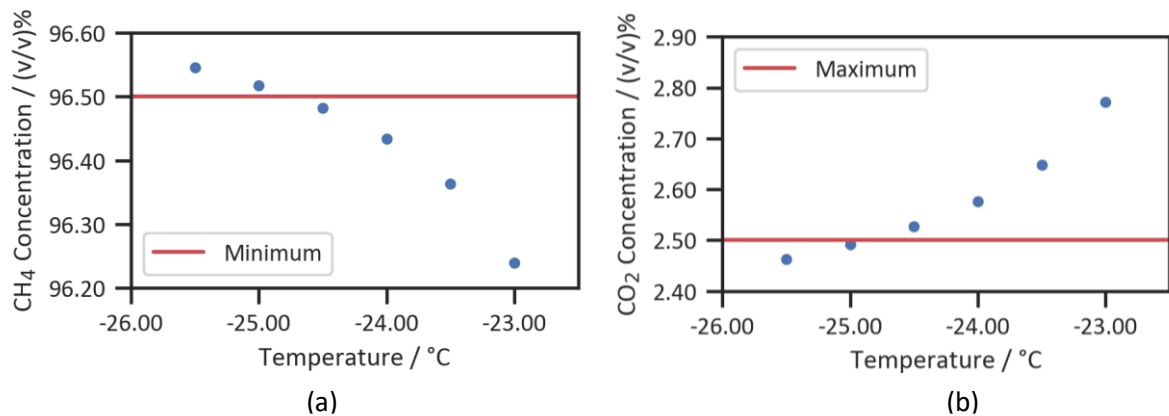


Figure 4.15 - CH₄ (a) and CO₂ (b) composition in the upgraded biogas for Configuration 3 as function of the condenser temperature.

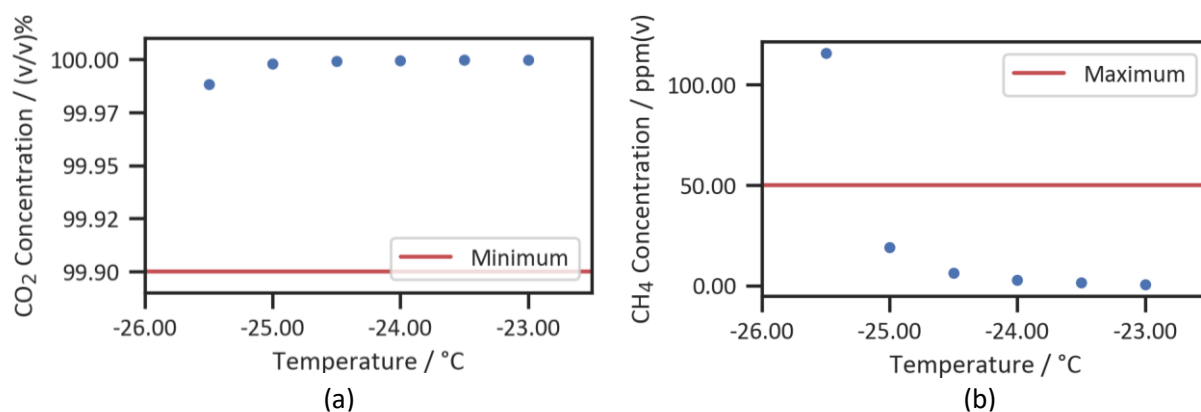


Figure 4.16 - CH₄ (a) and CO₂ (b) composition in the liquid CO₂ for Configuration 3 as function of the condenser temperature.

Like in Configuration 2, raising the temperature of the condenser lowers the quality of the upgraded biogas and increases the quality of the liquid CO₂. However, for Configuration 3, only a condenser temperature of -25.00 °C will allow a proper operation of the system. The simulation for the selected temperature was performed, and its results are shown in Appendix C.

A summary table was made with the main parameters and compositions for the four configurations to compare the results. The results are presented in Table 4.4.

Table 4.4 – Summary of the results of the 3-stage configurations.

Parameters	Bolt-on	Conf. 1	Conf. 2 Optimized	Conf. 3
Carborex®MS				
Compressor's Flow Rate (Nm ³ h ⁻¹)	1577.41	1676.16	1677.34-1744.69	1700.57
Stage 1 Inlet Temperature (°C)	25.00	25.00	30.00	25.00
Upgraded biogas CH ₄ % (v/v)	96.80	96.51	96.53-96.67	96.52
Upgraded biogas CO ₂ % (v/v)	2.29	2.50	2.34-2.47	2.49
Upgraded Biogas Flow Rate (Nm ³ h ⁻¹)	641.70	646.75	645.53-646.60	646.29
LCO₂ unit				
Inlet Flow Rate (Nm ³ h ⁻¹)	559.16	596.95	645.70-670.63	629.40
Condenser's temperature (°C)	-24.9	-24.4	- 25.50 to -23.50	-25.00
CH ₄ slip % (v/v)	0.48	0.00	0.00	0.00
CO ₂ in CO ₂ product % (v/v)	100.00	100.00	100.00	100.00
CH ₄ in CO ₂ product (ppmv)	4.54	2.46	0.41-6.86	19.13
CO ₂ product flow rate (Nm ³ h ⁻¹)	517.27	553.23	533.20-554.17	553.40

By analyzing Table 4.4 is visible that the integration of the LCO₂ in Carborex®MS will lead to an increase in the product flow rates, especially in the case of the liquid CO₂. However, because the CH₄ content in this stream will be lower and the CO₂ will be closer to the upper limit, the integration will also negatively impact the biomethane quality. Additionally, since the Carborex®MS compressor and LCO₂ feed flow rates

will be higher, the operating costs will also increase, particularly in the case of the optimized version of Configuration 2.

As for the heat exchanger duties, there is no significant difference in the condenser temperature. The only significant difference regarding the heating is the first stage inlet temperature, which will be 30.00 °C instead of 25.00 °C for the optimized version of Configuration 2.

Each configuration has advantages and disadvantages when looked at in more detail. Configuration 1 has the lower Carborex®MS compressor duty and the LCO₂ flow rates and does not require a lot of heating or cooling duties. Because of this, this configuration works well from an economic standpoint. However, the quality of the biomethane is very near to the limit values, which is the downside of this configuration.

Of all the integration configurations, and after being optimized, Configuration 2 meets the quality specification in a wider range of operation conditions, making it a more flexible option. Depending on the condenser temperature, the quality of the product streams can be adjusted, as well as the system flow rates. Having said that, this configuration will require a higher heating duty in the Carborex®MS membrane stage.

Regarding compression costs, Configuration 3 is the least desirable of the three options. In addition, compared to other configurations, neither the quality of the biomethane nor the product flow rates change significantly.

4.2 2-stage results

The outcomes of the 2-stage configuration will be presented and discussed in this subsection. Due to the challenges in 2-stage configurations, there are some suggestions for system optimization in the following phase. The results from these configurations are presented in Appendix D.

4.2.1 Bolt on

Just like in the 3-stage Bolt-on Configuration, a smaller outlet gas/LCO₂ inlet ratio means more liquid CO₂. For that reason, a simulation was run considering that the outlet gas will be 7 % of the inlet stream of the liquefaction unit. However, in these conditions, the liquid CO₂ won't have the required quality to be used in food-grade applications. This happens because the tail gas will contain more CH₄ with the third membrane missing. Consequently, the condenser temperature will have to be reduced to control the outlet gas stream flow rate, and CH₄ and the other trace components will end up in the liquid CO₂ stream.

Since the selected outlet gas/LCO₂ inlet ration was too low, its value was increased gradually until the liquid CO₂ met the quality specifications. This happened for an outlet gas stream equal to 15 % of the LCO₂ inlet. Table 4.5 shows the quality of the liquid CO₂ for the 7 % and 15 % outlet gas/LCO₂ ratio.

Table 4.5 - Liquid CO₂ properties and composition from the 2-stage Bolt-on for 7% and 15% outlet gas/LCO₂ inlet ratio.

Parameters	Liquid CO ₂	
	7% outlet gas/LCO ₂ inlet	15% outlet gas/LCO ₂ inlet
Pressure (bar)	18.72	18.72
Temperature (°C)	-22.78	-21.53
Flow Rate (Nm ³ h ⁻¹)	521.84	480.05
CH ₄ slip %	1.90	2.14
Main Composition % (v/v)		
CO ₂	99.71	100.00
Trace Composition (ppmv)		
CH ₄	2916.61	1.89
N ₂	1.20 x 10 ⁻⁸	1.07 x 10 ⁻¹²
O ₂	7.82	6.71 x 10 ⁻⁵
H ₂ O	0.87	0.93

Increasing the outlet gas flow/LCO₂ inlet ratio increased the condenser temperature from -31.31 to -27.42 °C. Table 4.5 shows that, as expected, the liquid CO₂ composition improves drastically with the increased flow rate of the outlet gas stream. Even though this is the minimum outlet stream flow rate, it still means that there will be a decrease of 8% in the flow rate of the liquid CO₂. Table 4.6 presents the results of the main streams for the 2-stage Bolt-on configuration.

Table 4.6 - Properties and composition of 2-stage Bolt-on's main streams.

Parameters	CH ₄ product	Inlet LCO ₂	Condenser's Inlet	PTSA outlet
Pressure (bar)	16.21	1.07	18.70	1.10
Temperature (°C)	32.47	17.89	-17.27	130
Flow Rate (Nm ³ h ⁻¹)	626.47	574.44	619.49	106.10
Composition % (v/v)				
CH ₄	97.50	2.33	3.23	14.91
CO ₂	1.59	97.39	96.62	83.86
N ₂	0.79	0.03	0.03	0.20
O ₂	0.12	0.09	0.12	0.49
H ₂ O	4.79 x 10 ⁻⁹	0.16	7.41 x 10 ⁻⁷	0.54

The Carborex® MS design and operating conditions were the same; hence the temperature adjustment of the condenser had no impact on the biomethane quality. Since the composition of the condenser inlet is known, it is possible to predict the maximum temperature for the condenser. For 96.62% of CO₂, and using the vapor-liquid equilibrium diagram, the operating range of temperature for this configuration is

from -31.31 to -23.14 °C. However, as already indicated; increasing the temperature further will result in more CO₂ being lost.

4.2.2 Integration

Based on the previous results, it is expected that for the integration of the 2 stages the prices associated with the compressor size will be too high, just like with the Bolt-on. For that reason, the Configurations 1 and 2 were integrated while optimizing the operating conditions of the Carborex®MS, following the same methodology presented in the Material and Methods chapter. Table 4.7 presents the main results of both configurations.

Table 4.7 – Summary of the results of the 2-stage integrated configurations.

Parameters	Conf. 1	Conf. 2
Carborex®MS		
Compressor's Flow Rate (Nm ³ h ⁻¹)	2326.85	1980.27
Membrane Count	8-33	11-34
Stage 1 Inlet Temperature (°C)	20.00	20.00
Extra heat exchanger Temperature (°C)	41.00	40.00
CH ₄ in biomethane % (v/v)	96.52	96.81
CO ₂ in biomethane % (v/v)	2.49	2.20
Upgraded Biogas Flow Rate (Nm ³ h ⁻¹)	649.92	644.77
LCO ₂ unit		
Inlet Flow Rate (Nm ³ h ⁻¹)	624.12	711.42
Condenser's temperature (°C)	-26.00	-26.50
CO ₂ in CO ₂ product % (v/v)	100.00	100.00
CH ₄ in CO ₂ product (ppmv)	4.89	1.90
CO ₂ product flow rate (Nm ³ h ⁻¹)	553.10	555.12

The greatest advantage of having the integration of the 2-stage Bolt-on is that the CH₄ slip will be eliminated. However, to meet the quality requirements of the product streams, it was essential to increase the membrane number in both configurations.

Comparing the two configurations in terms of compressor flow rate, it is perceptible that the first configuration has a significantly higher value, which will be reflected in the operating costs. Meanwhile, Configuration 2 has a larger number of membranes which will lead to a higher capital cost.

Quality-wise, all streams meet the quality specifications; however, the second configuration will provide product streams with better quality. This is visible by analyzing the table above, that shows that more CH₄ will stay in the biomethane, and more CO₂ will go to the liquid CO₂.

4.2.3 Bolt-on Design optimization

As an alternative to further decrease the outlet gas flow rate and achieve CO₂ of food-grade quality in the Bolt-on configuration, the initial strategy was to modify and adapt the Carborex®MS design. By decreasing the CH₄ amount going in the inlet of the LCO₂ unit, the condenser can operate at a higher temperature without increasing the outlet gas flow rate.

The optimization process was carried out following the methodology described previously, but for the fixed 7% outlet gas/LCO₂ inlet ratio, the system performance is not ideal due to challenges in maintaining the quality of both streams and high recycling rates, which will result in increased costs for the compressors.

Since the redesign of the Carborex®MS was not the optimal option, another approach is to change the design of the liquefaction unit. In this sense, two suggestions are presented in a tentative of decreasing the outlet gas flow rate to 7% of the LCO₂ inlet flow rate. The first suggestion is to have extra heating in the reboiler. With a higher temperature in the reboiler, some of the CH₄ and trace components going to the liquid CO₂ stream will become gas again and return to the distillation column. For these conditions, these components are expected to leave the distillation column at the top and thus not negatively affect the liquid CO₂ quality.

To simulate the extra heating in the reboiler, a heat exchanger was added after the reboiler. Figure 4.17 shows the LCO₂ schematic representation for this design.

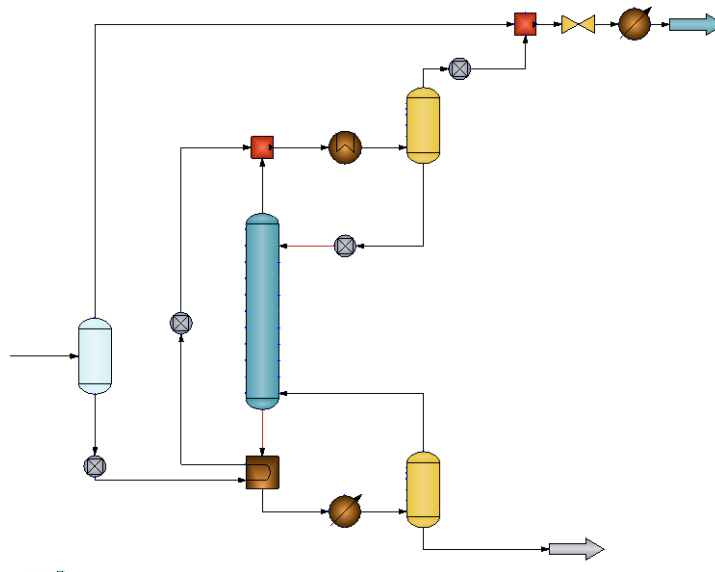


Figure 4.17 – Schematic representation of the 2-stage Bolt-on configuration with extra heating.

A sensitivity study was conducted with the output gas/LCO₂ inlet fixed at 7% to determine how much heating should be added. Figure 4.18 shows the CO₂ and CH₄ content of the liquid CO₂ as the heat exchanger duty increases.

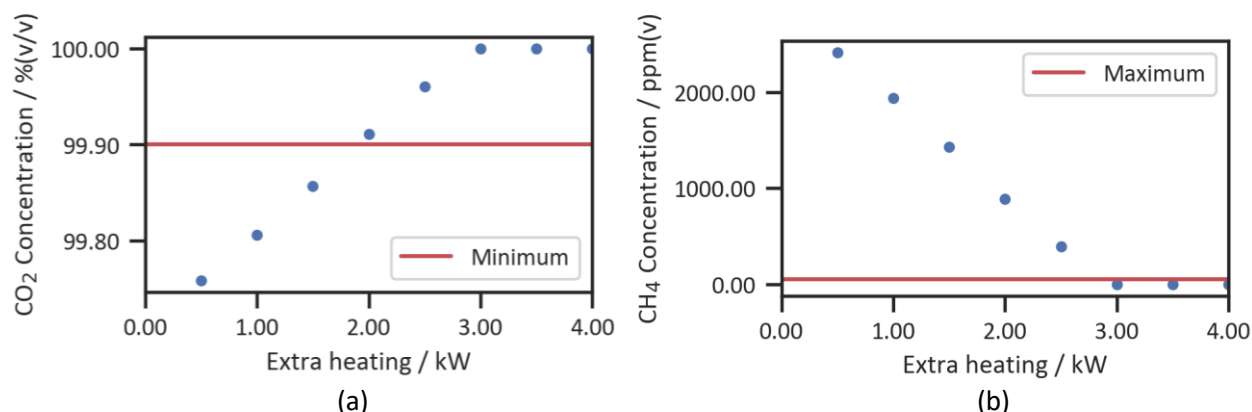


Figure 4.18 - CH₄ (a) and CO₂ (b) concentration in the liquid CO₂ for 2-stage Bolt on configuration as a function of extra heating.

By observing the figure, it is visible that up until a heating of 3.00 kW, increasing the reboiler temperature will result in a decrease in the CH₄ concentration and, as a result, an improvement in the quality of the liquid CO₂. After this, increasing the temperature has no further effect because most trace components were already volatilized for an extra duty of 3.00 kW. This way, for this design, the reboiler should operate with an additional 3.00 kW of heating.

The second suggestion to reduce the amount of CO₂ discarded in the outlet gas flow rate is to add a second condenser to the liquefaction unit. Previously, the condenser was simulated using both a heat exchanger and a flash unit. However, with the addition of the second condenser (heat exchanger and flash unit), there was no need to have a heat exchanger before the first flash unit. This is because the bottom stream from the second flash unit is being redirected to the first heat exchanger. Since this stream is already at a very low temperature, the flash unit alone will act as a condenser.

The outlet gas stream still has the controller to set a fixed flow rate for this stream. The controller will vary the temperature of the second condenser until this stream meets with the 7 % outlet gas/LCO₂ inlet ratio.

With the addition of the second condenser, some of the CO₂ that was being discharged will be recycled to the first condenser instead. After this point, this CO₂ will follow the normal path into the distillation column until the liquid CO₂ stream. Furthermore, as the temperature in the first condenser is not so low, the bulk of the CH₄ will also be separated and leave the system in the outlet gas stream. Figure 4.19 shows the schematic representation for the LCO₂ unit with the second condenser.

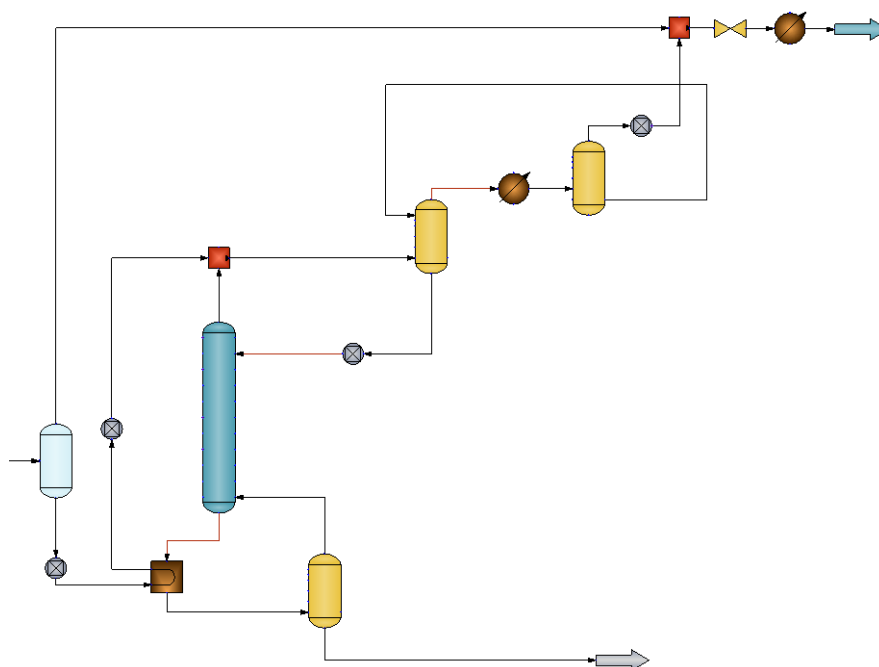


Figure 4.19 – Schematic representation of the 2-stage Bolt-on configuration with second condenser.

To compare the results of the two suggestions, the main results are summarized in Table 4.8. Table 4.8 shows the main results of the two suggestions.

Table 4.8 - Summary of the results of the 2-stage suggested configurations.

Parameters	Heating	2 nd Condenser
Condenser's temperature (°C)	-33.22	-33.24
CH ₄ slip %	2.10	2.14
CO ₂ in outlet gas stream % (v/v)	70.53	70.49
CH ₄ in outlet gas stream % (v/v)	26.90	26.93
CO ₂ in CO ₂ product % (v/v)	100.00	100.00
CH ₄ in CO ₂ product (ppmv)	6.49 x 10 ⁻⁵	0.93
CO ₂ product flow rate (Nm ³ h ⁻¹)	587.65	525.55

Both suggestions allow the liquid CO₂ to meet the food-grade quality with an outlet gas flow rate equal to 7% of the LCO₂ inlet. In terms of operating costs, the configurations have similar condenser temperature and the same flow rates in the compressors. Having additional heating duty after the reboiler will allow a better separation of CH₄ and CO₂, and thus a significant increase liquid CO₂ production. Nevertheless, the additional 3.00kW will make this alternative more expensive than the first option.

Quality-wise the two configurations have a better product quality when compared to the 2-stage configurations and even some of the 3-stage ones. As a result, these configurations present a visible potential for future applications as they require less equipment than the 3-stage configurations, namely one less membrane stage, and less operating costs than the 2-stage.

5 Conclusions

The multistage membrane-based upgrading system Carborex®MS aims to remove the bulk of CO₂ from biogas, while producing pure biomethane. The CO₂ emission may be considered CO₂ neutral because the biogas source is a sustainable energy source or third-generation waste. However, going one step further and using this CO₂ for useful purposes would be especially advantageous to achieve net-zero global emissions.

The simulation and modelling of the CO₂ liquefaction unit was successful as it was possible to obtain liquid food-grade CO₂ as a product for different configurations. The first case examined was a Bolt-on liquefaction unit into a 3-stage membrane system, with the outlet stream of the partial condenser to be used in the regeneration of the PTSA system upstream. Since the outlet gas from the distillation column needs to be at least 7 % of the feed of the LCO₂ unit for the PTSA regeneration, a sensitivity study was conducted. For 7 to 15 % outlet gas/LCO₂ inlet ratio the analysis showed that with higher flow rate of the outlet stream, less CO₂ is liquefied due to higher temperature in the condenser.

Moreover, a sensitivity study was conducted for a minimum concentration of CH₄ and CO₂ in the raw biogas, which reveal the that the system is sensitive to the presence of inert compounds (O₂, N₂). The increase of inerts will lead to a lower concentration of both CH₄ and CO₂ in the biomethane stream and an increase of the CH₄ content in the liquid CO₂, compromising the quality of both products. A limit was set for the concentrations of CH₄ and CO₂ in the feed of the Carborex®MS as the water content in raw biogas is fixed and the inerts composition is usually around 0.40 % N₂ and 0.10 % O₂. In this sense, for a proper operation of the full system, the raw biogas should have 45.00 to 50.28 % of CH₄ and 43.00 to 48.28 % of CO₂.

After the Bolt-on configuration, some alternative integrations were made to make the most of the outlet streams. The outlet gas flow rate was monitored similarly to the Bolt-on case, but this time the aim was to understand its impact on the system as this steam is recycled to the Carborex®MS. Because this stream has a high CO₂ concentration, the system is negatively impacted by an increase in its flow rate, which lead to the selection of a flow rate equal to 7 % of the LCO₂ inlet.

For the 3-stage design of the Carborex®MS, Configuration 2 did not allow the production of biomethane with the required quality. As a result, a design optimization was done, increasing the first membrane stage temperature to 30 °C.

Configurations 2 and 3 have two recycles to the Carborex®MS, varying merely in the second recycle tie-in point. The second recycle flow rate was set to 7 % of the LCO₂ inlet to reduce liquid CO₂ loss. To choose the better suited flow rate of the first recycle, the condenser temperature was controlled in a sensitivity

study. According to the results, while a temperature rise will improve the quality of the liquid CO₂, it will worsen the quality of the biomethane. For Configuration 2, the condenser temperature was restricted from -25.50 to -23.50 °C.

Given that the tie-in point for Configuration 3 is more conservative than the one for Configuration 2, this configuration could operate as intended with the pre-defined design. Nevertheless, the only temperature that will enable a proper operation of the system is -25.00 °C.

From a general point of view, integrating the liquefaction unit within the Carborex®MS will be beneficial in terms of product flow rate, increasing the liquid CO₂ production by approximately 7 % in comparison to the 3-stage Bolt-on configuration. The main advantage of this configuration is that they can operate with 0% methane slip. The downside is that the recycle will cause an increase in the operating costs associated with an increase from 6 to 14 % in the compressors flow rate.

Because the 2-stage Bolt-on configuration didn't show desirable results, several changes were proposed in the design of both Bolt-on and integrated configurations to have results that were most closely aligned with the DMT objectives towards minimizing the CH₄ content in the inlet of the LCO₂. For the integrated configurations, the Carborex®MS design was modified, adjusting the membrane count. The results show that similarly to the 3-stage integrated configurations, producing both products with the necessary quality and without methane slip is feasible. In terms of operating costs, the 2-stage configurations will have bigger operating costs as the compressor flow rate increase by 26 to 38 % compared to the 3-stage Bolt-on configuration.

Finally, for the Bolt-on, some design modifications were suggested aiming to reduce the outlet gas flow rate that is discharged into the atmosphere. The first suggestion implied the addition of a heat exchanger after the reboiler, and the second one the addition of a second condenser. Both recommendations were effective as they managed to lower the outlet gas flow rate to 7 % of the LCO₂ inlet and deliver high-quality performance. However, the configurations will require a condenser temperature of -33.22 and -33.24 °C, meaning that the operating costs will be higher for these cases.

The first suggestion will result in a 14 % increase in liquid CO₂ flow rate compared to the 3-stage Bolt-on configuration, but it will also require 3.00 kW more heating, which will increase operating costs. In contrast, the product flow rate for the second suggestion will not show any significant increase. For future work, these recommendations can be integrated within the Carborex®MS to reduce the methane slip.

6 Assessment of the work done

6.1 Objectives Achieved

- Overview of the CO₂ liquefaction configuration developed by DMT;
- Simulation of the 3-stage Bolt-on configuration to produce food-grade CO₂;
- Sensitivity study in the raw biogas composition of the 3-stage Bolt-on configuration;
- Integration of the LCO₂ unit within the 3-stage design of Carborex®MS and thus designing three different configurations with 0 % methane slip;
- Simulation of the 2-stage Bolt-on configuration to produce food-grade CO₂;
- Model and optimization of the 2-stage configurations, confirming that it is possible to replace the third membrane stage with the liquefaction unit;
- Improvement of the 2-stage Bolt-on configuration suggesting some design changes in the liquefaction unit.

6.2 Final Assessment

The work performed during this internship demonstrates that it is possible to implement a CO₂ liquefaction unit and produce food-grade CO₂ from the tail gas of Carborex®MS. Since both Bolt-on and integrated configurations worked properly, it is safe to assume that the system can also operate without methane and CO₂ emissions.

Furthermore, the 2-stage Bolt-on and integrated configuration also showed satisfactory results. This indicates that the third membrane stage can be replaced by the liquefaction unit, reducing capital costs. As the suggested design changes worked well for the Bolt-on configuration, the possibility of integration with these designs could be explored in the future.

Nevertheless, these conclusions are only based on the quality of the product. Since the integration of the LCO₂ and the operation with two membrane stages will increase the flow rates in the compressors, it's expected the operating costs to increase significantly. For this reason, is recommended for future works a business case of the configurations with more potential.

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Annex A - CO₂ temperature-pressure diagram

Annex A shows the temperature-pressure diagram of CO₂. This diagram is presented in Figure A.1.

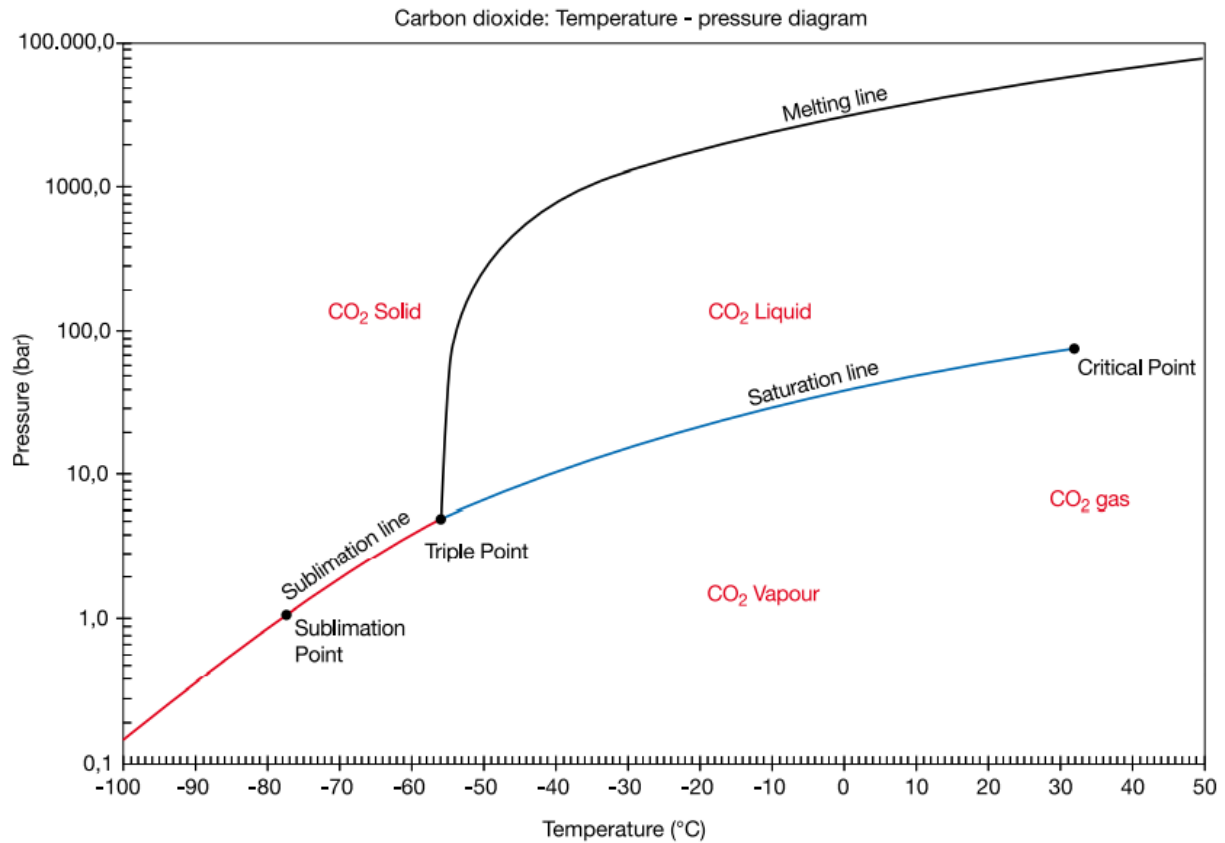


Figure A.1 - Phase diagram for CO₂, adapted from [36]

Annex B - Quality specifications according to the European Industrial Gases Association (EIGA)

The quality specifications for Food-grade CO₂ (Table B.1) are presented in Annex B.

Table B.1 - Quality specifications according to EIGA, adapted from [37].

Component	Concentration
Assay	99.9 % v/v min.
Moisture	20 ppm v/v max.
Ammonia	2.5 ppm v/v max.
Oxygen	30 ppm v/v max.
Oxides of nitrogen (NO/NO ₂)	2.5 ppm v/v max. each
Non-volatile residue (particulates)	10 ppm w/w max.
Non-volatile organic residue (oil and grease)	5 ppm w/w max.
Phosphine ***	0.3 ppm v/v max
Total volatile hydrocarbons (Calculated as methane)	50 ppm v/v max. of which 20 ppm v/v max non-methane hydrocarbons
Acetaldehyde	0.2 ppm v/v max.
Aromatic hydrocarbon	0.02 ppm v/v max.
Carbon monoxide	10 ppm v/v max.
Methanol	10 ppm v/v max.
Hydrogen cyanide*	0.5 ppm v/v max
Total sulphur (as S) **	0.1 ppm v/v max
Taste and odor in water	No foreign taste or odor
Appearance in water	No color or turbidity
Odor and appearance of solid CO ₂ (snow)	No foreign odor or appearance

* Analysis necessary only for carbon dioxide from coal gasification sources

** If the total sulfur content exceeds 0.1 ppm v/v as sulfur then the species must be determined separately and the following limits apply:

 Carbonyl Sulphide 0.1 ppm v/v max.

 Hydrogen Sulphide 0.1 ppm v/v max.

 Sulphur Dioxide 1.0 ppm v/v max.

*** Analysis necessary only for carbon dioxide from phosphate rock sources

Where carbon dioxide complies with the specification then by definition the requirements for acidity and reducing substances as required by European Law are met.

Annex C - VLE Diagram

Annex C shows the Vapor-Liquid Equilibrium of CH₄-CO₂ and O₂-CO₂. This data was collected by DMT using CHEMCAD software and is presented in Figure C.1.

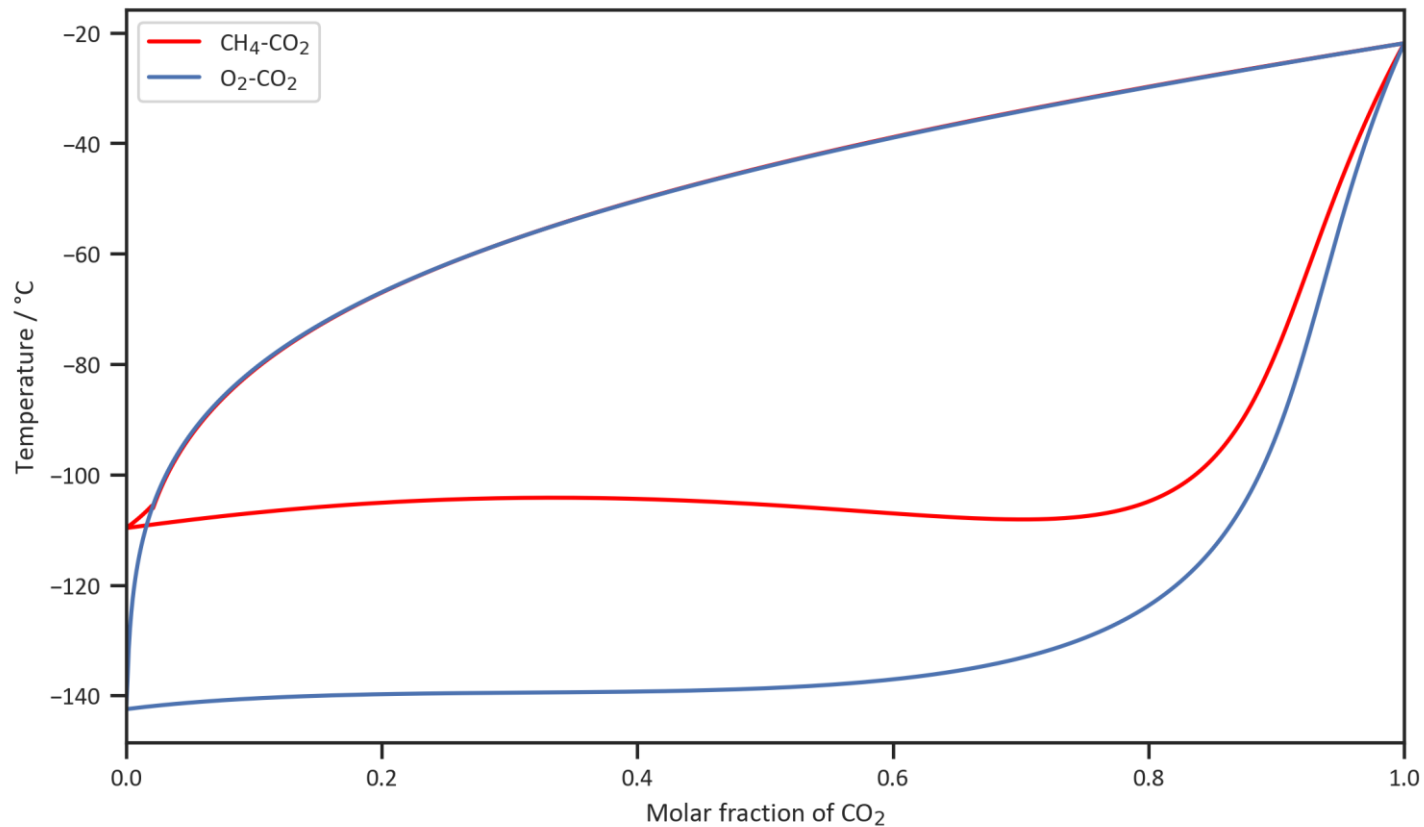


Figure C.1 – Full version of the CH₄-CO₂ and O₂-CO₂ vapor-liquid equilibrium curves.

Appendix A - PFD of the Configurations

This appendix introduces the PFD of the different configurations (Figures A.1 to A.4), as it is presented in CHEMCAD. The membrane part of the current simulation is automatically regulated with an Excel file. In this file, some by-pass can be activated or deactivated according to the needs of the user. As a result, every simulation shows 4 membrane stages.

For the 3-stage configurations, a by-pass is done for the “MEMBRANE STAGE 2B”, which means that the stream will not pass through this membrane stage. Similarly, for the 2-stage configurations, the “MEMBRANE STAGE 3” is not part of the simulation.

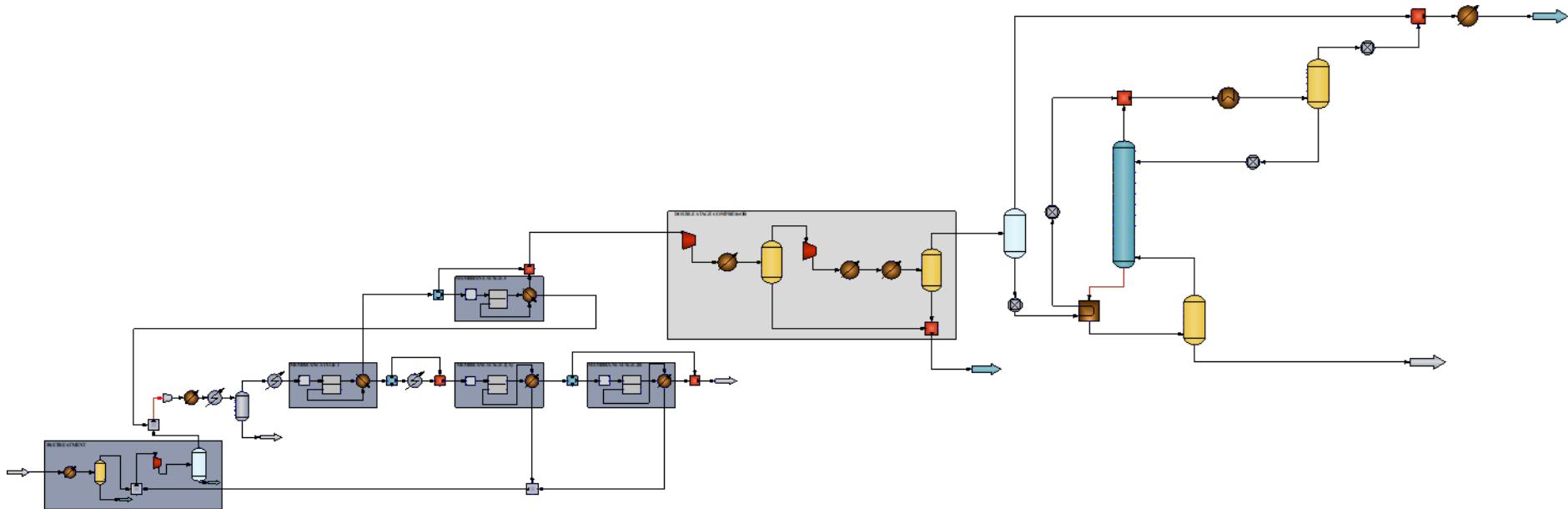


Figure A.1 - PFD of the Bolt-on Configuration.

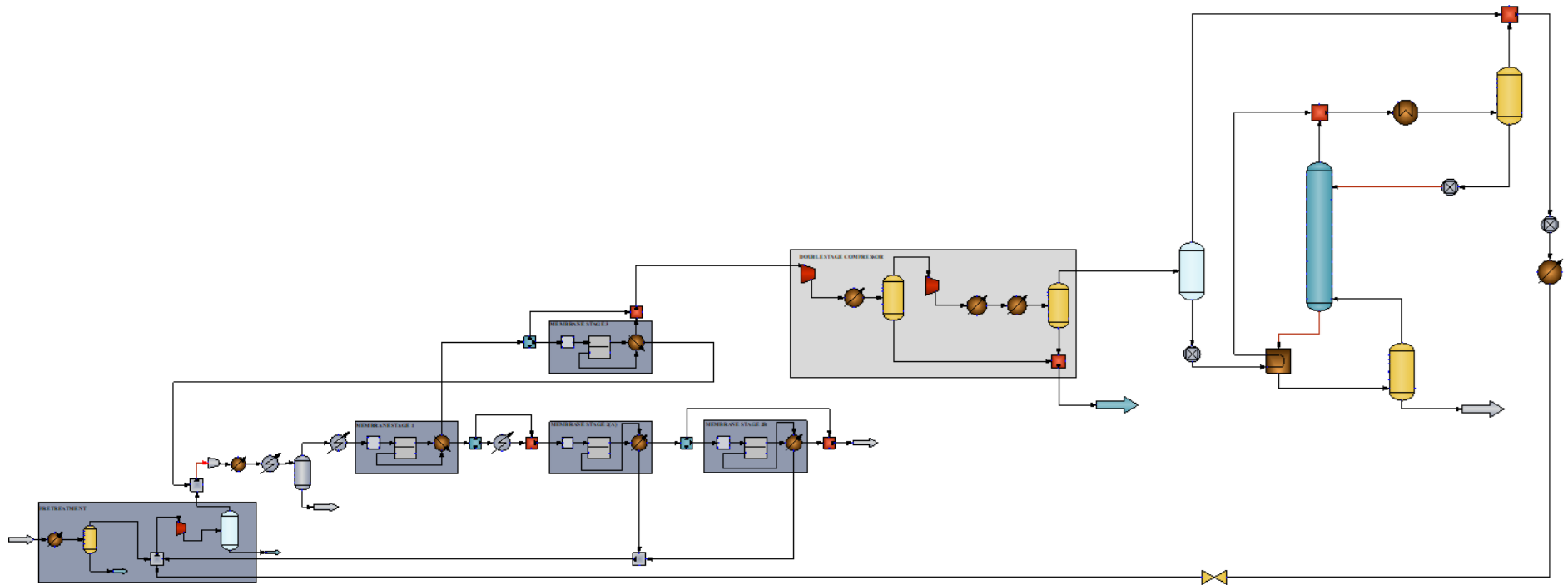


Figure A.2 - PFD of Configuration 1.

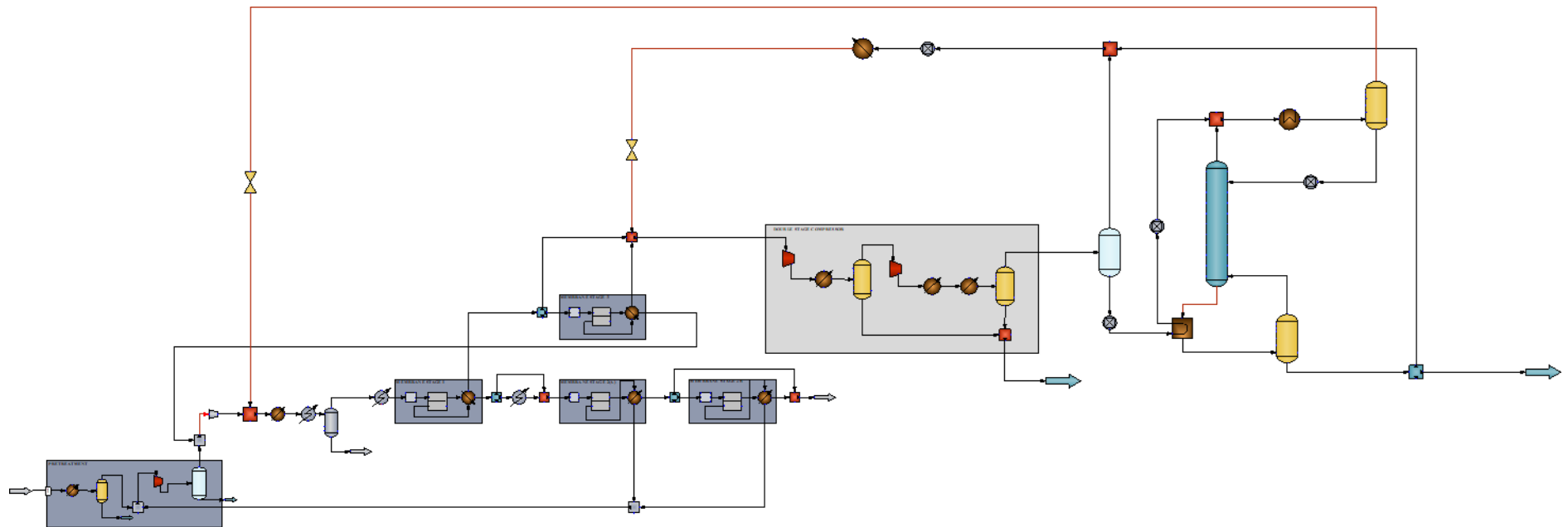


Figure A.3 - PFD of the Configuration 2.

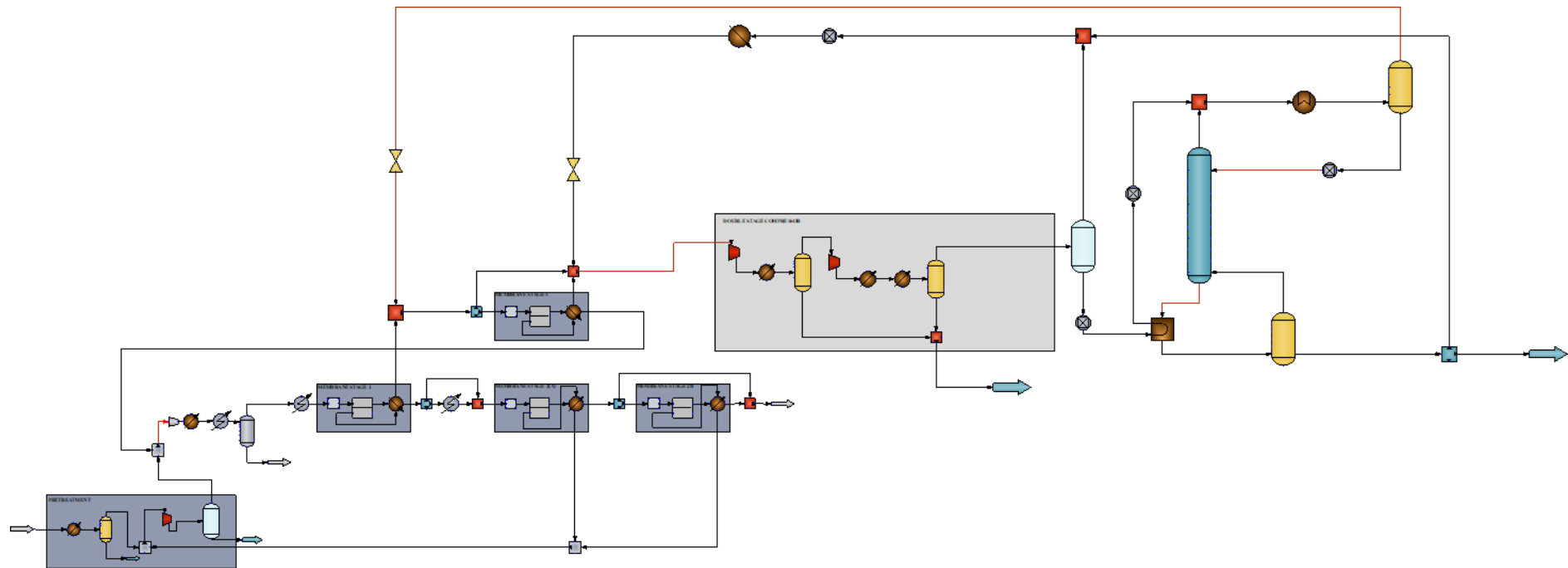


Figure A.4- PFD of the Configuration 3.

Appendix B - Sensitivity study results for 43% of CO₂ in the raw biogas

To verify that the quality of both product streams meets with the quality requirements, these streams compositions were monitored. Tables B.1 and B.2 show the properties and composition of the raw biogas and product streams.

Table B.1 - Properties and composition of the raw biogas and biomethane from the 3-stage Bolt-on.

Parameters	Raw biogas	Biomethane
Pressure (bar)	1.01	16.43
Temperature (°C)	37.00	14.10
Flow Rate (Nm ³ h ⁻¹)	1279.69	661.34
Composition % (v/v)		
CO ₂	43.00	2.35
CH ₄	50.28	96.77
N ₂	0.40	0.76
O ₂	0.10	0.12
H ₂ O	6.22	4.72 x 10 ⁻⁸

Table B.2- Properties and composition of the liquid CO₂ from the 3-stage Bolt-on.

Parameters	Liquid CO ₂
Pressure (bar)	18.72
Temperature (°C)	-21.54
Flow Rate (Nm ³ h ⁻¹)	498.81
Main Composition % (v/v)	
CO ₂	100.00
Trace Composition (ppmv)	
CH ₄	19.84
N ₂	3.35 x 10 ⁻¹²
O ₂	2.70 x 10 ⁻³
H ₂ O	0.85

Appendix C - Results from 3-stage configurations

Appendix C presents the properties and composition of the main streams of the 3-stage integrated configurations. This section is composed in 3 parts, each one for one configuration.

C.1 - Configuration 1

The results from configuration 1 are presented in this section. Tables C.1 and C.2 show the results of the main streams for this design.

Table C.1 Properties and composition of 3-stage Configuration 1 main streams.

Parameters	CH ₄ product	Inlet LCO ₂	Condenser's Inlet	Recycle
Pressure (bar)	16.43	1.05	18.70	1.10
Temperature (°C)	12.22	20.89	-17.07	130.00
Flow Rate (Nm ³ h ⁻¹)	646.75	596.95	650.98	43.38
Composition % (v/v)				
CH ₄	96.51	0.41	0.84	5.59
CO ₂	2.50	99.32	98.94	91.38
N ₂	0.79	0.01	0.01	0.11
O ₂	0.20	0.11	0.21	1.54
H ₂ O	2.87 x 10 ⁻⁶	0.15	7.32 x 10 ⁻⁵	1.39

Table C.2 - Liquid CO₂ properties and composition from the 3-stage Configuration 1.

Parameters	Liquid CO ₂
Pressure (bar)	18.72
Temperature (°C)	-21.53
Flow Rate (Nm ³ h ⁻¹)	553.23
Main Composition % (v/v)	
CO ₂	100.00
Trace Composition (ppmv)	
CH ₄	2.46
N ₂	3.39 x 10 ⁻¹²
O ₂	8.78 x 10 ⁻⁴
H ₂ O	0.85

C.2 - Configuration 2

Because Configuration 2 can operate in a range of temperatures, the results of the higher and lower temperature are presented. Tables C.3 and C.4 show the results of the main streams for a condenser's temperature of -25.00 °C. Tables C.5 and C.6 show the results of the main streams for a condenser's temperature of -23.50 °C.

Table C.3 - Properties and composition of 3-stage Configuration 2 main streams for a condenser temperature of -25.00 °C.

Parameters	CH ₄ product	Inlet LCO ₂	Condenser's Inlet	Recycle 1	Recycle 2
Pressure (bar)	15.62	1.05	18.70	18.70	1.10
Temperature (°C)	19.53	32.88	-17.12	-25.00	130.00
Flow Rate (Nm ³ h ⁻¹)	645.70	644.90	702.36	45.67	45.68
Composition % (v/v)					
CH ₄	96.67	0.50	1.03	7.04	6.76 x 10 ⁻⁴
CO ₂	2.34	99.12	98.71	91.03	98.58
N ₂	0.79	0.01	0.01	0.14	8.59 x 10 ⁻¹⁶
O ₂	0.20	0.13	0.24	1.79	3.45 x 10 ⁻⁷
H ₂ O	4.41 x 10 ⁻⁶	0.25	7.34 x 10 ⁻⁵	1.20 x 10 ⁻⁵	1.42

Table C.4 - Liquid CO₂ properties and composition from the 3-stage Configuration 2 for a condenser temperature of -25.00 °C.

Parameters	Liquid CO ₂
Pressure (bar)	18.72
Temperature (°C)	-21.53
Flow Rate (Nm ³ h ⁻¹)	554.17
Main Composition % (v/v)	
CO ₂	100.00
Trace Composition (ppmv)	
CH ₄	6.86
N ₂	8.72 x 10 ⁻¹⁰
O ₂	3.50 x 10 ⁻³
H ₂ O	0.85

Table C.5 - Properties and composition of 3-stage Configuration 2 main streams for a condenser temperature of -23.50°C.

Parameters	CH ₄ product	Inlet LCO ₂	Condenser's Inlet	Recycle 1	Recycle 2
Pressure (bar)	15.62	1.05	18.70	18.70	1.10
Temperature (°C)	18.72	32.88	-17.03	-23.50	130.00
Flow Rate (Nm ³ h ⁻¹)	646.60	670.63	733.72	68.80	47.46
Composition % (v/v)					
CH ₄	96.53	0.41	0.68	3.95	4.08 x 10 ⁻⁵
CO ₂	2.47	99.23	99.13	94.89	98.58
N ₂	0.79	0.01	0.01	0.08	2.37 x 10 ⁻¹⁶
O ₂	0.20	0.11	0.17	1.07	1.86 x 10 ⁻⁸
H ₂ O	3.90 x 10 ⁻⁸	0.25	7.29 x 10 ⁻⁵	1.29 x 10 ⁻⁵	1.42

Table C.6 - Liquid CO₂ properties and composition from the 3-stage Configuration 2 for a condenser temperature of -23.50°C.

Parameters	Liquid CO ₂
Pressure (bar)	18.72
Temperature (°C)	-21.53
Flow Rate (Nm ³ h ⁻¹)	553.20
Main Composition % (v/v)	
CO ₂	100.00
Trace Composition (ppmv)	
CH ₄	0.41
N ₂	2.41 x 10 ⁻¹²
O ₂	1.89 x 10 ⁻⁴
H ₂ O	0.88

C.3 - Configuration 3

This section shows the results of the main streams for Configuration 3. Tables C.7 and C.8 show the results of the main streams for this design.

Table C.7 - Properties and composition of 3-stage Configuration 3 main streams.

Parameters	CH ₄ product	Inlet LCO ₂	Condenser's Inlet	Recycle 1	Recycle 2
Pressure (bar)	16.43	1.05	18.70	18.70	1.10
Temperature (°C)	12.38	25.88	-24.11	-25.00	130.00
Flow Rate (Nm ³ h ⁻¹)	646.29	629.40	55.72	30.38	44.55
Composition % (v/v)					
CH ₄	96.52	0.30	6.43	6.28	1.86 x 10 ⁻³
CO ₂	2.49	99.32	91.30	91.04	98.58
N ₂	0.79	0.01	0.06	0.12	1.02 x 10 ⁻¹⁵
O ₂	0.20	0.12	2.21	2.56	1.17 x 10 ⁻⁶
H ₂ O	2.61 x 10 ⁻⁶	0.25	1.21 x 10 ⁻⁸	1.18 x 10 ⁻⁷	1.42

Table C.8 - Liquid CO₂ properties and composition from the 3-stage Configuration 3.

Parameters	Liquid CO ₂
Pressure (bar)	18.72
Temperature (°C)	-21.54
Flow Rate (Nm ³ h ⁻¹)	553.40
Main Composition % (v/v)	
CO ₂	100.00
Trace Composition (ppmv)	
CH ₄	19.13
N ₂	1.04 x 10 ⁻¹¹
O ₂	0.01
H ₂ O	0.83

Appendix D - Results from 2-stage configurations

Appendix D presents the properties and composition of the main streams of the 2-stage configurations. This section is composed in three parts. The first part includes section A, that provide the results from the Bolt-on configuration with an outlet gas equal to 7 % of the LCO₂ inlet. The second part, composed of sections B and C will show the results from the integrated configurations. Finally, the third part incorporates the remaining sections that present the results from the suggested configurations.

D.1 - Bolt-on configuration with 7% outlet gas/LCO₂ inlet ratio

The results from the Bolt-on configuration with an outlet gas equal to 7 % of the LCO₂ inlet are presented in this section. Table D.1 shows the results of the main streams for this design.

Table D.1 - Properties and composition of the main streams from 2-stage Bolt-on configuration with 7 % outlet gas/LCO₂ inlet ratio.

Parameters	CH ₄ product	Inlet LCO ₂	Condenser's Inlet	PTSA outlet
Pressure (bar)	16.21	1.07	18.70	1.10
Temperature (°C)	32.47	17.89	-19.95	130.00
Flow Rate (Nm ³ h ⁻¹)	626.47	574.45	616.32	52.29
Composition % (v/v)				
CH ₄	97.50	2.33	3.78	22.71
CO ₂	1.59	97.39	96.03	74.88
N ₂	0.79	0.03	0.04	0.34
O ₂	0.12	0.09	0.15	0.97
H ₂ O	4.79 x 10 ⁻⁷	0.16	7.44 X 10 ⁻⁵	1.11

D.2 - Configuration 1

The results from configuration 1 are presented in this section. Table D.2 and D.3 show the results of the main streams for this design.

Table D.2 - Properties and composition of 2-stage Configuration 1 main streams.

Parameters	CH ₄ product	Inlet LCO ₂	Condenser's Inlet	Recycle 1
Pressure (bar)	16.07	1.07	18.70	1.10
Temperature (°C)	23.67	17.76	-17.20	130.00
Flow Rate (Nm ³ h ⁻¹)	646.92	624.12	676.12	70.56
Composition % (v/v)				
CH ₄	96.49	1.21	1.96	10.69
CO ₂	2.52	98.52	97.90	87.59
N ₂	0.79	0.02	0.02	0.14
O ₂	0.20	0.08	0.12	0.68
H ₂ O	6.14 x 10 ⁻⁷	0.18	7.37 x 10 ⁻⁵	0.89

Table D.3 - Liquid CO₂ properties and composition from the 2-stage Configuration 1.

Parameters	Liquid CO ₂
Pressure (bar)	18.72
Temperature (°C)	-21.53
Flow Rate (Nm ³ h ⁻¹)	553.10
Main Composition % (v/v)	
CO ₂	100.00
Trace Composition (ppmv)	
CH ₄	4.89
N ₂	3.61 x 10 ⁻¹²
O ₂	3.99 x 10 ⁻⁴
H ₂ O	0.89

D.3 - Configuration 2

This section shows the results of the main streams for Configuration 2. Tables D.4 and D.5 show the results of the main streams for this design.

Table D.4 - Properties and composition of 2-stage Configuration 2 main streams.

Parameters	CH ₄ product	Inlet LCO ₂	Condenser's Inlet	Recycle 1	Recycle 2
Pressure (bar)	15.36	1.05	18.70	18.70	1.10
Temperature (°C)	29.38	25.41	-17.21	-26.50	130.00
Flow Rate (Nm ³ h ⁻¹)	645.56	694.50	750.48	90.46	48.75
Composition % (v/v)					
CH ₄	96.69	1.55	2.35	11.89	3.46 x 10 ⁻⁴
CO ₂	2.32	98.08	97.49	87.23	98.57
N ₂	0.79	0.02	0.02	0.16	5.86 x 10 ⁻¹⁶
O ₂	0.20	0.09	0.13	0.72	3.45 x 10 ⁻⁸
H ₂ O	8.13 x 10 ⁻⁷	0.26	1.25 x 10 ⁻⁸	1.20 x 10 ⁻⁵	1.43

Table D.5 - Liquid CO₂ properties and composition from the 2-stage Configuration 2.

Parameters	Liquid CO ₂
Pressure (bar)	18.72
Temperature (°C)	-21.53
Flow Rate (Nm ³ h ⁻¹)	553.99
Main Composition % (v/v)	
CO ₂	100.00
Trace Composition (ppmv)	
CH ₄	3.51
N ₂	5.95 x 10 ⁻¹²
O ₂	3.45 x 10 ⁻⁴
H ₂ O	0.90

D.4 - Configuration with extra heating

As a suggestion for the LCO₂ unit, an extra heat exchanger was added after the reboiler. For this configuration, a simulation was done and the main results are presented in Tables D.6 and D.7.

Table D.6 Properties and composition of the main streams from 2-stage Bolt-on configuration with extra heating.

Parameters	Inlet LCO ₂	Condenser's Inlet	PTSA outlet
Pressure (bar)	1.07	18.70	1.10
Temperature (°C)	17.89	-17.26	-32.28
Flow Rate (Nm ³ h ⁻¹)	574.48	622.89	53.28
Composition % (v/v)			
CH ₄	2.33	4.19	25.22
CO ₂	97.38	95.62	73.48
N ₂	0.03	0.04	0.34
O ₂	0.09	0.15	0.96
H ₂ O	0.16	7.37 x 10 ⁻⁵	9.12 x 10 ⁻⁶

Table D.7 - Liquid CO₂ properties and composition from 2-stage Bolt-on configuration with extra heating.

Parameters	Liquid CO ₂
Pressure (bar)	18.72
Temperature (°C)	-21.53
Flow Rate (Nm ³ h ⁻¹)	520.57
Main Composition % (v/v)	
CO ₂	100.00
Trace Composition (ppmv)	
CH ₄	6.13 x 10 ⁻³
N ₂	7.45 x 10 ⁻¹³
O ₂	3.41 x 10 ⁻⁷
H ₂ O	0.87

D.5 - Configuration with second condenser

The second suggestion was to add a second condenser. The main results from this configuration are shown in this section in Tables D.8 and D.9.

Table D.8 - Properties and composition of the main streams from 2-stage Bolt-on configuration with a second condenser.

Parameters	Inlet LCO ₂	1 st Condenser Inlet	2 nd Condenser Inlet	PTSA outlet
Pressure (bar)	1.07	18.70	18.70	1.10
Temperature (°C)	17.89	-17.04	-23.30	130.00
Flow Rate (Nm ³ h ⁻¹)	574.27	629.29	614.49	47.73
Composition % (v/v)				
CH ₄	2.33	2.49	4.40	26.93
CO ₂	97.38	97.39	95.40	70.50
N ₂	0.03	0.03	0.04	0.36
O ₂	0.09	0.09	0.15	1.03
H ₂ O	0.16	7.29 x 10 ⁻⁵	1.30 x 10 ⁻⁵	1.19

Table D.9 - Liquid CO₂ properties and composition from 2-stage Bolt-on configuration with a second condenser.

Parameters	Liquid CO ₂
Pressure (bar)	18.72
Temperature (°C)	-21.53
Flow Rate (Nm ³ h ⁻¹)	525.54
Main Composition % (v/v)	
CO ₂	100.00
Trace Composition (ppmv)	
CH ₄	0.93
N ₂	5.68 x 10 ⁻¹³
O ₂	4.41 x 10 ⁻⁵
H ₂ O	0.87