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TECHNO-ECONOMIC ANALYSIS OF WASTEWATER TREATMENT PLANT BIOGAS METHANATION

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Abstract

The methanation of the CO_2 present in biogas, which is the production of CH_4 from CO_2 and H_2 , the latter being produced via water electrolysis, is getting more and more interesting over the years, especially if that hydrogen is obtained from renewable electricity. This process is usually referred to as Power-to-Gas and it shows great interest in the concept of wastewater treatment plants (WWTP), namely in Portugal. The produced CH_4 , called biomethane, can then be injected into the natural gas grid, if complying with the required specifications.

The biogas resulting from anaerobic digestion can be separated into a CH_4 and a CO_2 -rich stream, using an adequate gas separation technology, after which the CO_2 goes into the methanation section; alternatively, the biogas can go directly into the reaction section with no separation. These are two of the alternatives studied in this work. The type of reactors used was also analyzed, since there are two types of state-of-the-art methanation reactors, the cooled fixed-bed and the adiabatic fixed-bed reactors.

Cooled reactors present a significant advantage (in comparison with the adiabatic ones) that is the formation of different reaction zones inside the reactor, that allows for a simpler one-reactor approach. When using adiabatic reactors, two reactors must be used in order for the second one to be at a lower temperature, so that a higher conversion can be attained, which results a more complex reaction process even more so because of the gas recycle. The results show exactly that, while the cooled reactor that had no previous CO_2 separation from the biogas, showed a conversion of 91.8 %, the adiabatic reactors, showed conversions of 59.6 and 67.2 %, resulting in an overall conversion of 93.0 %.

In economic terms, all the scenarios studied showed negative net present worth (NPW) values. Scenarios with CO_2 membrane separation upstream of the reaction section showed the lowest NPW values, -962 and -982 k€ for the cooled and adiabatic reactors, respectively. The NPW obtained for the scenarios with no membrane were -638 and -669 k€, for the cooled and adiabatic reactors, respectively.

Since all scenarios were able to obtain biomethane with enough quality to be injected into the grid, meaning a Wobbe Index higher than 48.17 MJ Nm^{-3} , the best scenario is considered to be the one with the highest NPW, which is the scenario with the cooled reactors, with no membrane. This scenario presented a payback time of little over 10 years, meaning that the investment could easily be paid off the next year. Also, a sensitivity analysis showed that by decreasing the renewable electricity price by 18% or by increasing the biomethane by 25%, the NPW would have been 0 by the end of the considered lifetime.

Keywords: biogas, methanation, economic analysis

Resumo

A metanação do CO_2 presente no biogás, que consiste na produção de CH_4 a partir de CO_2 e H_2 , sendo o último produzido através da eletrólise da água, tem ganho cada vez mais interesse ao longo dos anos, especialmente se o hidrogénio é produzido a partir de energia renovável. Este processo é conhecido como *Power-to-Gas*, e demonstra grande interesse no âmbito das estações de tratamento de águas residuais, em Portugal. O CH_4 produzido pode, então, ser injetado na rede de gás natural, quando produzido com a qualidade necessária.

O biogás resultante da digestão anaeróbia pode ser separado em duas correntes ricas em CO_2 e CH_4 , respetivamente, utilizando uma tecnologia de separação adequada, para depois seguir para a secção da metanação; alternativamente, o biogás pode ir diretamente para os reatores de metanação. Estas são duas das possíveis alternativas estudadas neste trabalho. O tipo de reatores utilizados foi também analisado, uma vez que existem dois tipos de reatores considerados estado-de-arte da metanação, os de leito fixo arrefecidos e adiabáticos.

Os reatores arrefecidos apresentam uma vantagem significativa, em comparação com os adiabáticos que é a formação de diferentes zonas de reação dentro do reator, que permite uma abordagem mais simples (um reator) ao processo de metanação. Quando se utiliza reatores adiabáticos, são normalmente necessários dois ou mais, de modo a que o segundo esteja a uma temperatura mais baixa para que se consiga obter conversões mais altas, o que resulta numa secção de metanação mais complexa, também devido ao reciclo de gás. Os resultados mostram exatamente isso, enquanto que o reator arrefecido, sem separação prévia com membrana, mostrou uma conversão de 91.8 %, os reatores adiabáticos mostraram conversões de 59.6 e 67.2 %, resultando numa conversão total de 93.0%.

Em termos económicos, todos os cenários estudados apresentaram valores atuais líquidos (VAL) negativos. Os cenários em que o CO_2 é previamente separado do biogás, resultaram em VAL mais baixos, -962 e -982 k€ para os reatores arrefecidos e adiabáticos, respetivamente. O VAL obtido para os cenários sem membrana foi -638 e -669 k€ para os reatores arrefecidos e adiabáticos, respetivamente.

Uma vez que todos os cenários foram capazes de produzir biometano com qualidade suficiente para ser injetado na rede, ou seja, um Índice de Wobbe maior que $48.17 \text{ MJ Nm}^{-3+}$, o melhor cenário é considerado aquele com o maior VAL, que neste caso é o cenário com o reator arrefecido, sem membrana. Este cenário apresentou um prazo de retorno de pouco mais de 10 anos, podendo facilmente ser pago no ano seguinte. Para além disso, uma análise de sensibilidade mostrou que diminuindo em 18% o preço da eletricidade renovável, ou aumentando em 25% o preço de venda do biometano, o VAL teria sido 0 no fim dos 10 anos considerados.

Palavras-chave: biogás, metanação, análise económica

Declaration

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

A handwritten signature in black ink, appearing to read 'Yawara Silva'.

July 5, 2021

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Notation and Glossary

a	year of operation	y
A	area	ft ²
A_{ext}	external heat transfer surface	m ²
A_{in}	internal heat transfer surface	m ²
A_v	cross-sectional area for vapor flow	m ²
C	cost of the case at the operation condition considered	€ y ⁻¹
C_B	base cost of equipment	\$
C_{base}	base case cost	€ y ⁻¹
C_{CAPEX}	annual capital expenditures	€ y ⁻¹
C_{OPEX}	operational expenditures	€ y ⁻¹
$C_{O\&M}$	cost of operation and maintenance	€ y ⁻¹
C_p	purchase cost	€
C_{PL}	platforms and ladders cost	\$
$C_{raw materials}$	cost of raw materials	€ y ⁻¹
C_{TCI}	total capital investment cost	€
$C_{utilities}$	cost of utilities	€ y ⁻¹
C_v	empty vessel cost	\$
CF_a	cash flow at year of operation a	€ y ⁻¹
d	relative density	
D_i	internal diameter	ft
d_m	membrane thickness	m
D_p	catalyst particle diameter	m
D_t	tube diameter	m
D_v	vessel diameter	m
dC	costs difference	
E	weld efficiency	
$F_{CO_2,in}$	molar flow of CO ₂ at the inlet	mol h ⁻¹
$F_{CO_2,out}$	molar flow of CO ₂ at the outlet	mol h ⁻¹
F_D	drive factor	
F_i	moles produced of component i	mol h ⁻¹
F_L	length factor	
F_M	material factor	
F_P	pressure factor	
G	mass flux in each tube	kg m ⁻³
i	interest rate	
J_i	molar flow of each component through the membrane wall surface area	mol m ⁻² h ⁻¹
$K_{CH_4}, K_{H_2}, K_{CO}$	adsorption constants of CH ₄ , H ₂ and CO, respectively	Pa ⁻¹
K_{H_2O}	adsorption constant of H ₂ O	
K_C, K_H	adsorption constants of C and H	Pa ^{-0.5}
K_{Meth}	equilibrium constant of CO methanation reaction	Pa ⁻²
K_{WGS}	equilibrium constant of the water-gas shift reaction	
k_1	kinetic constant of the CO methanation reaction	kmol kg _{cat} ⁻¹ s ⁻¹
k_2	kinetic constant of the RWGS reaction	kmol Pa ^{-1.5} kg _{cat} ⁻¹ s ⁻¹
L	membrane length	m
L_v	vessel length	in
m_{cat}	catalyst mass	kg
N_i	molar flow of each component i through the cross-sectional area of the membrane	mol m ⁻² h ⁻¹
P	shell side pressure	psig
P_C	consumed power of compressors	hp

P_d	design pressure	psig
P_j	partial pressure of component j	Pa
P_r, P_p	pressure on the retentate and the permeate side, respectively	Pa
P_o	operating pressure	psig
Q_{feed}	feed volumetric flow	$m^3 s^{-1}$
$Q_{v,m}$	vapor mass flow rate	$m^3 s^{-1}$
$Q_{v,v}$	vapor volumetric flow rate	$kg h^{-1}$
r	radius	m
R	universal gas constant	$m^3 Pa K^{-1} mol^{-1}$
$r_{CO\ methanation}$	reaction rate of CO methanation reaction	$kmol kg_{cat}^{-1} s^{-1}$
r_{RWGS}	reaction rate of RWGS reaction	$kmol Pa^{-1.5} kg_{cat}^{-1} s^{-1}$
S	stress	in^2
S_i	selectivity of component i	
T	temperature	K
t	income tax rate	
t_s	shell thickness	in
U	overall heat transfer coefficient	$W m^{-2} K^{-1}$
u_t	settling velocity	$m s^{-1}$
u_v	vapor velocity	$m s^{-1}$
V_{cat}	catalyst volume	m^3
$\dot{V}_{in}$	volumetric flow of gas at normal conditions	$Nm^3 h^{-1}$
W	weight of the shell and two heads	lb
X_{CO_2}	CO ₂ conversion	
$x_{i,feed}$	molar fraction of component i in the feed stream	
$x_{i,p}$	molar fractions of component i in the permeate	
$x_{i,r}$	molar fractions of component i in the retentate	
Y_i	yield of component i	

Greek Letters

a_{ext}	heat transfer coefficient on the external side of the tubes	$W m^{-2} K^{-1}$
a_i	heat transfer coefficient on the internal side of the tubes	$W m^{-2} K^{-1}$
ΔG	Gibbs free energy	$kJ mol^{-1}$
ΔH_r^0	Standard enthalpy of reaction	$kJ mol^{-1}$
Δz	longitudinal element of the membrane	m
λ_{gas}	gas thermal conductivity	$W m^{-1} K^{-1}$
μ	dynamic viscosity	Pa s
ρ	mass density of construction material	$lb in^{-3}$
ρ_L	liquid mass density	$kg m^{-3}$
ρ_v	vapor mass density	$kg m^{-3}$

Indexes

j	component j (CO, H ₂ , CH ₄ , H ₂ O, CO ₂)
n	component n (CH ₄ , H ₂ , CO, H ₂ O, C, H)

List of Acronyms

AEL	Alkaline Electrolysis
AD	Anaerobic Digestion
CAPEX	Capital Expenditures
CEPCI	Chemical Engineering Plant Cost Index
CF	Cash-flow
CHP	Combined Heat and Power
EU	European Union

GHG	Greenhouse Gases
GHSV	Gas Hourly Space Velocity
HHV	Higher Heating Value
LHHW	Langmuir-Hinshelwood-Hougen-Watson
LHV	Lower Heating Value
NG	Natural Gas
NPW	Net Present Worth
OPEX	Operational Expenditures
PE	Population Equivalents
PEMEL	Proton Exchange Membrane Electrolysis
PSA	Pressure Swing Adsorption
PtG	Power-to-Gas
PtM	Power-to-Methane
ROI	Return on Investment
RWGS	Reverse Water-Gas Shift
SOEL	Solid Oxide Electrolysis
USA	United States of America
WI	Wobbe Index
WWTP	Wastewater Treatment Plant

1 Introduction

1.1 Framing and presentation of the work

The increase in the Earth's average temperature, as a result of global warming, has been one of the most pressing issues of the last decades. That is precisely why the Paris Agreement came to be, in 2015, as an action plan conducted to limit the global warming. This Agreement, ratified by over 55 countries, including all of the European Union (EU), thus representing at least 55 % of the worldwide greenhouse gases (GHG) emissions, has a great objective that consists in limiting the global temperature to 1.5 °C above the pre-industrial temperature, when the GHG emissions were yet significant (Council of the EU, 2020b).

The EU is responsible for a great share of the global GHG emissions, with a share of 9.1 % in 2017, right behind China and the United States of America (USA), with 24.3 % and 13.4 %, respectively (Center for Climate and Energy Solutions, 2020). In 2008, the EU adopted a series of policies, fixed until 2020, related to the climate and energy. Among these, there was the reduction of 20 % GHG emissions, relatively to 1990, with a reduction of 23 % already achieved in 2018. The goal was then established to a 40 % reduction, relatively to 1990, until 2030 (Council of the EU, 2020a).

A great part of the reduction of GHG emissions is due to the reduction of the dependence on fossil fuels for global energy production, with a growing preference for renewable energy sources in order to promote environmental sustainability. It is due to the development of three main renewable energy sources, wind, solar and hydro, that the renewable energy shares have been increasing so much in the last decade.

In order to achieve the goal of carbon neutrality by 2050, it is necessary to not only reduce the GHG emissions, but also to promote the concept of circular economy, with a better resource management. It is precisely in this theme of increasing interest in renewables and circular economy that the use of biogas shows great interest. Produced as a final element in the process chain of biomass degradation, biogas presents itself as a renewable energy carrier and could thus help in the process of decarbonization of certain sectors.

Biogas is produced through the degradation of organic matter, performed by microorganisms, under anaerobic conditions, thus being considered a renewable fuel. Nowadays, biogas produced through anaerobic digestion (AD) of agricultural residues, municipal waste and wastewater has become one of the most attractive methods regarding renewable energy. In Europe, most biogas produced is used for combined heat and power (CHP), however,

over the past few years, biogas used for biomethane production for injection in the natural gas grid has been preferred over CHP (Scarlat et al., 2018).

The production of biomethane for injection in the gas grid started gaining special interest due to the evolution of the technologies and also due to the preference for more energy efficient methods. A stream of biomethane is produced through a separation process, that also produces a CO₂-rich stream that can be used to produce methane through a methanation reaction with hydrogen. This way, instead of just being emitted to the atmosphere after CHP, since it is not a combustible gas, CO₂ can be used for methane production. This process becomes very interesting when the production of hydrogen for the methanation reaction is performed using renewable energy in excess, the so-called Power-to-Methane (PtM) concept.

Electricity is considerably easy to produce and transform, however, one of the current issues regarding the implementation of renewables, is its storage. Renewables, like wind and solar, work in a discontinuous way but it is still necessary to guarantee that energy is available whenever it is needed, in spite of those discontinuities. The concept of Power-to-Gas (PtG) presents itself as an added value regarding this issue. This process, and particularly PtM, connects the electricity grid with the natural gas grid, producing hydrogen through water electrolysis, using excess renewable energy, followed by the CO₂ methanation process, thus producing methane (Götz et al., 2016).

This work aimed to perform a series of different simulations, considering different scenarios, in order to better understand the technical part of the process and to evaluate which technologies were better suited for the main goal of this work, which was to obtain biomethane to inject into the gas grid. All of this was done involving a techno-economic analysis of the whole process, analyzing costs, revenues in the different scenarios, in order to decide which one would bring the desired goal at a lower cost. This was done to determine the viability of the process described in this work for use in wastewater treatment plants (WWTP), since it is a process that is currently not used for this purpose, in Portugal.

1.2 Presentation of the company

SIMDOURO, S.A. - Saneamento do Grande Porto, S.A. is a society initially created in 2009 by the Decree-Law 312/2009, having initiated its activity in 2010. It is composed of Águas de Portugal, SGPS, that holds 51 % of the social capital, and the municipalities of Arouca, Baião, Castelo de Paiva, Cinfães, Paredes, Penafiel and Vila Nova de Gaia, that hold the remaining 49 %. In 2015, Águas do Norte, S.A. is formed following the aggregation of Águas do Douro e Paiva, S.A., Águas de Trás-os-Montes e Alto Douro, SIMDOURO, S.A. and da Águas do Noroeste, S.A. A year later, in 2016, the General Meeting of Águas do Norte, S.A. agreed to the creation of the multimunicipal sewage system of Porto with SIMDOURO, S.A. as the managing entity. That is

how, in 2017, SIMDOURO, S.A. came to be, an anonymous society of public capital responsible for the sewage system in the area of Grande Porto for 50 years, with the responsibility of collecting, treating and safely disposing of the municipal wastewater. It comprises an area of 1 300 km², providing service to around 519 000 people, and is composed of Grupo Águas de Portugal, SGPS, S.A., that holds 58.52 % of the social capital and the municipalities previously mentioned that hold the remaining 41.48 % (SIMDOURO, 2017b).

Since its creation until the end of 2019, SIMDOURO has invested around 155 M€ in new infrastructures and rehabilitation of the existing ones for improvement of the municipal sewage system. Currently, it has 22 working WWTP, and is planning on investing 9.7 M€ in the sewage system (SIMDOURO, 2017b).

This work focuses on the WWTP of Gaia Litoral, that started operating in 2003, built to serve a population of up to 300 000 population equivalents (PE) (SIMDOURO, 2017a).

1.3 Contribution of the author to the work

This work was conducted by the author in a simulation environment, in the program Aspen Plus.

The process studied in this work can be divided into three parts. The reaction section for which the author studied and researched the best suited kinetic model. The electrolysis section, for which the author was also responsible for researching and developing a simulation model that would provide the required needs for the process.

There was also the separation of the CO₂ from the biogas section, for which the author did not contribute. The membrane model used was provided and developed by the research group Laboratory LSRE-LCM, in Aspen Custom Modeler.

The author was also responsible for conducting the economic analysis performed in this study, for the three sections mentioned above.

1.4 Organization of the dissertation

This work is divided into 5 main sections.

In the first section, which is the State of the Art (Chapter 2), all the technologies involved are briefly explained, as well as important data and calculations for the work done.

After that, in the Aspen Plus process simulation section (Chapter 3), all the process scenarios studied in this work are presented along with a brief explanation of the flowsheet of each one.

Following that there is the Results and discussion (Chapter 4), in which all the process optimizations done are presented, along with the most important results for this work in terms of the methanation reaction.

Then there is the Economic Analysis (Chapter 5), in which the scenarios are compared in economic terms, to determine whether or not the best one in terms of performance is also the best one in economic terms.

Finally, after that, some conclusions about the study conducted in this work were withdrawn and some suggestions for future work were provided (Chapters 6-7).

2 Context and State of the art

2.1 Biogas

Biogas is the product of an anaerobic degradation of organic matter, such as animal manure, sewage sludge, food and agricultural waste and others, performed by microorganisms. This renewable fuel is mainly composed of methane (50-75 %) and carbon dioxide (25-50 %) and can sometimes contain smaller amounts of other gases like nitrogen, oxygen, carbon monoxide and hydrogen sulfide (Plugge, 2017).

Biogas is a very promising energy carrier since it can heavily contribute to the decrease of the use of fossil fuels for energy production and for vehicle fuels as well (Weiland, 2010). Biogas has a great potential, even though its average calorific value (21.5 MJ Nm^{-3}) (Hosseini et al., 2014) is below natural gas' and other fuels', as according to the values from Table 2.1. That is because, since biogas is about 98 % composed of a mixture of CO_2 and CH_4 , its characteristics, namely its calorific value, is dictated by these two gases. Since CO_2 is not a combustible gas, the lower heating value (LHV) of biogas should be in between 17.15 and 25.73 MJ Nm^{-3} for 50 % and 75 % of methane, respectively.

Table 2.1: Calorific value of fuels. Retrieved from Carvill (1993)

Fuel	Higher heating value (HHV)	Lower heating value (LHV)
Liquid (MJ kg^{-1} ; 15°C)		
Petrol (gasoline)	47.00	43.90
Kerosene	46.25	43.25
Diesel	46.00	43.25
Gas (MJ m^{-3} ; 15°C ; 1 atm)		
Natural Gas	36.20	32.60
Hydrogen	11.85	10.00
Carbon Monoxide	11.79	11.79

In WWTP, biogas is a by-product of the sludge treatment, that is produced from the wastewater treatment. This sludge treatment is necessary since most EU countries forbid the disposal of non-treated sludge in soils and, in certain countries, there are mandatory treatments like chemical and biological stabilization. Sludge stabilization is a very important procedure since it consists in the transformation of putrescible organic matter in more stable substances to avoid unpleasant odors and uncontrolled biogas emissions into the atmosphere (Canziani, 2021).

Anaerobic digestion is the most used stabilization process in the EU, with 24 out of the 27 countries using it. This process is further described in Appendix A. The criterion for the need to use a stabilization process in WWTP, namely AD, is the number of PE that the WWTP serves. This depends on the country's policies, some require AD for WWTP serving over 5 000 PE, like Czech Republic, others, like Italy and Austria only require it for PE over 50 000 (Kelessidis et al., 2012).

2.2 Biogas applications

2.2.1 Combined heat and power (CHP)

Currently, most of the biogas produced is used in CHP. This technology has been evolving in the last few years, along with its efficiency with the main focus in the electricity production since heat is usually produced in sufficient amounts. In terms of electric energy, a typical CHP unit has an electrical efficiency ranging from 25 to 45 % (Bachmann et al., 2015), depending on the power output.

There are five technologies currently used in CHP, reciprocating engines, gas turbines, microturbines, steam turbines and fuel cells, all but the latter classified as heat engines. While fuel cells convert the chemical energy in the fuel to electric energy electrochemically, heat engines use the heat produced from the combustion of the fuel to produce electricity, through an alternator, while the remaining heat is exhausted, available to other end uses (Darrow et al., 2017), for the case of gas engines.

The use of biogas for cogeneration of heat and electricity, in WWTP, ensures the facility with a certain autonomy. The electricity can be used for the aeration systems in the biological treatment of the wastewater, since this process is responsible for 67 % of the electrical consumption in WWTP (Au et al., 2013), while the heat is usually used to heat the sludge going into the digestors and ensuring its working temperature. Thermal autonomy is quite easily achieved, from 90 to 100 %, while electrical autonomy is usually harder to achieve, ranging from 37 % in WWTP with less than 10 000 PE to 68-100 % in WWTP with more than 100 000 PE (Bachmann et al., 2015).

One of the biggest advantages of the use of biogas for CHP, is the fact that there is no need to use a high-quality fuel, meaning the biogas produced in the AD can be used almost directly without the need of upgrading processes. There is, however, the need to remove certain biogas components like hydrogen sulfide (H_2S), and humidity, due to the corrosive effects they have on certain pieces of equipment. The limit values for these parameters depend on the type of equipment since some are more sensible than others. The limit values for the amount of H_2S , relative humidity and particulate matter for the CHP unit used in the WWTP of Gaia Litoral are reported in Table 2.2.

Table 2.2: Limit values for the parameters of gas quality for the CHP unit at the WWTP of Gaia Litoral. Retrieved from Silva (2021)

Parameter	Limit value
Hydrogen sulfide (H ₂ S)	1 500 ppm/10 kWh
Particulate matter	10 mg/10 kWh
Relative humidity	80 %

CHP engines can also work in “dual fuel” mode, meaning that when the biogas production is not enough to work continuously, some other fuel, usually natural gas, can be used to ensure the continuous functioning of the equipment.

2.2.2 Injection in the natural gas grid

Another option for biogas use is its injection in the national natural gas grid. There are, however, certain quality requirements that a gas must fulfill in order for it to be able to be injected into the gas grid, requirements which depend on the country. In fact, European countries’ regulations are quite heterogenous, as reported in Table 2.3. The parameters usually considered are the CO₂ and H₂ content, in %, the H₂S concentration and the Wobbe Index (WI). The WI is used to evaluate the interchangeability of various gaseous fuels, comparing the energy produced by their combustion, for a determined equipment. It is calculated as the quotient of the HHV of the fuel and the square root of the relative density of the gas, d , according to Eq. (2.1) (Bidlemaier et al., 2017).

$$WI = \frac{HHV}{\sqrt{d}} \quad (2.1)$$

Table 2.3: Limit values of gas properties for natural gas grid injection, in some European countries. Retrieved from Thema et al. (2019)

Country	% CO ₂	% H ₂	H ₂ S (mg Nm ⁻³)	WI (MJ Nm ⁻³)	
				Lower	Higher
Holland	-	12	5.0	41.23	42.13
Italy	3.0	0.5	6.6	47.31	52.33
Spain	2.5	5.0	15*	45.65	54.70
Denmark	3.0	-	5*	48.19	52.93
Latvia	-	-	20	39.06	51.67

*H₂S and COS

The parameters reported in this table are some of the most common but there are some more specific depending on each country’s regulations. All the specific regulations for natural gas grid injection in Portugal are in Table 2.4.

Table 2.4: Portugal's natural gas grid quality parameters. Retrieved from Entidade Reguladora dos Serviços Energéticos (2017)

Parameter		Minimum value	Maximum value
Wobbe Index	MJ Nm ⁻³	48.17	57.66
Relative density		0.5549	0.7001
Hydrogen sulfide	mg Nm ⁻³	-	5
Total sulfur	mg Nm ⁻³	-	50
Water dew point	°C	-	-5*

*at maximum operation pressure

Usually, biogas straight out of AD will not fit these standards and that is because these quality parameters are somewhat different than those for CHP, as seen before. While for CHP the restrictions are more related with corrosive components, for grid injection the restrictions have more to do with the energetic content of the gas. Even though there are no CO₂ limitations in Portugal, a high amount of CO₂ in the biogas will lower its calorific value so, in a way there is a certain limit of CO₂, as well as a minimum CH₄ content, even if it is implicit.

This is why biogas upgrading to biomethane is so important. Biogas upgrading consists in a separation process that allows to obtain a CH₄-rich stream, that can be referred to as biomethane, and a CO₂-rich current that can further be converted to methane through a methanation process, with hydrogen produced via electrolysis using renewable energy. This whole process is usually referred to as Power-to-Methane.

This is a process that has shown growing interest precisely for complying with the decarbonization goals, especially when the hydrogen used in the methanation process is obtained from renewable energy. This way, not only the CH₄ in biogas is used but the CO₂ as well, instead of just being emitted to the atmosphere like it happens in CHP applications, therefore losing a possible energy source. Biomethane can then be used, among other possible applications, for injection in the natural gas grid and, since this process is not yet used in WWTP in Portugal, it is of great interest to study its technical and economic viability.

2.3 Biogas upgrading

The production of a CH₄-rich stream, biomethane, from biogas is usually referred to as biomethanation, that consists in a separation process to separate the CH₄ from the CO₂.

There are several technologies able to perform this separation, meaning that the ideal one needs to be chosen according to the specific application depending on its advantages and disadvantages. These technologies are based on certain physical, chemical and thermodynamical properties of the different gaseous components. Some of these technologies

are reported in Fig. 2.1, where it is possible to see which of these were the most used in the 503 existing biogas upgrading plants, in Europe, in 2016. The number of biomethane producing plants has been increasing with 725 in Europe, in 2019 (Arnau et al., 2021).

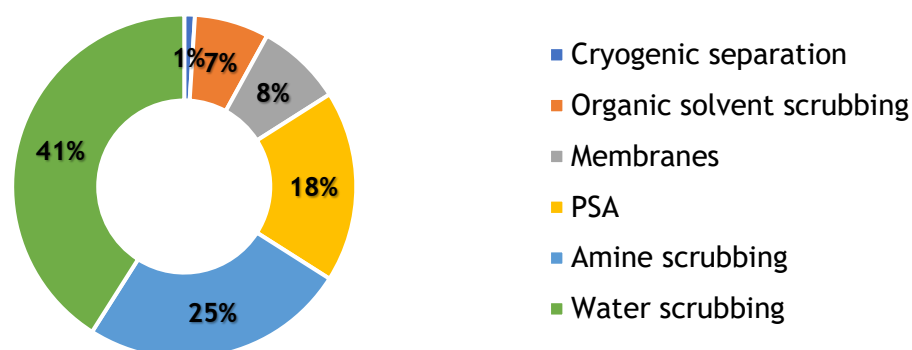


Figure 2.1: Share of biomethanation technologies used in European biogas upgrading plants, in 2016. Retrieved from Kapoor et al. (2019).

Out of all the technologies, the membrane separation was the one chosen for this work. That is because it can reach a high value of biomethane purity, with a small CH_4 loss. Besides that, it is also one of the cheapest technologies with a CAPEX of $0.22 \text{ € Nm}^{-3}_{\text{biogas}}$ and an OPEX of $25\,000 \text{ € year}^{-1}$, as reported in Table B.1, in Appendix B.

Membrane separation is based on the selective permeation of gaseous components through a membrane. In gas-gas systems, biogas is pressurized and is fed to the membrane unit where CH_4 is retained while CO_2 permeates through the membrane, with CO_2/CH_4 selectivity factors up to 1000/1 (Kapoor et al., 2019), due to the pressure gradient. Sometimes, due to the elevated pressure, CH_4 can also permeate the membrane, leading to a poor recovery of up to 92 % and so, in order to obtain higher purity biomethane, up to 99.5 %, two or more membrane modules are sometimes needed (Kapoor et al., 2019).

Recently, gas-liquid processes have been developed, with hydrophobic microporous membranes that divide the gas from the liquid flux, flowing in counter-current. CO_2 passes through the membrane and is absorbed by the liquid, therefore resulting in biomethane up to 96 % (Kapoor et al., 2019).

A simple counter-current membrane module, as the one used in this work, is described in Fig. 2.2. The gas mixture flows inside the membrane and most of the CO_2 in the initial gas mixture permeates through the membrane wall whilst only a small fraction of the CH_4 does, thus obtaining a permeate stream that is CO_2 -rich and a CH_4 -rich retentate stream. Further information about the model used in this work is reported in Appendix C.

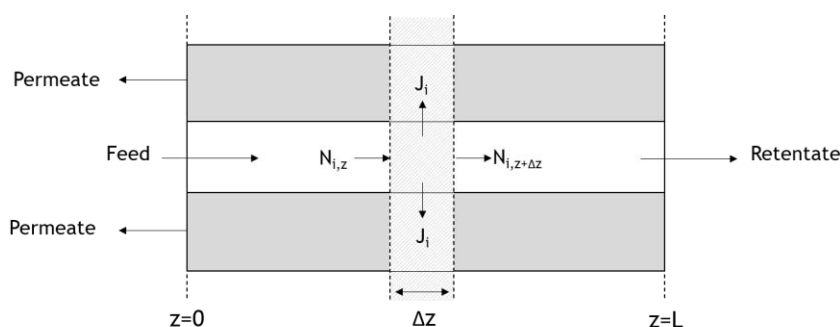


Figure 2.2: Counter-current membrane module scheme. Adapted from Witte et al. (2018b).

There are a lot of different types of materials that a membrane can be made out of but, nowadays, the most used ones for gas separation are organic polymers, such as polycarbonate, cellulose acetate, polyesters, polysulfide, polyimide, polyetherimide and polypyrrolones, with cellulose acetate, polysulfide and polyimide being the most used at an industrial level. The permeability and selectivity of each of these materials are reported in Table 2.5.

For CO_2 separation from CH_4 , polyimide membranes are the most suited ones. They have the highest CO_2 selectivity over CH_4 , and they have excellent thermal, chemical and mechanical properties, and that is why this was the material considered for the membrane module in this work.

Table 2.5: Permeability, in Barrer, and selectivity of some membrane materials. Retrieved from Chen et al. (2015)

Material	Permeability at 30 °C (Barrer)			Selectivity (-)	
	H_2	CH_4	CO_2	H_2/CO_2	CO_2/CH_4
Cellulose acetate	2.63	0.21	6.30	0.41	30.00
Polycarbonate	-	0.13	4.23	-	32.50
Polyimide	28.10	0.25	10.70	2.63	42.80
Polysulfide	14.00	0.25	5.60	2.50	22.40

2.4 Power-to-Gas (PtG)

The concept of PtG consists in the use of electricity obtained from renewables for the production of hydrogen, through the electrolysis of water. Hydrogen is considered an energy vector, storing large amounts of energy in the form of chemical energy. It can be stored for a variety of uses, or it can be used for the production of methane, like in Fig. 2.3, the so-called Power-to-Methane process. Hydrogen can also be directly injected into the natural gas grid, which can be seen as an advantage since its combustion does not produce any CO_2 , resulting in a reduction of the emissions related to this gas (Quarton et al., 2018). However, it is necessary

to consider that the amount of hydrogen allowed in the gas grid, for some countries, is very limited, as seen in Table 2.3.

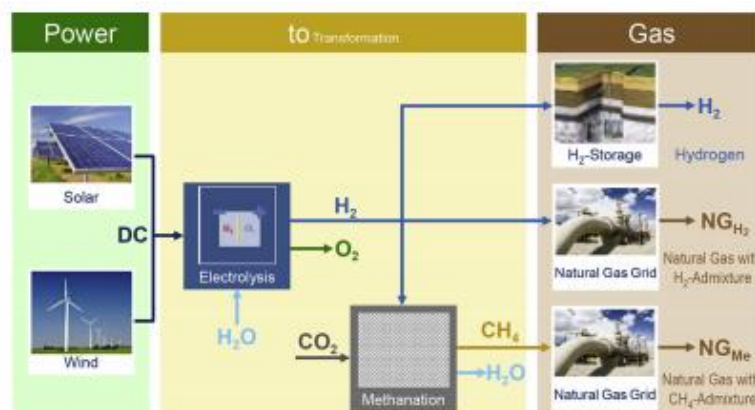


Figure 2.3: Principle of the Power-to-Gas concept. Retrieved from Schiebahn et al. (2015).

The present work focuses, however, in the use of hydrogen for the methanation of CO₂. Even though this is a very interesting and promising technology from the energetic and environmental point of view, it is necessary to evaluate its efficiency as well as economic feasibility with other technologies already used, in order to decide if it is worth it to implement it in WWTP in Portugal.

2.4.1 Water electrolysis

Water electrolysis is one of the main processes in PtG, that consists in the conversion of electricity into chemical energy, through the production of hydrogen via water electrolysis, according to Eq. (2.2).



The dissociation of water occurs in electrolyzers that combine two electrodes and an electrolyte. When a certain tension is applied to both electrodes, it is possible to split the water molecule into its components, hydrogen and oxygen, in the cathode and the anode, respectively.

For the specific use in PtG applications, it is convenient that the electrolyzer used has certain characteristics. The most important ones are high efficiency, so that the energy losses are as little as possible, adequate dynamic behavior, to correspond to the fluctuations in renewable energy, capacity to produce hydrogen at high pressures to reduce in the costs of compressors, and a long life time and reduced investment cost (Schiebahn et al., 2015).

There are three different types of electrolysis technologies, that differ on the type of electrolyte used, alkaline electrolysis (AEL), proton exchange membrane electrolysis (PEMEL) and solid oxide electrolysis (SOEL).

AEL was the technology chosen for this work since it is a more well studied and established technology than PEMEL and SOEL, with a CAPEX and OPEX that, in current years, is still lower, as seen in Table D.1, in Appendix D, even though the PEMEL technology costs have been lowering the past years.

This technology has been available in the market for a few decades with modules up to 2.5 MW_{el} and operating pressures up to 30 bar (Schiebahn et al., 2015).

In these electrolyzers, an alkaline solution (KOH or NaOH) is used as the electrolyte, conducting OH⁻ ions. The electrodes are made of perforated steel with nickel, cobalt or iron catalysts and they are separated by a diaphragm that acts as an insulator, separating the two gases.

Hydrogen is produced in the cathode, according to Eq. (2.3), and oxygen is produced in the anode, according to Eq. (2.4).

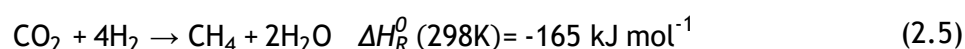


These electrolyzers usually operate at 80 °C (Schiebahn et al., 2015) and can either operate at atmospheric or high pressures, with the latter having the advantage of not needing further hydrogen compression (Götz et al., 2016). Depending on the capacity of the electrolyzer and the pressure of the produced hydrogen, the efficiency of these systems can range from 66 to 74 %, for 4.8 and 5.4 kWh_{el} Nm_{H₂}⁻³, respectively (de Bucy, 2016). They can operate in between 20 and 150 % of its design capacity, which is a great advantage since the system will be working with a fluctuating energy source (Götz et al., 2016). However, one disadvantage is the corrosivity of the alkaline solution used as electrolyte since it increases the OPEX.

The CAPEX of this equipment, including transport, installation and commissions, ranges from 1 000 to 2 000 EUR kWh_{el}⁻¹ (de Bucy, 2016). Currently, the main focus of manufacturers is the cost reduction, which is not so easy for such a studied and well implemented technology, but it is possible that the CAPEX will go down to 500-600 EUR kWh_{el}⁻¹ (Schiebahn et al., 2015).

2.4.2 Methanation

The methanation process consists in the hydrogenation of carbon dioxide to produce methane through the following Sabatier reaction (de Bucy, 2016).



Even though this is a thermodynamically favorable reaction ($\Delta G_{298\text{K}} = -130.8 \text{ kJ mol}^{-1}$) (Wei et al., 2011), it is an eight-electron process with kinetic limitations that therefore requires the use of a catalyst to obtain acceptable rates and selectivities.

There are two technologies available for this process, catalytic methanation, that will be the main focus of the present work, that uses metal catalysts like Ni and Ru, and biological methanation, that uses bio-catalysts.

Biological methanation is a process that produces methane from carbon dioxide, operating with methanogenic microorganisms as catalysts. It is a process similar to the AD process in the sense that it also occurs under anaerobic conditions, at atmospheric pressure or under pressure, and between 20 and 70 °C.

Instead, catalytic methanation uses metal catalysts to operate under high temperatures (200-650 °C) (Peters et al., 2019) and pressures between 1 and 100 bar (de Bucy, 2016). Several metals can be used as catalysts like Ru, Rh and Pd; however, Ni is often considered the optimum catalyst due to its relatively high activity, good CH₄ selectivity and affordable cost (Götz et al., 2016).

In order to talk about how the methanation reaction performs and the process itself, there are a few parameters that must be discussed. CO₂ conversion, X_{CO_2} , and CH₄ yield, Y_{CH_4} , are probably the most important ones but selectivity, S_i , is also an important parameter. These parameters are calculated according to Eqs. (2.6), (2.7) and (2.8), respectively (Garbarino et al., 2015):

$$X_{CO_2} = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \quad (2.6)$$

$$Y_i = \frac{F_i}{F_{CO_2,in}} \quad (2.7)$$

$$S_i = \frac{F_i}{F_{CO_2,in} - F_{CO_2,out}} \quad (2.8)$$

where $F_{CO_2,in}$ and $F_{CO_2,out}$ are the molar flow rates of CO₂ at the inlet and at the outlet, respectively and F_i is the molar flow rate of the component i that is produced.

Another parameter is the gas hourly space velocity, GHSV, that can be calculated in terms of ratio of gas inlet flow, in normal conditions, and reactor active volume, that is essentially the catalyst volume (Eq. (2.9)), or in terms of ratio of gas inlet flow, in normal conditions, and catalyst mass (Eq. (2.10)) (Thema et al., 2019).

$$GHSV [h^{-1}] = \frac{\dot{V}_{in}}{V_{cat}} \quad (2.9)$$

$$GHSV [Nm^3 h^{-1} g_{cat}^{-1}] = \frac{\dot{V}_{in}}{m_{cat}} \quad (2.10)$$

where $\dot{V}_{in}$ is the volumetric flow of the gas inlet and m_{cat} and V_{cat} are the mass and volume of the catalyst inside of the reactor, respectively.

Since the methanation reaction is highly exothermic, a good temperature control is the main concern when it comes to methanation reactors to prevent thermodynamic limitation or catalyst sintering (Gruber et al., 2021).

There are a few catalytic reactors that are currently used for the CO_2 methanation like fixed-bed reactors, adiabatic and cooled, structured reactors, micro and honeycomb reactors, fluidized bed reactors and three-phase reactors (Gruber et al., 2021), being that the last two are still considered to be in development stage (Sun et al., 2017).

Fluidized-bed reactors present almost ideal isothermal conditions, due to the mixing of fluidized solids, which makes it easy in terms of temperature control and allows for the use of a single reactor with a simplified design (Sun et al., 2017). However, one of the main drawbacks of this technology is the catalyst deactivation due to attrition and also the fact that bubbling can occur resulting in incomplete CO_2 conversion (Götz et al., 2016).

Fixed-bed reactors are the most commonly used ones for the methanation reaction and are therefore the ones that are going to be taken into consideration in this work.

For **adiabatic fixed-bed reactors** the usual approach is to use a series of reactors, usually 2 to 6, with intermediate cooling and gas recirculation (Sun et al., 2017), where the first reactor is usually at a higher temperature, and then the other ones at a lower temperature to ensure a better product formation, according to the thermodynamic equilibrium. Due to the adiabatic mode of operation, the used catalyst needs to be able to withstand temperatures that can go up to $700\text{ }^\circ\text{C}$, depending on the catalyst used (Götz et al., 2016). A very well-known process that uses this assembly of adiabatic reactors in series is the TREMP™ process, exemplified Fig. 2.4, developed by the Danish company Haldor Topsøe in the 1980s.

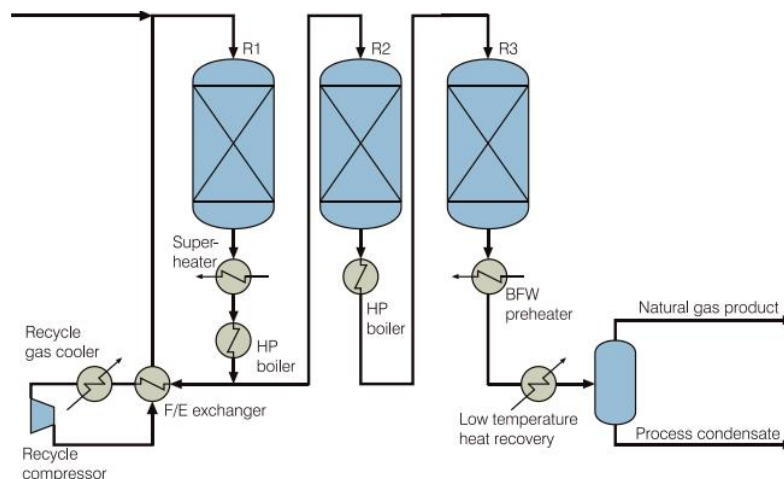


Figure 2.4: Example of the TREMP™ process. Retrieved from Haldor Topsøe (2009).

Cooled fixed-bed reactors can also be used and they offer the advantage of formation of different reaction zones, due to the temperature profile created along the reactor. Usually there is an accentuated increase in the temperature at the reactor inlet, which provides faster reaction rates, and then the temperature gradually decreases along the reactor, favoring the formation of products, according to the thermodynamic equilibrium, thus allowing high conversions to be attained (Gruber et al., 2021).

Evaporating water is often used as cooling fluid ((Giglio et al., 2018),(Salomone et al., 2019)) in these fixed-bed cooled reactors, since it ensures a high heat transfer coefficient in the shell side of the reactor. The overall heat transfer in the coefficient, U , can be determined through Eq. (2.11) (Giglio et al., 2018), in which the conductive term is neglected because its contribution to the overall resistance is almost insignificant due to the metallic surface in the reactor.

$$\frac{1}{U} \cong \frac{1}{\alpha_i} + \frac{1}{\alpha_{ext}} \frac{A_{in}}{A_{ext}} \quad (2.11)$$

In Eq. (2.11), α_i and α_{ext} are the heat transfer coefficients on the internal and external sides of the tubes, respectively, and A_i and A_{ext} are the internal and external heat transfer surfaces.

For the external heat transfer coefficient, α_{ext} , in the case of evaporating water, a constant value of $10 \text{ kW m}^{-2} \text{ K}^{-1}$ (Giglio et al., 2018) can be considered since this is a typical value reported in the literature. The internal heat transfer coefficient, α_i , can be determined through Eq. (2.12), for fixed catalytic beds (Giglio et al., 2018):

$$\frac{\alpha_i D_t}{\lambda_{gas}} = 3.5 \left(\frac{D_p G}{\mu} \right)^{0.7} \exp \left[\frac{-4.6 D_p}{D_R} \right] \quad (2.12)$$

where D_t and D_p are the reactor's tubes and catalyst particle diameters, in m, respectively, G is the mass flux in each tube, in kg m^{-3} , λ_{gas} is the gas thermal conductivity, in $\text{W m}^{-1} \text{ K}^{-1}$, and μ is the dynamic viscosity of the gas, in Pa s.

2.5 Economic analysis

Implementing a new process in an existing plant requires an analysis of the costs associated, in order to select the best alternative available in terms of process equipment and operational conditions. The main objective of an economic analysis is to analyze the profitability of all the scenarios available in order to know the best one in terms of technical and economic advantages, before making any type of investment.

2.5.1 Total capital investment

The total capital investment, which can be seen as the amount of capital needed to start construction and operation of the plant, is determined based on the purchased equipment cost, C_p , and it is usually multiplied by a factor of 1.2 to 1.3, that corresponds to installation fees and a factor of 1.1 to 1.2 that accounts for construction, according to SIMDOURO. Average values of these factors were selected for this work. The TCI is estimated as in Eq. (2.13) (Seider et al., 1999).

$$TCI = 1.25 \cdot 1.15 \sum_i \left(\frac{CEPCI_i}{CEPCI_{base}} \right) C_{p_i} \quad (2.13)$$

The sum of all equipments purchase cost, C_p , is considered, which is multiplied by the ratio between the current and the base Chemical Engineering Plant Cost Index (CEPCI), to account for cost inflation over the years. The $CEPCI_{base}$ value is 500, which is the value for the year 2006, since that is the base year for the purchase cost estimation correlations used in this work and the current CEPCI value is 607.5 (Jenkins, 2020), which is the value for 2019. A more recent CEPCI was not used due to recent fluctuations in this value that could cause incorrect estimations.

The correlations used to determine the purchase cost of each equipment are further described in detail in Appendix G.

Based on the TCI, the capital expenditures, CAPEX, which are basically an annualization of the TCI, can be determined on a yearly basis, in € y^{-1} , as in Eq. (2.14) (Witte et al., 2018a),

$$C_{CAPEX} = C_{TCI} \frac{(1+i)^a i}{(1+i)^a - 1} \quad (2.14)$$

where a is the operational lifetime, in years, and i is the interest rate.

2.5.2 Operating costs

Besides the capital costs, the operational costs must be considered as well. These can be divided into fixed and variable operating costs.

The fixed operational costs are the ones that include equipment maintenance, labour and taxation, while the variable costs are the ones that account for raw materials and utilities costs (Vo et al., 2018).

In terms of fixed operational costs, the main expenses to consider are operating labour, meaning the manpower needed to operate and run the plant, maintenance and repairs, operating supplies, such as safety equipment, cleaning supplies, among others. There are other expenses that can be considered as well such as laboratory and supervisory charges, taxation and insurance but those are not so relevant for this work since this is not a new plant that is being implemented and so most of those charges are already considered in the running WWTP.

These costs are usually estimated as a percentage of capital investment costs, as can be seen in Table 2.6.

Table 2.6: Fixed operating costs estimation. Retrieved from SIMDOURO and Seider et al. (1999)

Operating labour	1 labour shift ⁻¹
	1 shift day ⁻¹
	25 000 € labour ⁻¹ year ⁻¹
Maintenance and repairs	3 % of fixed capital investment
Operating supplies	15 % of maintenance and repairs

The variable operating costs are, as described before, the utilities and raw materials used for the process, which will include the water needed for the electrolysis, the electricity needed to run the plant and all the other utilities needed for heating and cooling.

The operational expenditures, OPEX, in € y⁻¹, are then calculated as in Eq. (2.15).

$$C_{OPEX} = C_{O\&M} + C_{utilities} + C_{raw\ materials} \quad (2.15)$$

2.5.3 Delta-costs method

The delta-costs method allows for comparison of differences in costs for different operating conditions, such as pressure or temperature. With this method, these operating conditions are evaluated regarding their economic outcome. For this, a base case is used, C_{base} , for which the capital and operational expenditures are calculated. In terms of operational expenditures, only the ones that are varying with the variable that is being optimized are to be considered, like yearly electricity consumption, catalyst costs, and more.

The costs difference, dC , is calculated as follows,

$$dC = \left(\frac{C}{C_{base}} - 1 \right) \cdot 100\% \quad (2.16)$$

where C is the cost of the case at the operating condition being considered.

2.5.4 Absolute economic analysis and project evaluation

In order to evaluate the viability of certain projects, when compared to others, there have to be some financial and economic criteria to serve as a basis.

Cash-flows (CF) are a very important financial factor that needs to be considered when performing an economic analysis, since it represents the net passage of money in or out of a company related to a certain investment. The net CF can be calculated as the after-tax net

earnings, as in Eq. (2.17), where the costs represent the product cost, meaning the yearly expenses, C_{OPEX} , and t represents the income tax rate (Seider et al., 1999).

$$CF_a = (1 - t)(Sales - Costs) \quad (2.17)$$

The net CF is considered to be the net future worth, NFW, at each year since it is calculated for each year specifically. On the other hand, since money earned at the beginning of the project is more valuable than the money earned later on, since it can be reinvested, the net present worth (NPW) of the CF in each year should be brought to its present worth, at the start of the project, which can be done by discounting it at a certain discount rate, as in Eq. (2.18) (Sinnott, 1983).

$$NPW \text{ of } CF \text{ in year } a = \sum_a \frac{CF_a}{(1+i)^a} \quad (2.18)$$

There are other important methods to evaluate the profitability of a project that do not account for the time value of money such as the return on investment (ROI), which, in a simple way, is defined as calculated as the profit over the total investment, and it is calculated as in Eq. (2.19)(Glandt et al., 2003). The payback time is another important method, which accounts for the amount of time needed for the CF to equalize the initial investment, meaning the TCI, and it can be calculated by Eq. (2.20)(Glandt et al., 2003).

$$ROI = \frac{CF_a}{TCI} \quad (2.19)$$

$$\text{Payback time} = \frac{TCI}{CF_{a, \text{average}}} \quad (2.20)$$

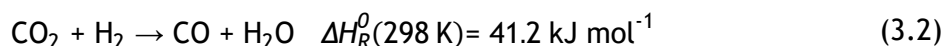
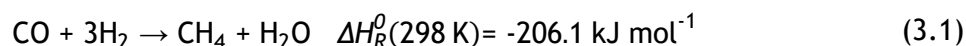
3 Aspen Plus process simulation

The techno-economic analysis was performed using the Aspen Plus® software. The simulation was performed using the Redlich-Kwong-Soave equation of state with modified Huron-Vidal mixing rules, RKSMHV2, model, which can be used for mixtures of polar and non-polar compounds, with light gases (Er-rbib et al., 2013). The simulation was divided into three sections according to the processes previously mentioned in this work, the separation of the CO₂ and the CH₄ in the biogas, the CO₂ methanation and the electrolysis.

3.1 Reaction kinetics

First, the reaction kinetics had to be validated and for that the CO₂ methanation reaction was simulated in a *RPlug* reactor in similar conditions to those reported on previously executed experiments.

The previously mentioned Sabatier reaction (Eq. (2.5)), is usually accompanied by the exothermic CO methanation reaction (Eq. (3.1)) and by the slightly endothermic reverse water-gas shift (RWGS) reaction (Eq. (3.2)) (Sun et al., 2017).



The most common kinetics used for the CO₂ methanation is the approach proposed by Xu et al. (1989), over Ni-based catalysts; however, this model is not well suited for temperatures below 500 °C. More recently, adjustments have been made and the kinetic model proposed by Zhang et al. (2013), with adjustments by Rönsch et al. (2016) for a commercial 50 % wt. Ni/Al₂O₃ catalyst, is well accepted and is well adjusted to experimental results of CO₂ methanation on Ni-based catalysts. This model is represented by the Langmuir-Hinshelwood-Hougen-Watson, LHHW, approach, whose kinetic expressions are provided in Eqs. (3.3) and (3.4), which represent the reaction rates of Eqs. (3.1) and (3.2), respectively (Neubert et al., 2017)).

$$r_{\text{CO methanation}} = \frac{k_1 K_C K_H^2 \left(p_{\text{CO}}^{0.5} p_{\text{H}_2} - \frac{p_{\text{CH}_4} p_{\text{H}_2\text{O}} p_{\text{CO}}^{-0.5} p_{\text{H}_2}^{-2}}{K_{\text{Meth}}} \right)}{\left(1 + K_C p_{\text{CO}}^{0.5} + K_H p_{\text{H}_2}^{0.5} \right)^3} \quad (3.3)$$

$$r_{\text{RWGS}} = \frac{\frac{k_2}{p_{\text{H}_2}} \left(\frac{p_{\text{H}_2} p_{\text{CO}_2}}{K_{\text{WGS}}} - p_{\text{CO}} p_{\text{H}_2\text{O}} \right)}{\left(1 + K_{\text{CO}} p_{\text{CO}} + K_{\text{H}_2} p_{\text{H}_2} + K_{\text{CH}_4} p_{\text{CH}_4} + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}} p_{\text{H}_2}^{-1} \right)^2} \quad (3.4)$$

The kinetic constants, k_i , the equilibrium constants, K_{Meth} and K_{WGS} , and the adsorption constants, K_i , used in Eqs. (3.3) and (3.4), are reported in Appendix E. Since in *Aspen Plus* the adsorption constant values must be inserted according to Eq. (3.5) those parameters are included as well.

$$\ln(K_n) = A_n + \frac{B_n}{T} + C_n \ln(T) + D_n T \quad (3.5)$$

These kinetic equations were inserted in *Aspen Plus* and were validated using the experimental data of Garbarino et al. (2015). The validation results are provided in Appendix F. The results show that the kinetic model chosen for this work represents quite well the experimental results. Only a small deviation was observed between the *Aspen Plus* and the experimental results, at a temperature of about 400 °C, that probably results from the difference in the catalyst used, since the catalyst being used in this work is 50 % Ni/Al₂O₃ and the one used for the experimental results is 20 % Ni/Al₂O₃.

It is also really important for this work to better understand how the equilibrium conversion for this reaction is affected by the reaction conditions. In order to do so, the CO₂ conversion was obtained for different temperatures and pressures, with a gas inlet mixture with a H₂/CO₂ molar ratio of 4, with no inert gases, in a *RGibbs* reactor in *Aspen Plus*. The results are shown in Fig. 3.1.

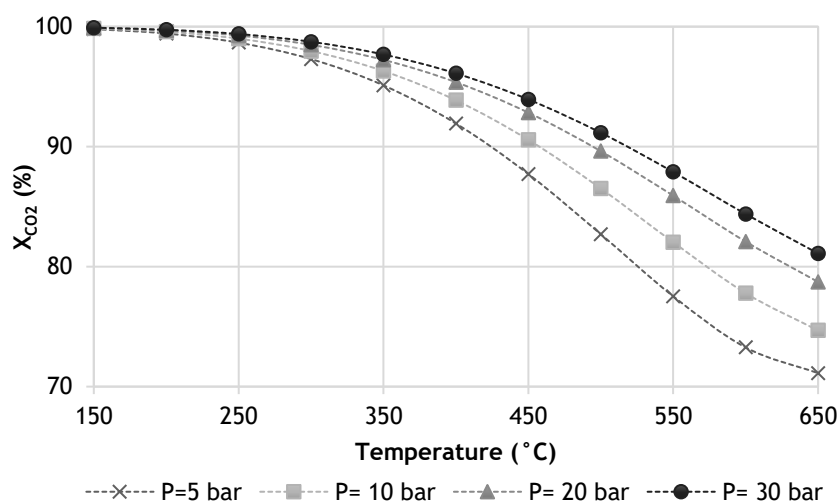


Figure 3.1: Equilibrium CO₂ conversions as a function of temperature, in °C, obtained in a *RGibbs* reactor in *Aspen Plus* for the operating pressures of 5, 10, 20 and 30 bar, with an inlet H₂/CO₂ molar ratio of 4, with no inert gases.

By analyzing the results in Fig. 3.1, the first thing that can be seen is that the conversion decreases as the operating temperature increases; this is a consequence of the CO₂ methanation being an exothermic reaction, which causes an increase in temperature leading to a shift of the equilibrium towards the reagents, which results in a subsequent reduction in CO₂ conversion. Regarding the pressure, it is noticeable that, for the same temperature, an increase in pressure

results in a higher CO₂ conversion. That is because, according to Le Chatelier's principle, as the amount of moles in the reagents side of Eq. (2.5) is higher, the equilibrium will shift in order to promote the formation of products in order to try to counteract the increase of partial pressure of the components.

3.2 Flowsheeting scenarios

In terms of process flowsheeting and equipment selection in general, there were a few options studied, more specifically in the separation and methanation sections. In terms of the methanation section, as was previously mentioned, it was important to determine which of the reactor technologies was the most suitable for this process, between the fixed-bed adiabatic and cooled reactors. According to Jürgensen et al. (2015), at pressures above 8 bar, the presence of methane in the reactor feed has a very small influence on the conversion of CO₂, therefore the possibility of not using any separation technology was studied as well.

The biogas composition obtained at SIMDOURO is reported in Table 3.1. There is about 200 ppm of H₂S in the biogas produced in the digestors but, since there is the need of biogas purification in terms of this component both for the membrane module and the reactor, it is considered in this work that the H₂S content is already low enough to be implemented in the process. Since the maximum H₂S content supported by the nickel catalyst in the methanation reactors is about 1 ppm (Götz et al., 2016), due to possible catalyst poisoning, that is the value considered for the purified biogas stream.

Table 3.1: SIMDOURO's biogas composition. Retrieved from Silva (2021)

Component	Molar composition	
	Without H ₂ S purification	With H ₂ S purification
N ₂	1.1 %	1.11 %
CO ₂	36.5 %	36.5 %
H ₂	<0.1 %	0.06 %
CH ₄	61.8 %	61.8 %
O ₂	0.5 %	0.51 %
CO	<0.1 ppm	>83 ppm
H ₂ S	>500 ppm	<1 ppm

The membrane model used in this work is an in-house model developed by the research group Laboratory LSRE-LCM, in the Aspen Custom Modeler program. The isothermal membrane model operates in countercurrent and does not consider any pressure drops, meaning that the pressure in the retentate and permeate side are constant throughout the membrane length. For the permeate side there was no sweeping gas or vacuum considered, the pressure was set

at 1 bar; as for the pressure on the retentate side, it was considered to be 30 bar, that was the pressure set to prevent obtaining very long membranes (pressure set for lengths between 1 and 2 m). Some of the membrane properties and the permeability of the components for a polyimide membrane are reported in Table 3.2. Since the permeability values for CO, H₂O and H₂S were not available, those values had to be estimated. For CO it was estimated the same as CO₂ and for H₂O and H₂S, since their presence in the biogas is almost negligible, they were neglected regarding the membrane.

Table 3.2: Membrane properties and permeabilities of the components, in Barrer.

Permeability values retrieved from Falbo et al. (2014)

Membrane thickness		m	1·10 ⁻⁶		
Number of tubes			10 000		
Tube diameter		m	0.01		
Permeate pressure		bar	1		
Retentate pressure		bar	30		
Permeability (Barrer)					
CO ₂	CH ₄	N ₂	H ₂	O ₂	CO
20.60	0.6269	0.6567	44.50	2.896	20.60

For the electrolyzer section, the conditions of the hydrogen obtained were assumed to be the ones of the electrolyzer A300 from the company Nel Hydrogen, chosen according to the H₂ flow rate needed, that is about 290 Nm³ h⁻¹, which corresponds to a H₂/CO₂ ratio of 4. The characteristics are given in Table 3.3.

Table 3.3: Characteristics of the electrolyzer used. Retrieved from Nel Hydrogen (2019)

Type of electrolysis	Alkaline	
H ₂ flow rate	Nm ³ h ⁻¹	150-300
Flow range	%	15-100
Energy consumption	kWh Nm ⁻³	3.8-4.4
Delivery pressure	barg	1-200
Ambient temperature	°C	5-35
Water feed	L _{H₂O} Nm _{H₂} ⁻³	0.9

The electrolyzer outlet temperature was assumed to be 35 °C and the pressure was assumed to be the maximum allowed by the electrolyzer being considered, 200 barg, for storage purposes, since a hydrogen tank is advised, for cases of electrolyzer malfunction or maintenance, or even in cases in which renewable energy sources are being used and the hydrogen production is not continuous, so that the methanation section can still operate

continuously. The hydrogen tank is considered to assure a 24 h supply of hydrogen to the methanation reactor.

3.2.1 Cooled fixed-bed reactors without membrane separation

In this scenario, the biogas stream coming from the digestors, at about 40 °C and 1 bar, is compressed in a multistage compressor, with intermediate cooling, exiting at 50 °C and 15 bar, which is the optimized process operating pressure, as will be discussed later on. That stream is then mixed with the hydrogen coming from the electrolyzer, in stoichiometric conditions, i.e., in a H_2/CO_2 molar ratio of 4. That stream is then heated to 350 °C, by exchanging heat with the stream that exits the reactor at a higher temperature. This is considered to be the minimum inlet temperature required to obtain a satisfactory CO_2 conversion inside the reactor.

After that, the gas mixture enters the reaction section which consists of a tubular reactor, working in a similar way to a heat exchanger. The process gas flows inside the tubes, where the reaction takes place, while the cooling fluid, the evaporating water, flows through the shell, allowing for heat removal. This provides certain advantages when comparing with the adiabatic reactors, due to the different reaction zones that are created by the temperature gradient along the reactor. This cooling fluid also allows for a better control of the maximum temperature allowed inside the reactor, that is about 650 °C (Peters et al., 2019), to prevent catalyst deactivation. The evaporating water is then run through a turbine, in order to produce electricity.

After the methanation section and going through a heat exchanger to heat the reactor inlet stream, the gas mixture is further cooled to 50 °C, in order to condensate the water vapor, which is then removed in a flash drum. That water is recycled to the electrolyzer, since it does not contain any salts or other components that may cause any electrolyzer malfunction (Jürgensen et al., 2015).

The flowsheet of this scenario is represented in Fig. 3.2.

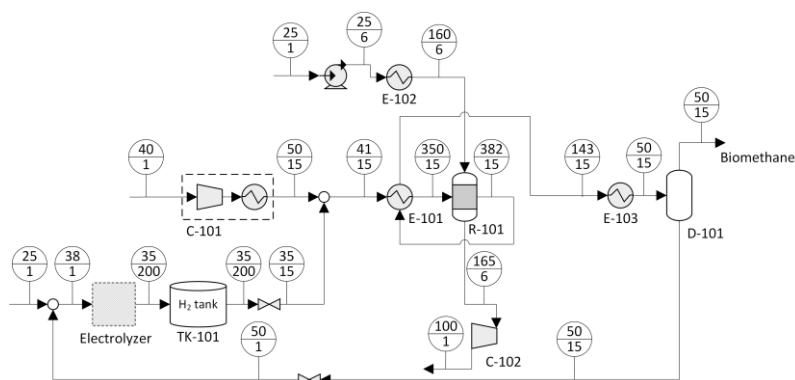


Figure 3.2: Flowsheet of the cooled fixed-bed reactors without membrane separation scenario.

4 Results and discussion

4.1 Cooled fixed-bed reactor without membrane separation

As said before, the maximum temperature allowed inside the reactor is 650 °C and some of the reactor characteristics had to be defined in order to obtain the best results in terms of CO₂ conversion without surpassing this temperature value.

The tube diameter was fixed at 50 mm, which corresponds to the minimum tube diameter over catalyst particle diameter ratio of 10, in order to avoid channeling in the catalytic bed, which is a phenomenon that causes an uneven catalytic packing (Giglio et al., 2018). The number of tubes and the coolant temperature, which affects both the reactor temperature and, therefore, the CO₂ conversion, were chosen in order to minimize the catalyst loading. The reactor length was chosen to be the minimum one in order to reach the thermodynamic equilibrium, since the reactor void fraction is fixed at 0.33 and the catalyst loading only changes with the reactor length, whilst having a L/D ratio in between 2 and 5. The pressure drop inside the reactor was neglected.

In Table 4.1, there are a few values obtained for 3 different number of tubes, 10, 20 and 30. It can be seen that for a higher number of tubes, the CO₂ conversion is slightly higher. This is because the catalyst loading increases with the number of tubes, and the gas flow per tube decreases, which subsequently decreases the GHSV and increases the CO₂ conversion. On one hand, the heat formation in each tube is lower as the number of tubes increases, due to the lower gas flow; on the other hand, the fact that the conversion increases with a higher number of tubes, also increases the amount of heat released, per mole of CO₂ reacted. The latter probably outweighs the first one, seeing as the maximum temperature attained inside the reactor is higher when a higher number of tubes is used.

Since the conversion was only slightly lower for a lower number of tubes (10), and that was the option that allowed for L/D ratio between 2 and 5, that was the number of tubes chosen.

Table 4.1: Values of catalyst mass, CO₂ conversion and maximum temperature in the reactor for 30, 20 and 10 tubes, at 5 bar

N° tubes		30	20	10
Tube diameter	mm	50	50	50
T _{coolant}	°C	160	160	160
Catalyst loading	kg	37.37	26.99	14.53
Maximum temperature	°C	603.76	603.49	601.42
X _{CO₂}	%	91.19	91.00	89.96

In terms of coolant temperature, the lower the temperature, the higher the driving force of the heat transfer between the process and the cooling fluid will be, thus decreasing the maximum temperature attained inside the reactor, as can be seen in Table 4.2. One thing to look out for is that if the cooling temperature is too low, it can cause reactor light-off (Giglio et al., 2018), meaning that the catalytic reaction may not initiate, thus resulting in low conversions. Since that did not happen with any of the cooling fluid temperatures chosen, the one that provided the smallest maximum temperature inside the reactor was chosen, which is 160 °C (only shown in Table 4.1). This results both in a smaller amount of cooling fluid needed, as well as a smaller amount of steam needed to heat it to the desired temperature, thus avoiding unnecessary costs.

Table 4.2: Maximum temperature and CO₂ conversion obtained in the reactor with 10 tubes, operating at 5 bar, with different cooling fluid temperatures

N° tubes		10			
Tube diameter	mm	50			
T _{coolant}	°C	180	190	200	210
P _{coolant}	bar	10.35	13.01	16.18	19.92
Catalyst mass	kg	18.89	20.34	21.80	23.87
Maximum temperature	°C	601.96	602.21	602.46	602.70
X _{CO₂}	%	90.20	90.33	90.47	90.63

As previously mentioned, the process operating pressure is a parameter that had to be optimized, not only in terms of obtaining the required NG grid requirements but also in terms of choosing the pressure that requires lower costs. That was done applying the delta-costs method, previously mentioned in the State-of-the-Art chapter.

The operating expenditures that were considered to change with the pressure are the electricity consumed, the amount of catalyst used and other utilities like the boiler-feed water that is used for the reactor cooling. The base case was considered to be 8 bar. The costs obtained for the equipment and utilities, whose costs are changing with the pressure, are portrayed in Fig. 4.1. The dC method results, CF and WI values are reported in Table 4.3. The costs values used in Fig. 4.1 are further reported in detail in Table H.1, in Appendix H.

As can be seen in Fig. 4.1, both the equipment (Fig. 4.1 a)) and the utilities (Fig. 4.1 b)) cost tend to increase with the increasing process pressure, that is due to the additional compression costs required, in terms of the compressor cost and in terms of electricity used, respectively.

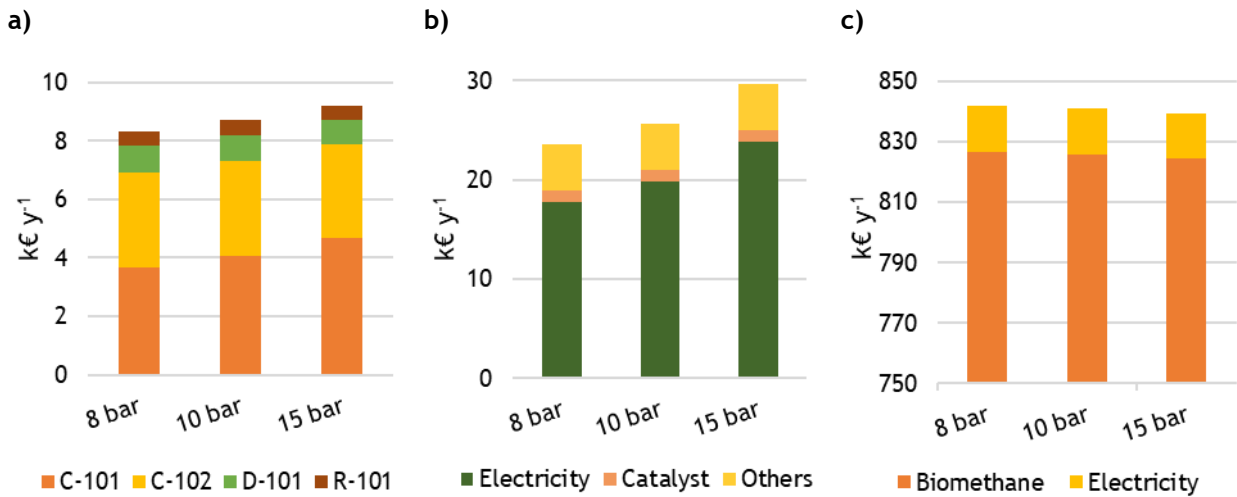


Figure 4.1: Costs for: a) equipment annualized, b) utilities and c) revenues, in k€ y^{-1} , for pressures of 8, 10 and 15 bar.

Table 4.3: CF, dC and Wobbe Index values for pressures of 8, 10 and 15 bar

Pressure	bar	8	10	15
Total CF	k€ y^{-1}	809.7	806.4	800.2
dC	%	-	-0.41	-1.17
Wobbe Index	MJ Nm^{-3}	47.27	47.64	48.19

However, there is a slight decrease in the reactor cost and the catalyst as well, as can be seen in Table H.1, in Appendix H. This decrease in catalyst and reactor costs is not enough to surpass the increasing compression costs. Moreover, as pressure increases, the biomethane and electricity revenues from the turbine decrease because the molar flow of biomethane, and the water needed for reactor cooling, decrease as well. The biomethane flow decreases because with higher operating pressures, the water separation in the flash drum is more efficient as well as a higher amount of water is produced, according to the reaction stoichiometry (Eq. (2.5)) and thus a higher amount of water is removed from the gas stream. This amount of water removed is higher than the increase in CH_4 production when the pressure is increased, which causes an overall lower biomethane flow rate, evidenced by an increase of the WI by 0.78 and 1.95 %, for pressures of 10 and 15 bar, respectively. The amount of water needed for reactor cooling is smaller because the evaporating water is considered to exit the reactor as superheated steam, at 165 °C, and, as the pressure in the reactor increases, so does the temperature, which increases heat transfer and reduces the amount of evaporating water needed.

In terms of gas grid quality parameters, the minimum pressure that provides biomethane with a high enough value of WI (in between 48.17 and 57.66 MJ Nm^{-3}) is 15 bar and, since increasing the pressure, even though it increases the conversion of CO_2 , increases the costs and

decreases the CF, the best option is to operate at the minimum pressure possible to obtain good quality biomethane, that is 15 bar.

The reactor dimensions had to be slightly altered, reducing the reactor length from 0.730 to 0.605 m and thus the catalyst loading from 15.15 to 12.56 kg, in order to increase the temperature at the exit of the reactor from 310 to 382 °C. On the one hand, this slightly decreases the conversion from 92.4 to 91.1 %, but it also allows for heat integration with the stream entering the reactor, discarding the need to use any other utility to heat that stream.

The final reactor properties are reported in Table 4.4.

Table 4.4: Reactor R-101 properties, temperature at the inlet, maximum temperature attained and CO₂ conversion, for an operating pressure of 15 bar

N° tubes		10
Tube diameter	m	0.05
Tube length	m	0.605
Catalyst mass	kg	12.56
Inlet temperature	°C	350
Exit temperature	°C	382
Maximum temperature	°C	647
X_{CO_2}	%	91.83

4.2 Cooled fixed-bed reactors with membrane separation

When it comes to the cooled reactors with previous membrane separation, whose flowsheet is represented in Fig. 3.3, since a split fraction of the CO₂-rich stream is advised, as previously reported, in order to not obtain too high temperatures inside the reactor, that split factor was chosen so that both reactor temperatures would be below 650 °C, which was 0.25 for the first reactor and 0.75 for the second reactor.

In this case, the temperature at the entrance of the reactors had to be lower than the temperature selected for the scenario without the membrane separation, since with an inlet temperature of 350 °C, the maximum temperature would exceed 650 °C. In this case, the temperature had to be lowered, whilst still allowing acceptable reaction rates. A temperature of 330 °C was fixed, as explained below. In this case, and to have a better comparison with the scenario without the membrane separation, the membrane length was chosen in order to obtain a CH₄ content in the biomethane to be injected into the grid similar to the scenario with no membrane separation. Pressure drop inside the reactors was neglected and the reactor length was adjusted so that the temperature at the exit of the reactors could allow for heat integration with the inlet streams. The results obtained for both reactors are reported in Table 4.5.

Table 4.5: Reactor properties, temperature at inlet and maximum temperature inside the reactor and CO₂ conversion for reactors R-201 and R-202

		R-201	R-202
N° tubes		10	10
Tube diameter	m	0.05	0.05
Tube length	m	0.25	0.45
Catalyst mass	kg	5.19	9.34
Inlet temperature	°C	330	330
Exit temperature	°C	351	391
Maximum temperature	°C	642.3	640.6
Per pass X_{CO_2}	%	98.78	91.47
Overall X_{CO_2}	%	93.69	

The fact that the temperatures had to be lowered can be explained by the use of the membrane. That is because when the membrane is added, there is almost no CH₄ going into the reactor (thus a more concentrated CO₂ stream is fed) which, in comparison, results in higher conversions and higher temperatures. In this case, even when the temperature at the inlet is 330 °C, the maximum temperature inside the reactor almost goes above the allowed value, so that temperature at the inlet should be seen as the highest value possible. In terms of conversion inside the reactors, this scenario had an overall higher conversion in both reactors, probably because of the high feed CO₂ concentrations and maximum temperatures achieved.

The desired biomethane purity coming from the membrane was obtained by varying the membrane length, which in this case was 1.2 m, thus obtaining biomethane with a CH₄ molar fraction of 0.978, which, when mixed with the biomethane coming from the reaction section (with 0.817 fraction in CH₄), resulted in a final biomethane stream with a CH₄ molar fraction 0.891.

4.3 Adiabatic fixed-bed reactors without membrane separation

In terms of the adiabatic reactors, there were a few more parameters that had to be optimized. Those parameters were the temperature at the entrance of the reactors, the split factor of the stream that exits the first reactor and the operating pressure. Even though the temperature at the entrance of the reactors was an optimized parameter, it was fixed that the temperature at the entrance of the second reactor was always 100 °C smaller. This is because, in the case of adiabatic reactors, since there is not formation of different reaction zones, the second reactor needs to be at a lower temperature so that the CO₂ conversion is higher, according to the equilibrium. Pressure drop inside the reactors was neglected.

Considering first the split factor of the outlet stream of R-301, in the flowsheet in Fig. 3.4, that is recycled back to the inlet, what can be seen in Table 4.6 is that at the operating conditions being considered, which are operating pressure of 10 bar and temperatures of the gas streams of 350 and 250 °C at the entrance of R-301 and R-302, respectively, only a higher split factor allowed to obtain a WI value high enough in terms of NG grid requirements (48.17-57.66 MJ Nm⁻³). One thing that is also noticeable is the fact that that same option is very uneconomic, seeing that it has a difference in costs of -10.7 %, when compared to a split factor of 0.3. That can be explained by looking at the way the reactors and catalyst costs increase with an increasing split factor, in Fig. 4.2 a). The costs values used in this figure, are reported in detail in Table H.2, in Appendix H.

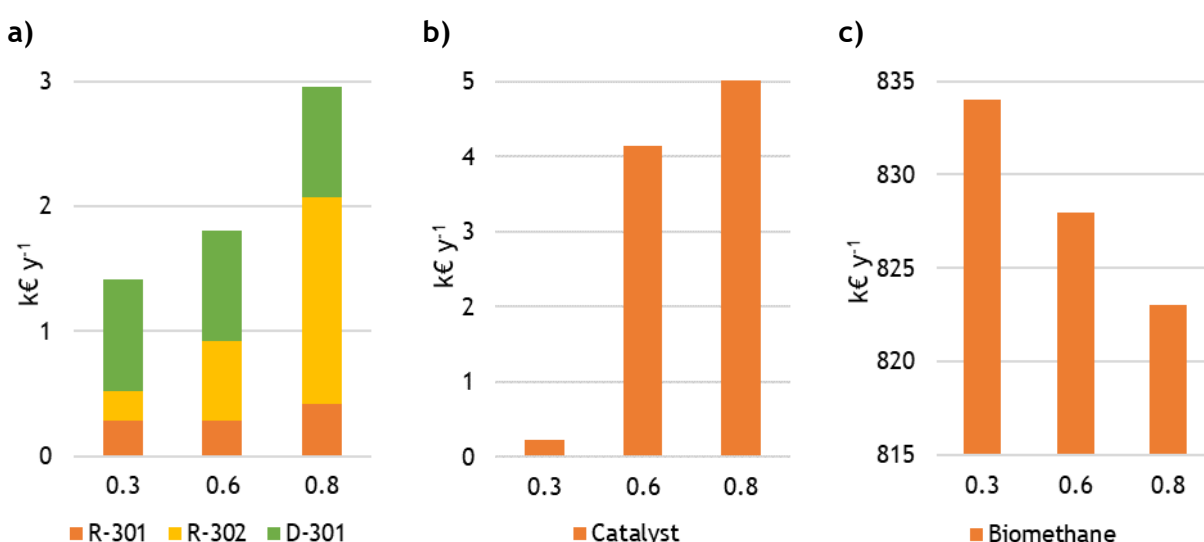


Figure 4.2: Costs for: a) equipment annualized, b) utilities and c) revenues, in k€ y⁻¹, for split factors of 0.3, 0.6 and 0.8, at 10 bar.

Table 4.6: CF, dC and Wobbe Index values for split factors of 0.3, 0.6 and 0.8, at an operating pressure of 10 bar and temperatures of 350 °C and 250 °C at the entrance of R-301 and R-302, respectively

Split fraction		0.3	0.6	0.8
Total CF	k€ y ⁻¹	833	822	744
dC	%	-	-1.31	-10.7
Wobbe Index	MJ Nm ⁻³	43.98	46.77	49.01

When the split factor increases, so does the amount of CH₄ that is recycled back to the first reactor, decreasing the conversion, which will prevent the temperature from rising too much, as can be seen in Table 4.7. The catalyst loading simply increases because the gas flow increases, with more product gas being recycled.

Table 4.7: Reactor dimensions and maximum temperature achieved for R-301 and R-302, with a split factor of 0.3, 0.6 and 0.8, at an operating pressure of 10 bar and inlet temperature of 350 and 250 °C for R-301 and R-302, respectively

Split factor		0.3		0.6		0.8	
Reactor		R-301	R-302	R-301	R-302	R-301	R-302
Length	m	0.37	0.28	0.38	1.10	0.65	2.94
Diameter	m	0.07	0.06	0.08	0.22	0.13	0.59
Catalyst mass	kg	1.68	0.73	1.82	44.2	9.12	840
Maximum temperature	°C	608	478	550	415	475	351
Per pass X_{CO_2}	%	62.6	43.5	54.8	58.7	50.5	67.3
Overall X_{CO_2}	%	83.31		89.76		94.64	

In both reactors, what can be seen is that lower gas flow rates result in lower conversions. If the amount of gas recycled to the first reactor is low (0.3), the conversion for that specific reactor, R-301, is higher, as said before but, for the second reactor, R-302, the amount of CH_4 is higher than the amount of CO_2 , due to the high conversion in the previous reactor, which induces the formation of products and thus reduces the conversion in the second reactor, as can be seen in Table 4.8. If the split factor is higher, 0.6 for instance, the amount of CH_4 recycled back to the first reactor is higher, thus reducing the conversion there.

For the second reactor, the maximum temperature inside the reactor decreases with the increasing amount of gas recycled back to the first reactor because the gas flow is so low that, even though the conversion is higher, the amount of heat released is not as significant as in the first reactor.

Table 4.8: Molar flows, in $kmol\ h^{-1}$, at the inlet and outlet of R-301 and R-302, and CO_2 conversion for the split factors of 0.3, 0.6 and 0.8, an inlet temperature of 350 and 250 °C for R-301 and R-302, respectively, and an operating pressure of 10 bar

Split factor		0.3				0.6				0.8			
Reactor		R-301		R-302		R-301		R-302		R-301		R-302	
Molar flows		In	Out	In	Out	In	Out	In	Out	In	Out	In	Out
CO_2	$kmol\ h^{-1}$	3.65	1.37	0.96	0.54	4.45	2.01	0.80	0.33	5.37	2.66	0.53	0.17
CH_4	$kmol\ h^{-1}$	8.61	10.4	7.29	8.15	17.1	19.4	7.75	8.39	38.2	40.8	8.17	8.56
H_2	$kmol\ h^{-1}$	15.2	7.56	5.29	2.28	18.6	9.36	3.74	1.35	21.9	11.1	2.23	0.70
X_{CO_2}	%	62.6		43.5		54.8		58.7		50.5		67.3	

All things considered, a split factor of 0.6 is probably the best option, both in terms of costs and gas grid quality because even though there is an increase in costs, when compared with a split factor of 0.3, there is also an improvement in terms of the quality of the final

product, in terms of energetic content (WI). Even though at 10 bar the biomethane produced does not have a sufficient WI value to be injected into the grid, a small increase in the operating pressure should meet the requirements. A split factor of 0.3 would require high operating pressures, resulting in high compression costs, to obtain a biomethane stream that would fit the gas grid requirements since at 10 bar the WI obtained was only 43.98 MJ Nm^{-3} . On the other hand, a split factor of 0.8 has high reaction costs, even though the results show an acceptable biomethane WI even at pressures as low as 10 bar.

In order to evaluate the influence of the temperature, different temperatures at the entrance of the reactors were considered, while maintaining the stream entering the second reactor 100°C lower than the first one. The costs for the equipments whose costs varied are reported in Fig. 4.3. The dC method results, CF and WI values are reported in Table 4.9. The costs values used in Fig. 4.3 are further reported in detail in Table H.3, in Appendix H.

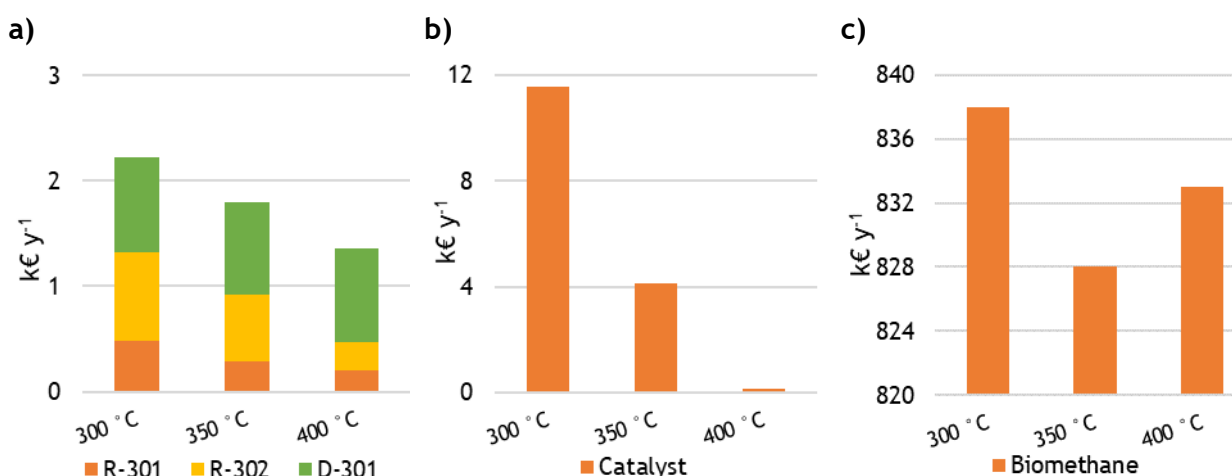


Figure 4.3: Costs for: a) equipment annualized, b) utilities and c) revenues, in k€ y^{-1} , for temperatures at the inlet of R-301 of 300, 350 and 400°C .

Table 4.9: CF, dC and Wobbe Index values for temperatures at the inlet of R-301 of 300, 350 and 400°C , at an operating pressure of 10 bar and a split factor of 0.6

Temperature at the inlet of R-301	$^\circ\text{C}$	300	350	400
Total CF	k€ y^{-1}	799	800	810
dC	%	-	0.12	1.33
Wobbe Index	MJ Nm^{-3}	42.50	46.77	44.54

By analyzing Table 4.9, what can be seen right away is that when comparing with a temperature of 300°C at the first reactor with higher temperatures, the CF is lower, in fact at 350°C the total CF is 0.12 % higher and at 400°C it is 1.33 % higher.

Once again, the major difference in costs is related to the reaction section, with higher temperatures requiring smaller reactors, as well as lower catalyst loadings, as can be seen in

Fig. 4.3. By increasing the temperature at the entrance of the reactors it is natural that the exit temperature will increase as well, thus resulting in lower conversions, according to the equilibrium; at the same time, higher temperature increases the kinetics, thus decreasing the amount of catalyst needed, as is reported in Table 4.10.

Table 4.10: Reactor dimensions, maximum temperature achieved and CO₂ conversion obtained for R-301, for temperatures at the inlet of R-301 of 300, 350 and 400 °C, at an operating pressure of 10 bar and a split factor of 0.6

		R-301			R-302		
Temperature at the inlet	°C	300	350	400	200	250	300
Length	m	0.79	0.38	0.2	3	1.1	0.35
Diameter	m	0.16	0.08	0.04	0.6	0.22	0.07
Catalyst mass	kg	16.4	1.82	0.27	897	44.2	1.42
Maximum temperature	°C	522	550	577	232	415	467
Per pass X _{CO₂}	%	59.1	54.8	51.5	1.49	58.7	43.7

For temperatures as low as 200 °C at the entrance of the second reactor, the kinetics are extremely slow, resulting in an exceedingly large amount of catalyst needed. In fact, the results reported in Table 4.10, for the minimum catalyst loading, correspond only to a CO₂ conversion of 1.49 %, since in order to attain the equilibrium conversion, a much larger reactor and a subsequent larger amount of catalyst would have been required. That is why the reactor dimensions were considered as mentioned above.

Even though the higher temperature provides a higher CF value, a temperature of 350 °C provides the best gas quality. All things considered, temperatures of 350 and 250 °C at the inlet of the first and second reactor, respectively, were deemed ideal.

When previously comparing the split factor and temperature it was seen that very few options corresponded to the minimum WI required in Portugal for biomethane injection in the NG grid. That is why it is important to evaluate the effect of the operating pressure in the whole process in order to see if the increased compression costs are overcome by the profits in terms of biomethane quality or not.

The costs for the equipments whose costs varied with the pressure are reported in Fig. 4.4. The dC method results, CF and WI values are reported in Table 4.11. The costs values used in Fig. 4.4 are further reported in detail in Table H.4, in Appendix H.

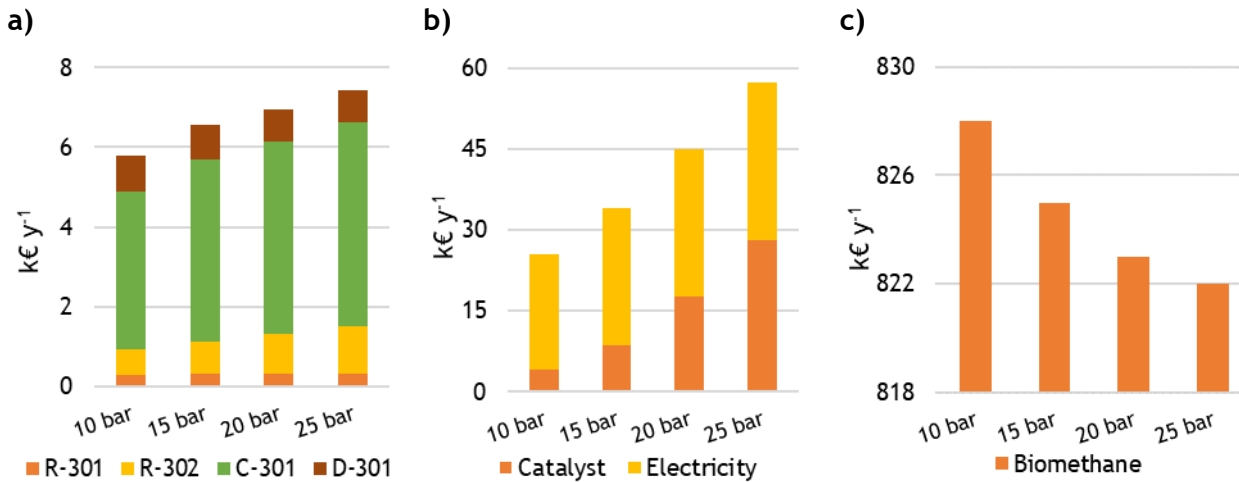


Figure 4.4: Costs for: a) equipment annualized, b) utilities and c) revenues, in k€ y^{-1} , operating pressures of 10, 15, 20 and 25 bar, with temperatures of 350 and 250 °C at the inlet of R-301 and R-302, respectively, and a split factor of 0.6.

Table 4.11: CF, dC and Wobbe Index values for operating pressures of 10, 15, 20 and 25 bar, with temperatures of 350 and 250 °C at the inlet of R-301 and R-302, respectively, and a split factor of 0.6

Operating pressure	bar	10	15	20	25
Total CF	k€ y^{-1}	796	784	771	757
dC		-	-1.51	-3.14	-4.95
Wobbe Index	MJ Nm^{-3}	46.77	47.88	48.57	49.05

In terms of operating pressure effect, what can be seen is that an increasing pressure does, in fact, increase the energetic content in the biomethane, since the conversions obtained in the reactors are higher and thus the CH_4 purity in the biomethane is higher as well. What can be seen as well is that an increase in pressure does not only increase the fraction of CH_4 in the biomethane, but it also decreases the amount of water, since the separation in the flash drum is more effective. Since the biomethane selling price is determined on a basis of energy per amount of gas, even if the energy increases, which it does, the amount of gas decreases in a greater extent, thus resulting in lower profits at higher pressures.

Contrary to what happens with the cooled reactors, by increasing the pressure, the reactor and catalyst costs are increasing. In the cooled reactors the operating pressures studied were lower (8 to 15 bar) than the pressures considered for the adiabatic reactors but, the maximum attained temperatures were higher (up to 647 °C). On the one hand, the increase in pressure decreases the kinetic rates, since it has noticeable effect on the products partial pressure, thus inhibiting the methanation reaction; on the other hand, an increase in pressure increases the CO_2 conversion (for thermodynamic reasons), which causes higher temperatures to be attained.

Since the temperatures attained in the cooled reactors are high, it is possible that the temperature effect of that parameter in the kinetic rate (faster rates), overcomes the pressure effect (lower rates), resulting in faster kinetics with increasing pressure, thus decreasing the catalyst loading needed.

For the adiabatic reactors, in the first reactor, R-301, the maximum temperature attained for the pressure considered is considerably lower (564 °C), as can be seen in Table 4.12, while the operating pressures are higher (10 to 20 bar). The results show that, in this case, the effect of pressure in the kinetics is more notorious than the temperature's, which causes an increasing demand of catalyst loading with the pressure. In the second reactor, R-302, that effect is even more notorious because the maximum temperatures attained are even lower.

Table 4.12: Inlet and outlet temperatures and CO₂ conversion for R-301 and R-302, for pressures of 10, 15 and 20 bar, and a split factor of 0.6

		10		15		20	
		R-301	R-302	R-301	R-302	R-301	R-302
Inlet temperature	°C	350	250	350	250	350	250
Outlet temperature	°C	550	415	558	409	564	406
Catalyst loading	kg	1.82	44.2	3.03	91.1	3.03	194
Per pass X_{CO_2}	%	54.84	58.66	57.61	63.72	59.60	67.22
Overall X_{CO_2}	%	89.76		91.75		93.01	

All things considered, the operating pressure should be the smallest one that would provide sufficient biomethane quality for injection into the grid which, in this case, corresponds to a pressure of 20 bar. The final reactor dimensions, maximum temperatures attained, and CO₂ conversions are reported in Table 4.13.

Table 4.13: Reactor dimensions, maximum temperature achieved and CO₂ conversion obtained for R-301 and R-302, for the final reactor settings

		R-301	R-302
Temperature at the inlet	°C	350	250
Length	m	0.45	1.80
Diameter	m	0.09	0.36
Catalyst mass	kg	3.03	194
Maximum temperature	°C	564	403
Per pass X_{CO_2}	%	59.6	67.2
Overall X_{CO_2}	%	93.01	

4.4 Adiabatic fixed-bed reactors with membrane separation

When the membrane is used along with the adiabatic reactors, as explained for the cooled reactors with the membrane, there is a higher temperature attained inside the reactor (due to the feed of a more concentrated CO₂ stream), which corresponds to a smaller conversion, as reported in Table 4.14. Therefore, while all the other parameters were maintained, the temperature at the entrance of the reactors, was lowered to obtain conversions similar to the ones obtained in the scenario without the membrane. In this scenario the pressure drop inside the reactors was also neglected.

Table 4.14: Reactor dimensions, maximum temperature achieved and CO₂ conversion obtained for R-401 and R-402, for temperatures at the inlet of R-401 of 350 and 330 °C

		350 °C		330 °C	
		R-401	R-402	R-401	R-402
Temperature at the inlet	°C	350	250	330	230
Length	m	0.25	0.7	0.4	1.5
Diameter	m	0.05	0.14	0.08	0.3
Catalyst mass	kg	0.52	11.39	2.13	112
Maximum temperature	°C	621	453	597	431
Per pass X_{CO_2}	%	58.16	58.72	59.54	64.26
Overall X_{CO_2}	%	90.84		92.36	

When adding the membrane, it is also important to understand the effect that the separation has on the reaction section. If a very short membrane is used, the amount of CO₂ that permeates is small. This results in higher amounts of CO₂ in the biomethane stream, thus reducing its purity; similarly, for the reaction section lower contents of CO₂ result in lower conversions. If, on the other hand, a larger membrane is used, there is also more CH₄ permeating the membrane, that can result in lower CO₂ conversions in the methanation section. For this scenario, the membrane was set at a length of 2 m, thus resulting in a biomethane stream obtained in the membrane with a molar fraction of CH₄ of 0.982, a biomethane obtained from the reaction section with a fraction of 0.800 and a final stream with 0.855. In this scenario, a larger membrane provides a higher purity in the biomethane obtained from the membrane, when compared with the value obtained for the 1.2 m long membrane in the cooled reactors scenario but, in contrast with that, the CH₄ molar fraction in the biomethane obtained from the reaction, is smaller.

4.5 Comparison of the scenarios studied

In order to sum up all the case-studied studied, the properties of the biomethane stream obtained for the four scenarios considered are reported in Table 4.15.

Table 4.15: Obtained biomethane properties for the different scenarios studied

		Cooled without membrane	Cooled with membrane	Adiabatic without membrane	Adiabatic with membrane
Mass flow	kg h ⁻¹	154.4	151.0	153.2	155.6
CH₄ mass flow	kg h ⁻¹	135.9	136.5	136.1	137.5
Molar fractions					
CO₂		2.45·10 ⁻²	1.81·10 ⁻²	2.26·10 ⁻²	2.43·10 ⁻²
CH₄		0.852	0.891	0.863	0.855
H₂O		9.05·10 ⁻³	4.90·10 ⁻³	6.92·10 ⁻³	4.84·10 ⁻³
H₂		9.98·10 ⁻²	7.15·10 ⁻²	9.28·10 ⁻²	1.01·10 ⁻¹
Wobbe Index	MJ Nm ⁻³	48.19	49.4	48.6	48.4
HHV	MJ kg ⁻¹	50.8	51.8	51.2	51.1
LHV	MJ kg ⁻¹	45.58	46.21	45.53	45.82
Overall X_{CO₂}	%	91.83	93.69	93.01	92.36

All in all, in terms of reactor performance, cooled fixed-bed reactors are probably a better choice, when compared with the adiabatic ones. That is because the adiabatic ones result in lower conversions because of the high temperatures attained inside and, even if a second or third reactor were to be used at a lower temperature than the ones performed in this work, the kinetics would be so low that a much larger reactor, which a much higher catalyst loading, would have been needed. In fact, all depends on the economic analysis because maybe that alternative, even if more expensive, could have resulted in a better quality biomethane, and therefore a higher profitability. However, that possibility was not accounted for in this work.

It is only possible to decide whether a scenario is better than other when an economic analysis is performed, and all the process costs are compared with the profits to determine which one will provide the better investment. This is discussed in the next chapter.

5 Economic analysis

The economic analysis performed in this work assumes a 10-year plant lifetime, considering that none of the equipments is replaced during that time, and 350 days of continuous operation throughout the year and a 5 % interest rate, as indicated by SIMDOURO. For each case, the capital costs, CAPEX, and the operational costs, OPEX, were calculated.

The main cost values used in this study are described in Table 5.1.

Table 5.1: Main cost values used in this study

	Value	Cost	Source
Utilities			
Electricity	0.105	€ kWh ⁻¹	SIMDOURO
Renewable electricity	0.041-0.108	€ kWh ⁻¹	(Salomone et al., 2019)
Catalyst	8.14	€ kg ⁻¹	(Giglio et al., 2015)
Cooling water	0.029	€ m ⁻³	(Michailos et al., 2021)
Boiler feed water	0.41	€ m ⁻³	(Seider et al., 1999)
Deionized water	11.5	€ m ⁻³	(Salomone et al., 2019)
High pressure steam	12	€ m ⁻³	(Vo et al., 2018)
Sales			
Biomethane selling price	0.027-0.045	€ kWh ⁻¹	SIMDOURO
Equipment			
Electrolyzer	800-1 500	€ kW ⁻¹	(Buttler et al., 2018)
Membrane	79	€ m ⁻²	(Hao et al., 2008)
Hydrogen storage	75	€ m ⁻³	(Gorre et al., 2019)

One of the most important costs is the biomethane because it is the source of most of the revenues in this work. There is, however, not yet a defined market value but, instead, a range of values that can be applicable, which is the one in Table 5.1. The lowest value of 0.027 € kWh⁻¹ corresponds to the natural gas purchase price for industrial clients, meaning that this would be NG equivalent value; the higher value, 0.045 € kWh⁻¹ is an estimate of the expected market value of the biomethane.

For the electrolyzer, the price range considered represents the current cost of the technology, but it should be kept in mind that, as said before, its price is decreasing over the years. The investment cost was determined as an average of the values mentioned above, 1 100 € kW⁻¹. It was considered that, in all four cases studied, the average H₂ production is 290 Nm³ h⁻¹, which corresponds to the H₂/CO₂ molar ratio of 4, considered for the H₂ feed to the reactors.

The energy consumption was set to be 4.4 kWh Nm^{-3} , which is the maximum energy consumption value for the electrolyzer being considered, according to the data in Table 3.3, and since the H_2 is exiting the electrolyzer at 200 barg, the maximum electricity consumption is defined to account for the compression costs in the electrolyzer. This corresponds to an electrolyzer cost of approximately 1.4 M€. As will be discussed further, the electrolysis section is the most expensive of the whole process. For the membrane, the investment cost was directly obtained from Aspen Plus, depending on the membrane area, considering a cost of 79 € m^{-2} (Hao et al., 2008).

In terms of understanding whether a determined investment is or not financially viable, financial indicators, such as the net present worth (NPW), the return on investment (ROI) and the payback time, are the most important values to be analyzed. These financial indicators are represented in Fig. 5.1 a) and b).

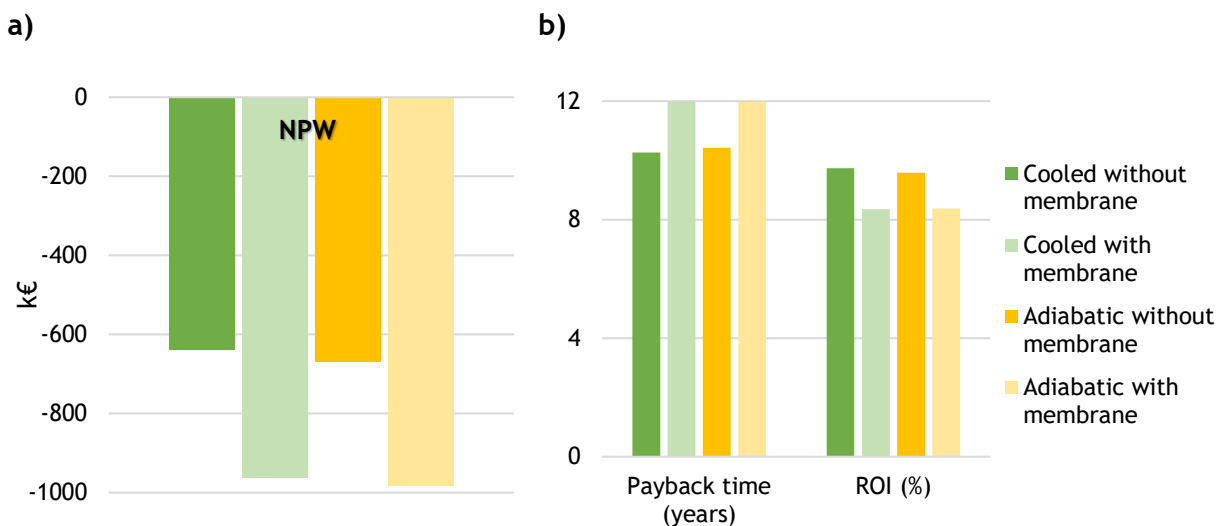


Figure 5.1: Values determined for: a) net present worth, in k€, and b) payback time, in years, and return on investment, in %, obtained for all the scenarios.

Right away what can be seen is that none of the scenarios represent a viable alternative in economic terms. That is because they all present a negative NPW, of over 600 k€ for the scenarios without membrane and almost 1 000 k€ for the ones with membrane. By looking at the data in Fig. 5.1 b), it can be seen that the payback time of the scenarios with no membrane is slightly above 10 years, meaning that the invested capital would have been recovered at the end of next (11th) year. As for the other scenarios, about 2 years more would have been needed.

First, it is important to understand that the electrolysis section is the most expensive section of the process, both in terms of equipment, as can be seen in Fig. 5.2 a) and in terms of utilities used (renewable electricity and deionized water), as can be seen in Fig. 5.2 b). The utilities consumption for all the scenarios is reported in Table H.5, in Appendix H.

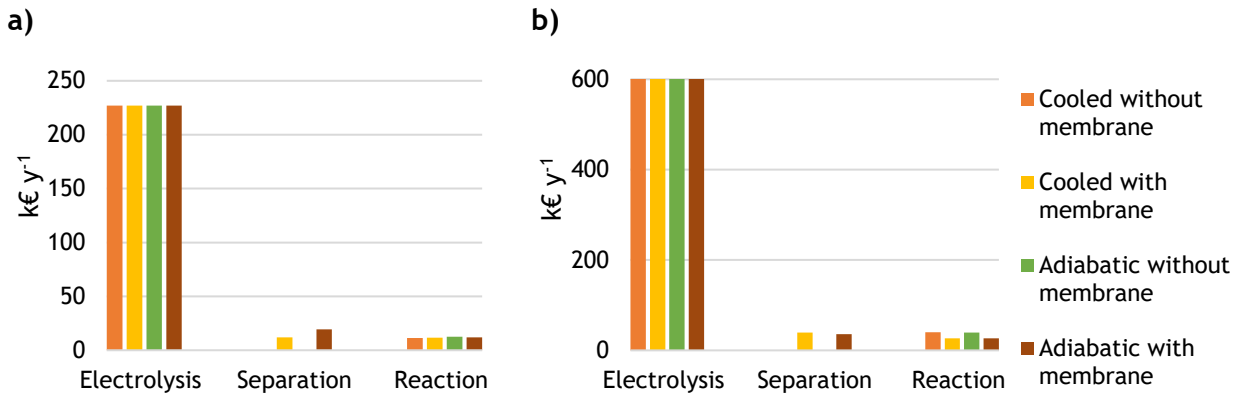


Figure 5.2: Cost values of: a) annualized equipment, in k€ y⁻¹ and b) utilities, in k€ y⁻¹, for the three sections of the process.

The electrolysis section, that accounts for the electrolyzer and hydrogen tank (the separation section accounts for the compressor before the membrane and the membrane and the reaction section accounts for the rest of the equipment), corresponds to approximately 90 % of the whole equipment costs and 91 % of the electricity consumption. This goes more or less according to literature data reported by Witte et al. (2018a), who report an electricity consumption of about 75 % of the operating costs, due to the large consumption of the electrolyzer, being that the electricity costs in their work represent about 83 % of the total OPEX.

Then, it is necessary to take a better look at the individual capital and operational costs, as well as revenues, represented in Fig. 5.3, in order to better understand the difference in costs between the scenarios. The cash-flows, CF, is considered to be the same every year, considering a yearly catalyst replacement, due to the high temperatures attained inside the reactor (Salomone et al., 2019). The values represented in Fig. 5.3 are reported in Table H.6, in Appendix H, along with all the equipment costs, in Tables H.7 and H.8.

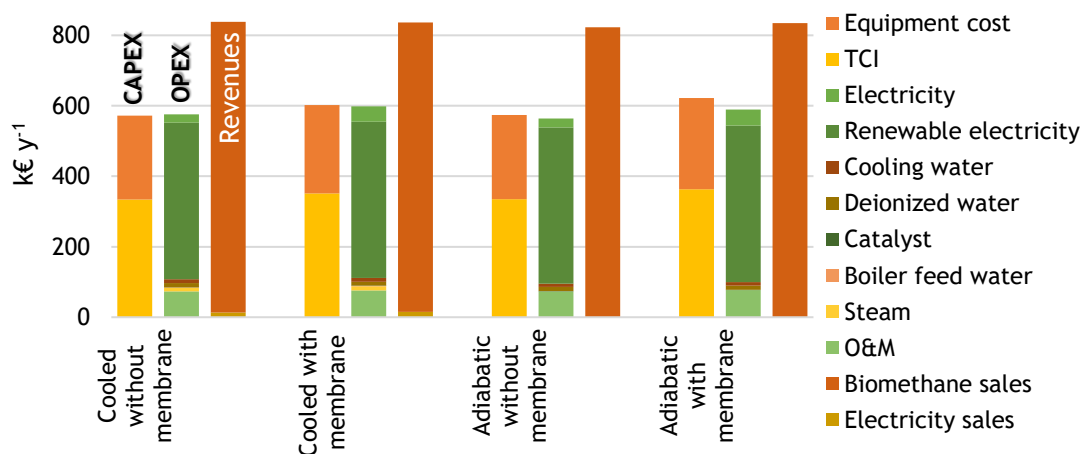


Figure 5.3: Capital and operational costs and revenues, in k€ y⁻¹, for the four scenarios studied.

In terms of total capital investment (TCI), what can be seen is that, as would be expected, both alternatives without the membrane have smaller capital investment costs, as reported in Fig. 5.3, because the membrane is an expensive equipment, and so the absence of that equipment is notorious in terms of TCI. Between cooled and adiabatic reactors without membrane, there is almost no difference in TCI. When comparing the two types of reactors with membrane there is, however, a more notorious difference. This is due to the higher costs of the compressor after the membrane because the operating pressure is higher in the case of the adiabatic reactors, thus increasing the compressor cost.

In terms of utilities, the electricity costs are higher in the cases where there is a membrane separation, due to the extra compression costs required. Besides that, what can be seen is that electricity represents the majority of the utilities required.

As reported before, the energy consumption for the electrolyzer was considered to be 4.4 kWh Nm^{-3} , already accounting for the compression of the hydrogen stream. The electricity value used for the electrolyzer is not the same as used for other equipment. That is because the electricity price of 0.105 € kWh^{-1} applies to electricity coming from the national grid and, it is not justified to use such electricity to produce hydrogen to obtain methane as an energy carrier. In that way, electricity used in the electrolyzer should be considered renewable, and with a lower price.

The results presented above were obtained considering a renewable electricity cost of 0.04 € kWh^{-1} (an in-between value for the range considered in Table 5.1). In fact, if the results would have been obtained with an electricity cost of 0.105 € kWh^{-1} , considering the use of electricity from the grid for the electrolyzer, as was considered for the other equipment, the NPW would have been more than five times lower, as it is possible to see in Fig. 5.4. It is, however, relevant to determine the cost of renewable electricity for which the NPW would have been zero for all the scenarios, as well as the biomethane selling price. These values are reported in Table 5.2.

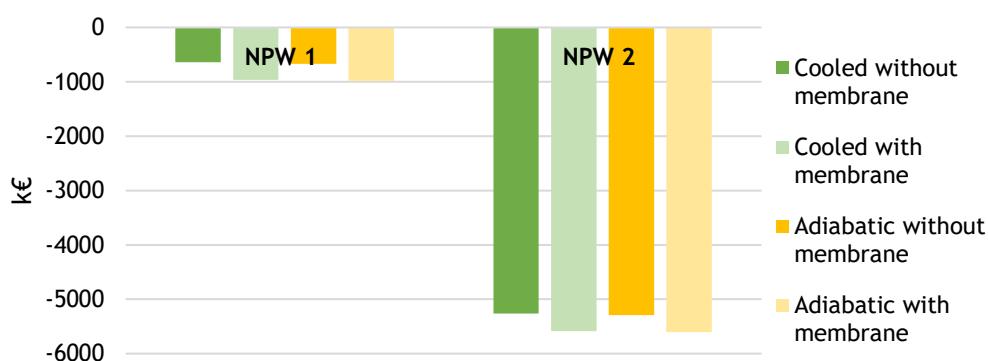


Figure 5.4: NPW 1, for an electricity price of 0.04 € kWh^{-1} , for the electrolyzer, and NPW 2, for an electricity price of 0.105 € kWh^{-1} , for the electrolyzer.

Table 5.2: Renewable electricity and biomethane prices, in € kWh^{-1} , needed to obtain a NPW of zero, each calculated using the other's base value

		Base value	Cooled without membrane	Cooled with membrane	Adiabatic without membrane	Adiabatic with membrane
Renewable electricity price	€ kWh^{-1}	0.04	0.033	0.029	0.033	0.029
Biomethane selling price	€ kWh^{-1}	0.045	0.050	0.052	0.050	0.052

These values help to understand how high the biomethane selling price and how low the electricity price would have to be for the project to be worth investing in, in order to gain back the investment made in the considered lifetime of 10 years.

With these values it is once again possible to see that, in comparison with the base value used for this study calculations, the scenarios with membrane require a lower electricity price and/or a higher biomethane selling price, in comparison with the scenarios with no membrane. The electricity price would have to be 28 % lower and the biomethane price 16 % higher than in the base case, while for the projects with no membrane the electricity would only have to be 18 % lower and the biomethane 11 % higher.

It is also important to compare the economic results along with the technical results obtained in the previous chapter, in order to understand if higher investments lead to better results.

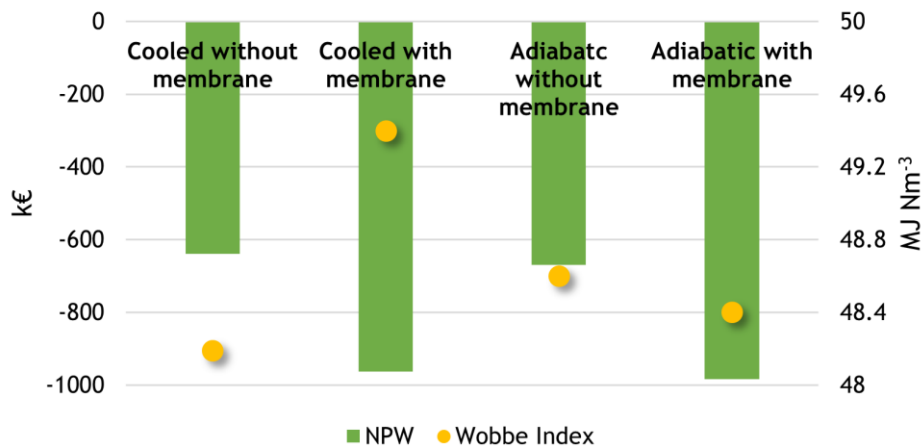


Figure 5.5: Wobbe Index, in MJ Nm^{-3} , of the biomethane obtained in each scenario and respective Net Present Worth, in k€ .

According to Fig. 5.5, the cooled reactor without the membrane was the scenario that presented the lowest WI value but also the highest NPW value (less negative). In economic terms, it can also be noticed that the cooled reactors both had higher NPW values, when comparing with the respective alternatives with the adiabatic reactors.

All in all, since all the scenarios resulted in a WI that is in the range of values allowed for injection in the grid, the best scenario should be the one with the higher NPW, meaning the scenario of the cooled reactor with no membrane separation. This goes according to the technical results in the previous chapter, which pointed to the cooled reactors being the best choice for this process, presenting a simpler reactor configuration, with just one reactor, and no recycle loops needed.

6 Assessment of the work done

6.1 Objectives achieved

One of the main objectives of this work was the study of the biomethanation process, which is the separation of CO_2 in the biogas followed by its methanation. This objective was successfully achieved, with the conclusion that the addition of the gas separation process did not present any advantage in terms of performance or costs for the project.

Another objective was the study of different methanation technologies, which was also done, by comparing the two types of reactors most used currently, the adiabatic and cooled fixed-bed reactors.

Finally, the economic analysis of all the scenarios was also conducted, which was also one of the main goals of this study.

6.2 Limitations and future work

One of the main limitations in this work is that there are a lot of variables that can be optimized in the process, and it was not possible to study all of them due to time constraints and the complexity of the optimization.

An interesting scenario that could not be studied, due to consistent numeric errors in the simulation, was the recycle of the biomethane stream obtained in the reaction section back to the membrane, in order to obtain biomethane with higher purity. This is, however, an interesting alternative that could make the scenarios with membrane separation more profitable, contrary to what was concluded in this work.

Another thing that could be interesting, in terms of future studies and investments, is the possibility of installing an on-site renewable source of electricity at the WWTP of Gaia Litoral, in order to determine whether those additional costs would compensate for the economic electricity demand of the electrolyzer.

6.3 Final assessment

The work developed in this study helped first and foremost in developing a more founded knowledge in the area of implementing a Power-to-Methane process and the required steps and thorough analysis it takes in order to decide the best choice.

This work and the way it was developed, during the pandemic, also helped in developing certain skills as resilience, autonomy and most of all time management.

7 Conclusions

The implementation of the PtM process was studied using a techno-economic analysis in which several scenarios possible studied. These scenarios involved using two different types of methanation reactors, cooled and adiabatic fixed-bed, as well as exploring whether or not the separation of the CO₂ from the CH₄ present in the biogas, previously to the methanation, had any advantage in terms of costs or final product quality.

Even though all the scenarios provided biomethane with quality enough to be injected into the natural gas grid, meaning a WI higher than 48.17 MJ Nm⁻³, the specific performance of the two types of reactors was clearly different. For the scenarios with no membrane, the cooled reactor showed a conversion of 91.8 %, while the two adiabatic reactors showed conversions of 59.6 and 67.2 %, respectively. This shows that the cooled reactors have a better performance, even more so because the adiabatic reactors operate at a higher pressure (20 bar) than the cooled ones (15 bar).

However, the operational expenses are higher for the cooled reactors, both with and without membrane, because of the cooling fluid, which is evaporating water. The yearly OPEX was 574 and 598 k€ for the cooled reactors without and with membrane, respectively, and 563 and 589 k€ for the adiabatic reactors without and with membrane, respectively.

All the scenarios ended up showing negative NPW values, indicating that, as they were studied in this work, none of them are financially feasible, considering the 10-year lifetime. It is, however, possible to cancel out the investment made in both scenario with no membrane separation, in little over 10 years (10.27 and 10.43 for the cooled and adiabatic reactors, respectively, with no membrane).

These values can also be associated with the conclusions withdrawn above related to the performance of the technologies studied. First, it was possible to determine that the addition of the membrane adds no advantage in economic terms, since the NPW values were the lowest for the scenarios with the membrane, meaning that the additional cost required for the acquisition of the membrane (and related additional equipment- e.g., compressor) is not covered by the possible better product quality. The NPW for cooled and adiabatic reactors with membrane was -962 and -983 k€, respectively, corresponding to payback times of 11.97 and 11.93 years, almost 2 years more than the considered lifetime of the project.

Between cooled or adiabatic reactors with no membrane, cooled reactors were eventually considered the best option due to the higher NPW of -639 k€, when comparing with the one obtained for the adiabatic reactors, -669 k€.

8 References

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Appendix A: Anaerobic digestion

AD is the process of organic matter decomposition, performed by microorganisms, under anaerobic conditions. The biogas produced from this process is considered one of the most energy and environmental efficient bioenergy producing technologies (Weiland, 2010).

The sludge digested in the AD process is usually a mixture of the primary and secondary sludge, produced in the primary and secondary treatments of the wastewater, respectively. To that mixed sludge, other substrates can be added to improve the CH_4 , this is called co-digestion. Co-digestion of certain substrates with higher energy content, like carbohydrates, raw fat and raw protein, can not only improve the overall biogas production yield, but the methane content in the biogas as well, as reported in Table A.1.

Table A.1: Maximal biogas yield, per ton of total solids of substrate consumed, and theoretical CH_4 and CO_2 content, for different substrates. Retrieved from (Weiland, 2010).

Substrate	Biogas ($\text{Nm}^3 \text{ t}_{\text{total solids}}^{-1}$)	CH_4 (%)	CO_2 (%)
Carbohydrates	790-800	50	50
Raw protein	700	70-71	29-30
Raw fat	1 200-1 250	67-68	32-33

Primary sludge, produced from the primary settling of the wastewater, has a great amount of easily biodegradable organic matter, which can result in a methane yield of 315-400 Nm^3 per ton of dry organic matter. Secondary sludge, product of the secondary treatment that is the biological treatment, has a smaller amount of easily biodegradable organic matter and thus results in a smaller methane yield, 190-240 Nm^3 per ton of dry organic matter. Sludge is usually thickened before it is mixed, in a mixing tank, in order to increase the dry matter content and reduce the water content, to prevent an excessive energy demand in the digestors (Bachmann et al., 2015).

The AD process, that is represented in Fig. A.1, consists of the four following stages, hydrolysis, acidogenesis, acetogenesis and methanogenesis. First, in the hydrolysis stage, complex organic molecules are decomposed into simpler ones, like sugars and amino and fatty acids (Abassi et al., 2012), then, these molecules are fermented in order to produce volatile fatty acids like propionic, butyric and valeric acids, alcohols, hydrogen and carbon monoxide in a process called acidogenesis. These fermentation products are then consumed by acetogenic bacteria to form acetic acid and carbon dioxide and hydrogen, followed by the work of methanogenic bacteria to produce methane, that can be either acetotrophic, and consume

acetic acid to produce CH_4 ($4 \text{ CH}_3\text{COOH} \rightarrow 4 \text{ CO}_2 + 4 \text{ CH}_4$), or hydrogenotrophic, and consume CO_2 and H_2 to produce CH_4 ($\text{CO}_2 + 4 \text{ H}_2 \rightarrow \text{CH}_4 + 2 \text{ H}_2\text{O}$) (Bharathiraja et al., 2018).

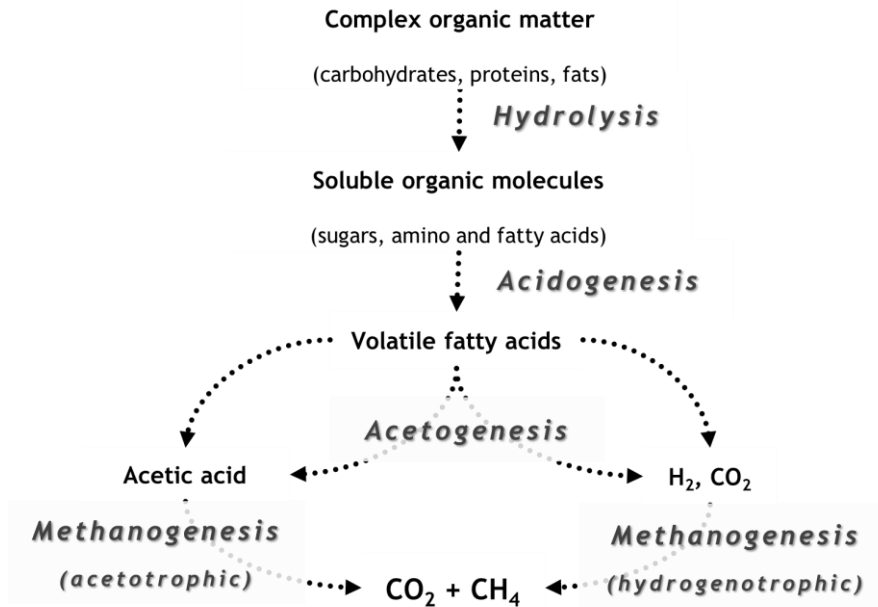


Figure A.1: Schematic representation of the four stages of AD. Adapted from (Bharathiraja et al., 2018) and (Abassi et al., 2012).

One of the most important process variables is the working temperature. Methanogenic bacteria can be classified according to their working temperature range as thermophilic (50-65 °C), mesophilic (20-40 °C) and psychrophilic (<10 °C) (Abassi et al., 2012), with most AD processes working with mesophilic bacteria and therefore in that same temperature range. In the WWTP of Gaia Litoral, the usual working temperature is in between 35 and 40 °C (Águas de Gaia, 2003). Besides the working temperature, a good mixing of the sludge should be maintained, in this case, it is ensured by injecting, in the digester, the same biogas that is being produced.

Appendix B: Comparison of CO₂ separation technologies

The choice of the adequate separation technology for biomethanation depends on a series of factors like CAPEX, OPEX, availability and good market development and, one of the most important things to consider, the specific application of the biomethane produced, that will dictate the purity needed, which will affect all the other aspects.

In terms of biomethane purity for natural gas grid injection, as mentioned before, there are not exactly any minimum values, however, it is convenient that that purity is as high as possible in order to obtain biomethane with a WI that respects the allowable range. In terms of CAPEX and OPEX, as well as energetic demand, it depends mainly on the biogas flow that is being treated, which in the WWTP of Gaia Litoral is about 230 m³ h⁻¹ (Águas de Gaia, 2003).

In Table B.1, it is possible to briefly analyze a few of the technologies differences in order to choose the best one. And the other separation technologies, besides membrane separation are briefly explained.

B.1 Water scrubbing

This technology is based on the absorption, in water, of a certain component from a gaseous stream, in order to remove that same component. This works based on the different solubility of gases in water, in fact, CO₂ is about 26 times more soluble in water than CH₄, at 25 °C (Kapoor et al., 2019), therefore being easily extracted through this process.

It is possible to obtain a biomethane stream of about 90 % CH₄, that can attain a purity of 99 % after drying. Economically and energetically, biogas compression before feeding to the absorption column and water recirculation through pumps are the most costly processes in this technology

B.2 Organic solvent scrubbing

This technology is pretty similar to the previous one with the exception of the type of solvent used. Instead of water, organic solvents are used, like mixtures of methanol and dimethyl ethers of polyethylene glycol and, since the CO₂ solubility in these solvents is higher than in water, the amount of solvent needed for the separation is reduced, thus reducing the investment and operational costs (Angelidaki et al., 2018).

Table B.1: Comparison of the different biogas upgrading technologies. Adapted from Sun et al. (2015), Angelidaki et al. (2018), Kapoor et al. (2019) and Adnan et al. (2019)

Technology		Membrane separation	Cryogenic separation	PSA	Amine Scrubbing	Organic Solvent Scrubbing	Water Scrubbing
Temperature	°C	25-60	-59 to -45	5-30	35-50	10-20	20-40
Pressure	bar	20-36	40	4-8	1	4-7	6-10
Biomethane purity	%	92-99	97-98	96-98	>98	96-98	95-99
CH ₄ loss	%	<1	<2	<4	<0.1	2-4	1-3
Energy consumption	kWk Nm ⁻³	0.18-0.35	0.2-0.79	0.16-0.35	0.05-0.25	0.10-0.33	0.2-0.5
Pre-treatment		Required	Recommended	Required	Required	No	No
CAPEX	€ Nm ⁻³ biogas	0.22	0.40-0.44	0.26	0.28	0.25	0.13-0.15
OPEX	€ year ⁻¹	25 000	-	56 000	59 000	39 000	15 000

B.3 Amine scrubbing

Amine scrubbing is based on the reversibility of the chemical reaction between the absorbed gases and the chemical solvent used, solvent which consists in a aqueous amine solution. The most used amines are diethanolamine, monoethanolamine and methyldiethanolamine, the latter being the most used one. Nowadays, it is also common to use activated methyldiethanolamine, that is a mixture of methyldiethanolamine and piperazine, that has a higher absorption capacity in comparison to methyldiethanolamine alone (Bauer et al., 2013).

The main disadvantages of this technology are the toxicity of the amine solutions, for the environment and the human being, the energy requirements for their regeneration and initial cost (Angelidaki et al., 2018).

B.4 Pressure Swing Adsorption (PSA)

PSA technology is a separation process based on the selective adsorption of several gaseous components on the surface of a determined adsorbent material. The most used ones are carbon molecular sieves, activated carbon and zeolites, and they are chosen according to the thermodynamic or kinetic selectivity of one component relatively to the others.

This is a dynamic process, operating in cyclic mode, with four stages, pressurization, feed, blowdown and purge, which implies that biogas is only being fed to the adsorption column in one of the stages and so this process is usually performed in four columns operating in parallel to ensure the continuity of the system (Bauer et al., 2013).

This is a very safe and compact technology that can produce biomethane up to 96-98 % purity (Angelidaki et al., 2018).

B.5 Cryogenic separation

This process is based on the different condensing properties of CO₂ and CH₄, since at 1 atm the boiling temperatures of these gases are -78,2 and -161.5 °C (Kapoor et al., 2019), respectively, meaning that there is a significant difference between these, allowing for an easy separation.

This way, through a gradual decrease in temperature, the CO₂ is liquified, allowing for its separation from the biomethane, that can reach a purity of over 97 % (Angelidaki et al., 2018). This is however a technology that is still in a developing stage, with only a few operating at a commercial scale, like seen in Fig. 2.2, and requires high investment and operating costs, for biogas compression.

Appendix C: Membrane model

The membrane module used in this work is an in-house model developed by the research group Laboratory LSRE-LCM.

The mass balance inside the membrane, meaning on the retentate side, is given as follows,

$$n\pi r^2 N_i|_z - n\pi r^2 N_i|_{z+\Delta z} - n\pi 2r \Delta z J_i = 0 \quad (C.1)$$

$$r N_i|_z - r N_i|_{z+\Delta z} - 2\Delta z J_i = 0 \quad (C.2)$$

$$-\frac{1}{\Delta z} (N_i|_{z+\Delta z} - N_i|_z) - \frac{2}{r} J_i = 0 \quad (C.3)$$

$$\frac{1}{L} \frac{\partial N_i}{\partial z} + \frac{2}{r} J_i = 0 \quad (C.4)$$

where N_i is the molar flow of each i component through the cross-sectional area of the membrane and J_i is the molar flow of each component through the membrane wall surface area in each longitudinal Δz element. L is the element that establishes the membrane length, since the axial direction, z , only has values from 0 to 1.

The boundary conditions considered for this differential equation are the ones in Eqs. (C.5) and (C.6).

$$N_i|_{z=0} = x_{i,feed} \frac{P_r(Q_{feed}/n\pi r^2)}{R T} \quad (C.5)$$

$$N_i|_{z=1} = 0 \quad (C.6)$$

In Eq. (C.5), $x_{i,feed}$ is the molar fraction of the component i in the stream feed, P_r is the pressure on the retentate side, in Pa, R is the gas constant, in $\text{m}^3 \text{Pa K}^{-1} \text{mol}^{-1}$, Q_{feed} is the feed volumetric flow, in $\text{m}^3 \text{s}^{-1}$ and T is the membrane operating temperature.

The mole flow of each component that permeates the membrane, J_i , is described by Eq. (C.7), where P_i is the permeability of each i component of the gas stream, in $\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$, d is the membrane thickness, in m, P_r and P_p are the pressures on the retentate and permeate side, respectively, in Pa, and $x_{i,r}$ and $x_{i,p}$ are the molar fractions of each component in the retentate and the permeate, respectively.

$$J_i = \frac{P_i}{d} (P_r x_{i,r} - P_p x_{i,p}) \quad (C.7)$$

Sometimes, instead of the permeability of each component, the permeance is given, which is essentially the ability of determined component to permeate a membrane of determined thickness. With that, Eq. (C.7) becomes as follows:

$$J_i = \text{Permeance}(P_r x_{i,r} - P_p x_{i,p}) \quad (\text{C.8})$$

The permeance units most commonly used are Barrer, which can be converted to SI units as according to Eq. (C.9).

$$1 \text{ Barrer} = 3,3485 \cdot 10^{-16} \frac{\text{mol} \cdot \text{m}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}} \quad (\text{C.9})$$

Appendix D: Comparison of water electrolysis technologies

There are a few characteristics that need to be considered when choosing between water electrolysis technologies. Table D.1 presents an overview of the main characteristics of the three technologies previously discussed for an easier comparison.

Table D.1: Summary of the main parameters of water electrolysis technologies. Retrieved from Buttler et al. (2018)

		AEL	PEMEL	SOEL
Operation parameters				
Cell temperature	°C	60-90	50-80	700-900
Typical pressure	bar	10-30	20-50	1-15
Current density	A cm ⁻²	0.25-0.45	1.0-2.0	0.3-1.0
Flexibility				
Cold start-up time		1-2 h	5-10 min	hours
Warm start-up time		1-5 min	<10 s	15 min
Efficiency				
Nominal stack efficiency (LHV)	%	63-71	60-68	100 ^a
Nominal system ^b efficiency (LHV)	%	51-60	46-60	76-81
Available capacity				
H ₂ production per stack	Nm ³ h ⁻¹	1 400	400	<10
Cell area	m ²	<3.6	<0.13	<0.06
Durability				
Life time	kh	55-120	60-100	8-20 ^c
Economic parameters				
CAPEX	EUR kW ⁻¹	800-1500	1400-2100	>2000 ^c
OPEX	% of CAPEX per year	2-3	3-5	-

^a Operating at thermoneutral voltage.

^b Including auxiliaries and heat supply (SOEL).

^c High uncertainty due to the pre-commercial stage of SOEL.

When looking at the characteristics of all three technologies, the first thing that comes forward is the fact that SOEL is still a really recent technology that still presents certain uncertainties and, even though it clearly has some advantages towards other technologies, such as a very high efficiency, those advantages probably aren't worth the risk with this technology for this specific application.

Between AEL and PEMEL, the latter has a great advantage when it comes to Power-to-Gas applications specifically, that is the good flexibility, meaning that they are able to deal with the renewable power fluctuations because they have a really short start-up time, when compared to AEL. But even though that is a really great advantage when it comes to PEMEL, AEL is still more studied and more well known, with a lower capital and operational cost.

D.1 Proton exchange membrane electrolysis (PEMEL)

When comparing with AEL, PEMEL is still a recent technology, with the first electrolyser available in the market in 1978 (Götz et al., 2016) and only for small scale applications and large scale demonstrations up to 2 MW_{el} (de Bucy, 2016). These electrolysers use a proton exchange membrane (PEM) that acts both as an electrolyte and diaphragm, separating the hydrogen produced in the cathode, according to Eq. (D.1), from the oxygen produced in the anode, according to Eq. (D.2).



The operating temperature is limited to 80 °C due to possible degradation of the polymeric material of the PEM (Schiebahn et al., 2015) and the efficiency is in the same range of AEL. Currently, PEM electrolysers have a higher CAPEX than alkaline electrolysers, which is one of the main disadvantages of this technology, and that is due to the use of noble metal catalysts (Pt, Ir, Ru) and the use of titanium bipolar plates. The current CAPEX of 2 000 EUR kWh_{el}⁻¹ is likely to go down to 700 EUR kWh_{el}⁻¹ by 2030 and 400 € kWh_{el}⁻¹ by 2050 with the use of alternative and cheaper materials (de Bucy, 2016).

D.2 Solid oxide electrolysis (SOEL)

SOEL, which is also called high temperature electrolysis, operates at temperatures between 700 and 1 000 °C. This technology is the most recent among the three, being first developed in Germany between 1975 and 1987 (Schiebahn et al., 2015), and is still in a developing stage.

Due to high operating temperatures, the electrolyte and the electrodes should be made of resistant ceramic materials, resistant to high temperatures. The electrolyte used is usually zirconium dioxide, ZrO₂, doped with 8 %mol yttrium oxide, Y₂O₃, conducting O²⁻ ions from the cathode to the anode (Götz et al., 2016). Hydrogen is produced in the cathode, according to Eq. (D.3), and oxygen is produced in the anode, according to Eq. (D.4).





The main advantage of SOEL is related to the high operating temperature, that reduces the equilibrium cell voltage, as seen in Fig. D.1, thus decreasing the energy demand. This way, theoretically, efficiencies of over 100 % can be achieved, since it is calculated as the quotient of the chemical energy produced and the electricity needed for its production (Götz et al., 2016), but usually efficiencies of 80-90 % are reported (de Bucy, 2016).

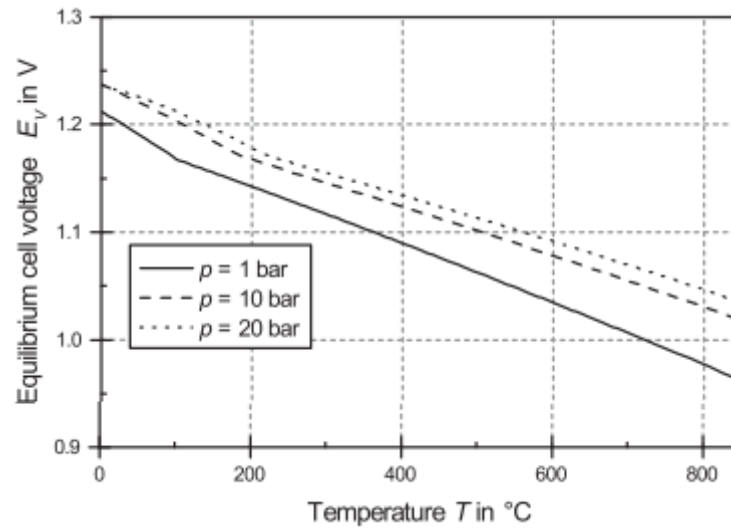


Figure D.1: Graphical representation of the equilibrium cell voltage, in V, as a function of the temperature, in °C, at different pressures. Retrieved from Götz et al. (2016).

The main disadvantages of this technology are the fast degradation of the materials, due to high temperatures, as well as the fact that these high temperatures imply that the product is a mixture of hydrogen and water vapor, thus requiring additional processing that comes with additional costs. There are not, however, any confirmed CAPEX values available for this technology, due to its initial stage.

Appendix E: Kinetic equation constants

Table E.1: Kinetic rate constants, equilibrium constants and adsorption constants for the CO₂ reaction kinetics. Retrieved from Neubert et al. (2017)

Parameter		Units	Aspen parameters
k_1	$1.94 \cdot 10^7 \exp\left(-\frac{103\,000 \text{ [J mol}^{-1}\text{]}}{RT}\right)$	[kmol kg _{cat} ⁻¹ s ⁻¹]	
$k_1^* = k_1 K_C K_H^2$	$9.13 \cdot 10^{-8} \exp\left(-\frac{29\,000 \text{ [J mol}^{-1}\text{]}}{RT}\right)$	[kmol Pa ^{-1,5} kg _{cat} ⁻¹ s ⁻¹]	$k_{1,0}^* = 9.13 \cdot 10^{-8}$ $E_{A,1}^* = 29 \text{ kJ mol}^{-1}$
k_2	$2.18 \cdot 10^{-2} \exp\left(-\frac{62\,000 \text{ [J mol}^{-1}\text{]}}{RT}\right)$	[kmol Pa ⁻¹ kg _{cat} ⁻¹ s ⁻¹]	$k_0^2 = 2.18 \cdot 10^{-2}$ $E_{A,2} = 62 \text{ kJ mol}^{-1}$
$\frac{1}{K_{Meth}}$	$1.027 \cdot 10^{-10} \exp\left(30.11 - \frac{26830}{T}\right)$	[Pa ²]	$A_{Meth} = 53.162$ $B_{Meth} = -26830$
$\frac{1}{K_{WGS}}$	$\exp\left(4.063 - \frac{4400}{T}\right)$		$A_{WGS} = 4.063$ $B_{WGS} = -4400$
K_C	$1.83 \cdot 10^{-2} \exp\left(-\frac{42\,000 \text{ [J mol}^{-1}\text{]}}{RT}\right)$	[Pa ^{-0,5}]	$A_C = -13.209$ $B_C = -5051.42$
K_H	$5.06 \cdot 10^{-5} \exp\left(-\frac{16\,000 \text{ [J mol}^{-1}\text{]}}{RT}\right)$	[Pa ^{-0,5}]	$A_H = -9.892$ $B_H = 1924.35$
K_{CO}	$8.23 \cdot 10^{-10} \exp\left(-\frac{70\,650 \text{ [J mol}^{-1}\text{]}}{RT}\right)$	[Pa ⁻¹]	$A_{CO} = -20.918$ $B_{CO} = 8497.20$
K_{H_2}	$6.12 \cdot 10^{-14} \exp\left(-\frac{82\,900 \text{ [J mol}^{-1}\text{]}}{RT}\right)$	[Pa ⁻¹]	$A_{H_2} = -30.425$ $B_{H_2} = 9970.53$
K_{CH_4}	$6.65 \cdot 10^{-9} \exp\left(-\frac{38\,280 \text{ [J mol}^{-1}\text{]}}{RT}\right)$	[Pa ⁻¹]	$A_{CH_4} = -18.829$ $B_{CH_4} = 4604.01$
K_{H_2O}	$1.77 \cdot 10^5 \exp\left(-\frac{88\,680 \text{ [J mol}^{-1}\text{]}}{RT}\right)$		$A_{H_2O} = 12.084$ $B_{H_2O} = -10665.70$

Appendix F: Kinetic model validation

The kinetic model validation was performed using an *RPlug* mirroring the same conditions reported in the experimental tests run by Garbarino et al. (2015). The operation conditions used by this author during the experiments performed over a temperature range of 250 to 500 °C, on a 20 % Ni/Al₂O₃ catalyst, are reported in Table F.1.

Table F.1: Operating conditions used in Aspen Plus to validate the kinetic model. Retrieved from Garbarino et al. (2015)

Gas inlet molar composition		
CO ₂	%	6
H ₂	%	30
N ₂	%	64
Inlet gas flow	Nm ³ min ⁻¹	7.5×10 ⁻⁵
GHSV	h ⁻¹	55 000

In this work a 50 % Ni/Al₂O₃ catalyst was considered since the kinetic rate equations used are adapted for this specific kind of catalyst. The properties of this catalyst are further reported in Table F.2. The diameters d_{ves} and d_{ses} are the diameters for spheres with equal volume and surface, respectively. The diameter of a sphere with the same volume was the one used in the present work.

Table F.2: Summary of the catalyst's properties. Retrieved from Gruber et al. (2021)

Length	mm	4.68
Diameter	mm	4.76
Diameter, d_{ves}	mm	5.41
Diameter, d_{ses}	mm	5.80
Density	kg m ⁻³	1578

The results obtained in the Aspen Plus simulation were compared with the experimental and thermodynamic equilibrium results reported by Garbarino et al. (2015) in terms of CO₂ conversion and CH₄ and CO yield. The results obtained are reported in Fig. F.1a) and b). The results are also reported in Table F.3, along with the experimental results obtained by Garbarino et al. (2015).

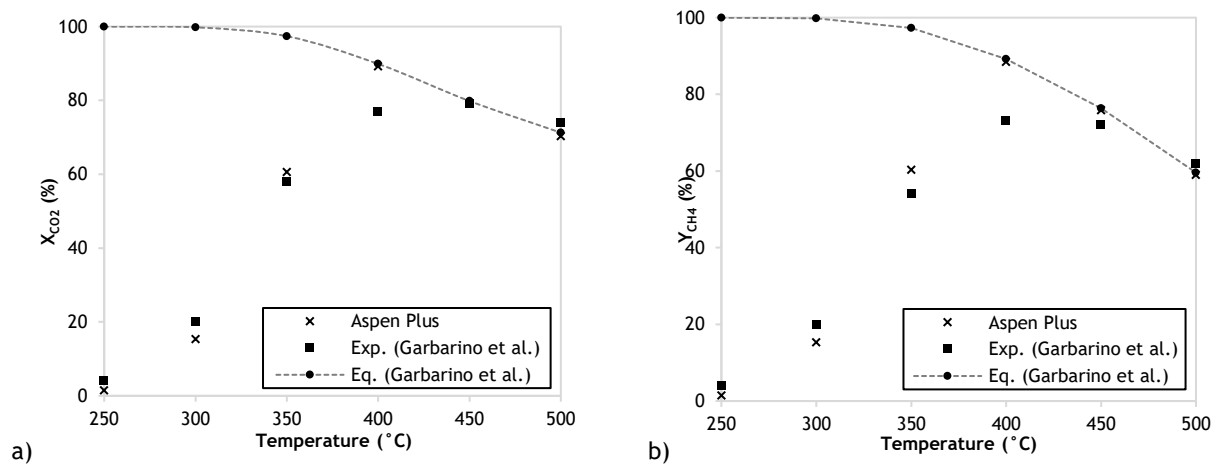


Figure F.1: Kinetic model validation with the results obtained by Garbarino et al. (2015) for:
a) CO₂ conversion and b) CH₄ yield

The results show that the kinetic model chosen for this work represents quite well the experimental results. The discrepancy between the Aspen Plus and the experimental results can be explained due the difference in the catalyst used, since the catalyst being used in this work is 50 % Ni/Al₂O₃ and the one used for the experimental results is 20 % Ni/Al₂O₃.

However, in terms of CO₂ conversion, it can be seen that the reaction grows closer to the equilibrium state as the temperature increases to about 400 °C, meaning that, more or less above that temperature, the reaction is controlled by the equilibrium. That is because the CO₂ methanation reaction is highly exothermic and therefore it is favored at lower temperatures by the thermodynamic equilibrium, resulting in CO₂ conversions close to 100 %, provided the required residence time in the reactor, the kinetics are slow at low temperatures and so, the equilibrium can only be attained at temperatures higher than 400 °C, where the kinetics increase. Above this temperature, the CH₄ formation is less favored by the equilibrium according to Le Chatelier's principle.

Table F.3: CO₂ conversion and CH₄ yield on 20 % Ni/Al₂O₃ and according to thermodynamic equilibrium. Retrieved from Garbarino et al. (2015)

T [K]	20% Ni/Al ₂ O ₃		Thermodynamic equilibrium	
	X _{CO₂} (%)	Y _{CH₄} (%)	X _{CO₂} (%)	Y _{CH₄} (%)
523	3	3	99.99	99.99
573	4	4	99.80	99.80
623	39	39	97.39	97.31
673	79	77	89.89	89.17
723	76	69	79.84	76.32
773	69	55	71.27	59.58

Appendix G: Equipment Costs

G.1 Heat Exchangers

The Shell-and-Tube heat exchangers purchase cost, C_P , in €, is obtained from Eq. (G.1), where C_B , in \$, represents the base cost of the equipment and F_M , F_P and F_L are material, pressure and length factors, respectively. The value 0.826 is the currency factor used to convert dollars to euros.

$$C_P = 0.826 \cdot F_M F_L F_P C_B \quad (\text{G.1})$$

The base cost is obtained from the heat exchangers outside tube area, A , in ft², through Eq. (G.2). This equation is valid for outside tube areas between 150 and 12 000 ft².

$$C_B = \exp \{11.0545 - 0.9228[\ln(A)] + 0.09861[\ln(A)]^2\} \quad (\text{G.2})$$

The material factor, F_M , is determined through Eq. (G.3), where a and b vary depending on the type of construction material. For this work a carbon steel/carbon steel construction was considered so a and b values were both 0.

$$F_M = a + \left(\frac{A}{100}\right)^b \quad (\text{G.3})$$

The length factor, F_L , relates to the tubes' length and the values for this factor are obtained from Table G.1.

Table G.1: Length factor, F_L , values for different tube lengths. Retrieved from Seider et al. (1999)

Tube length (ft)	F_L
8	1.25
12	1.12
16	1.05
20	1.00

The pressure factor is obtained from Eq. (G.4), where P represents the shell-side pressure, in psig.

$$F_P = 0.9803 + 0.018 \left(\frac{P}{100}\right) + 0.0017 \left(\frac{P}{100}\right)^2 \quad (\text{G.4})$$

Since it is quite time-consuming to use this process for all heat exchangers, this process can be done for just one heat exchanger and the other ones are determined through Eq. (G.5) that correlates the variation of cost with the equipment's capacity, that is the heat exchanged.

$$\frac{C_{P,1}}{C_{P,2}} = \left(\frac{Q_2}{Q_1}\right)^{0,6} \quad (\text{G.5})$$

G.2 Compressors and turbines

Centrifugal compressors purchase cost, C_P , in €, was determined through Eq. (G.6), where F_D and F_M are drive and material factors. Values for these factors are in Table G.2.

$$C_P = 0.826 \cdot F_D F_M C_B \quad (\text{G.6})$$

The base cost, C_B , in \$, for the compressors is determined through Eq. (G.7), where P_C corresponds to the compressors consumed power, in horsepower. This correlation is valid for P_C values in between 200 and 30 000 hp.

$$C_B = \exp \{7.5800 + 0.80[\ln(P_C)]\} \quad (\text{G.7})$$

Table G.2: Compressor drive factor, F_D , and material factor, F_M , values. Retrieved from Seider et al. (1999)

Compressor drive	F_D	Construction material	F_M
Electric motor	1.00	Cast iron or carbon steel	1.00
Steam turbine	1.15	Stainless steel	2.50
Gas turbine	1.25	Nickel alloy	5.00

In this work, electric motor and carbon steel compressors are considered so F_D and F_M values are both 1.00.

G.3 Tubular reactor

Tubular reactors' cost was determined in a similar way to a heat exchanger. The base cost, C_B , was determined through Eq. (G.2), where A represents the tubes outer surface area, in ft^2 .

The reactor was also assumed to be a carbon steel/carbon steel construction so the a and b values in Eq. (G.3) were both 0. The length factor was also determined based on the values in Table G.1.

The purchase cost, in €, was determined through Eq. (G.1).

G.4 Adiabatic reactor

The adiabatic reactors were designed as a pressure vessel. The purchase cost, C_P , in €, is determined as in Eq. (G.8), where F_M is the material factor, C_V is the empty vessel cost, including nozzles, manholes and supports, that depends on the weight, W , in lb, of the shell

and two heads (Eq. (G.9)), and C_{PL} is the cost for platforms and ladders, that depends on the vessel's internal diameter, D_i , in ft (Eq. (G.10)).

$$C_P = 0.826 \cdot (F_M C_V + C_{PL}) \quad (G.8)$$

$$C_V = \exp \left\{ 8.9552 - 0.2330 [\ln(W)] + 0.04333 [\ln(W)]^2 \right\} \quad (G.9)$$

$$C_{PL} = 2.005 (D_i)^{0.20294} \quad (G.10)$$

In Eq. (G.9), the weight, W , in lb, corresponds to the value given by Eq. (G.11), where t_s is the shell thickness, in in, given by Eq. (D.16), and ρ is the construction material's mass density, which in the case of carbon steel is considered 0.284 lb in^{-3} , an L is the vessel's length, also in in.

$$W = \pi (D_i + t_s) (L + 0.8 D_i) t_s \rho \quad (G.11)$$

$$t_s = \frac{P_d D_i}{2SE - 1.2 P_d} \quad (G.12)$$

In this last equation, P_d corresponds to the design pressure, in psig, given by Eq. (G.13), where P_o is the operating pressure of the vessel, in psig, S corresponds to the maximum allowable stress at the design pressure, in in^2 , which is considered to be approximately $15\,000 \text{ in}^2$, and E is the weld efficiency, that is 0.85 for thicknesses up to 1.25 in and 1.00 for larger ones.

$$P_d = \exp \left\{ 0.60608 + 0.91615 [\ln(P_o)] + 0.0015655 [\ln(P_o)]^2 \right\} \quad (G.13)$$

G.5 Flash drum

In order to determine the flash drum cost, it had to be properly sized first, as an horizontal vessel.

The first thing to consider is the ideal L/D ratio for the separator, which depends on the operating pressure of the vessel. For pressures in between 0 and 20 bar , the optimum L/D ratio is 3 (Sinnott, 1983). For preliminary design, the liquid height, h_v , is set as half of the vessel's diameter, D_v .

The settling velocity of the liquid droplets, u_t , in m s^{-1} , was determined through Eq. (G.14),

$$u_t = 0.15 \cdot 0.07 \left(\frac{\rho_L - \rho_v}{\rho_v} \right)^{0.5} \quad (G.14)$$

where ρ_L and ρ_v are the liquid and vapor mass densities, in kg m^{-3} .

The vapor volumetric flowrate, $Q_{v,v}$, in $\text{m}^3 \text{s}^{-1}$, is determined through Eq. (G.15), where $Q_{v,m}$ is the vapor mass flowrate, in kg h^{-1} .

$$Q_{v,v} = \frac{Q_{v,m}}{3600 \cdot \rho_v} \quad (\text{G.15})$$

The cross-sectional area for vapor flow, A_v , was determined from Eq. (G.16), where D_v is the vessel diameter.

$$A_v = \frac{\pi D_v^2}{4} \cdot 0.5 \quad (\text{G.16})$$

The vapor velocity, u_v , was determined through Eq. (G.17).

$$u_v = \frac{Q_{v,v}}{A_v} \quad (\text{G.17})$$

The vapor residence time required for the droplets to settle is determined as the quotient between the liquid height, h_v , and the settling velocity of liquid droplets, u_t , and the actual residence time required is determined as the quotient between the vessel length, L_v , and the vapor velocity, u_v (Sinnott, 1983). In order for the separation to be satisfactory, the required residence time and the actual residence time should be the same and so, by equalizing those equations, the vessel diameter can be determined, followed by the vessel length.

Knowing the flash drum dimensions, it is possible to determine its purchase cost, which was done in the same way as the adiabatic reactors.

Appendix H: Costs

Table H.1: Cost of equipment, utilities and revenues, for the scenario of cooled reactor without membrane, for pressures of 8, 10 and 15 bar

Pressure	bar	8	10	15
Equipment				
C-101	k€	28.51	31.23	36.18
C-102	k€	25.02	25.36	24.58
D-101	k€	6.95	6.80	6.56
R-101	k€	3.78	3.76	3.74
CAPEX	k€ y ⁻¹	8.32	8.70	9.20
Utilities				
Electricity	k€ y ⁻¹	17.72	19.85	23.87
Catalyst	k€ y ⁻¹	1.24	1.20	1.16
Others	k€ y ⁻¹	4.67	4.69	4.69
OPEX	k€ y ⁻¹	23.62	25.75	29.72
Revenues				
Biomethane	k€ y ⁻¹	826.62	825.82	824.41
Electricity	k€ y ⁻¹	15.05	15.00	14.72
Total CF	k€ y ⁻¹	809.7	806.4	800.2
dC	%	-	-0.41	-1.17
Wobbe Index	MJ Nm ⁻³	47.27	47.64	48.19

Table H.2: Cost of equipment, utilities and revenues, for the scenario of adiabatic reactors without membrane, for split factors of 0.3, 0.6 and 0.8, at an operating pressure of 10 bar and temperatures of 350 °C and 250 °C at the entrance of R-301 and R-302, respectively

Split fraction		0.3	0.6	0.8
Equipment				
R-301	k€	2.17	2.20	3.20
R-302	k€	1.83	4.91	12.8
D-301	k€	6.91	6.82	6.82
CAPEX	k€ y ⁻¹	1.41	1.80	2.95
Utilities				
Catalyst	k€ y ⁻¹	0.22	4.14	76.40
OPEX	k€ y ⁻¹	0.22	4.14	76.40
Revenues				
Biomethane	k€ y ⁻¹	834	828	823
Total CF	k€ y ⁻¹	833	822	744
dC	%	-	-1.31	-10.7
Wobbe Index	MJ Nm ⁻³	43.98	46.77	49.01

Table H.3: Cost of equipment, utilities and revenues, for the scenario of adiabatic reactors without membrane, for temperatures at the inlet of R-301 of 300, 350 and 400 °C, at an operating pressure of 10 bar and a split factor of 0.6

Temperature at the inlet of reactor 1	°C	300	350	400
Equipment				
R-301	k€	3.72	2.20	1.53
R-302	k€	6.51	4.91	2.09
D-301	k€	6.96	6.82	6.89
CAPEX	k€ y ⁻¹	5.35	1.80	1.36
Utilities				
Catalyst	k€ y ⁻¹	11.56	4.14	0.15
OPEX	k€ y ⁻¹	11.56	4.14	0.15
Revenues				
Biomethane	k€ y ⁻¹	838	828	833
Total CF	k€ y ⁻¹	799	800	810
dC	%	-	0.12	1.33
Wobbe Index	MJ Nm ⁻³	42.50	46.77	44.54

Table H.4: Cost of equipment, utilities and revenues, for the scenario of adiabatic reactors without membrane, for operating pressures of 10, 15, 20 and 25 bar, with temperatures of 350 and 250 °C at the inlet of R-301 and R-302, respectively, and a split factor of 0.6

Operating pressure	bar	10	15	20	25
Equipment					
R-301	k€	2.20	2.46	2.46	2.53
R-302	k€	4.91	6.10	7.75	9.03
C-301	k€	30.7	35.5	37.1	39.6
D-301	k€	6.82	6.57	6.41	6.31
CAPEX	k€ y ⁻¹	5.77	6.56	6.96	7.44
Utilities					
Electricity	k€ y ⁻¹	21.3	25.7	27.1	29.4
Catalyst	k€ y ⁻¹	4.14	8.48	17.71	27.99
Others	k€ y ⁻¹	0.06	0.08	0.06	0.06
OPEX	k€ y ⁻¹	25.6	34.2	44.9	57.4
Revenues					
Biomethane	k€ y ⁻¹	828	825	823	822
Total CF	k€ y ⁻¹	796	784	771	757
dC			-1.51	-3.14	-4.95
Wobbe Index	MJ Nm ⁻³	46.77	47.88	48.57	49.05

Table H.5: Utilities consumption for all the scenarios, separated by electrolysis, separation and reaction section

		Cooled without membrane	Cooled with membrane	Adiabatic without membrane	Adiabatic with membrane
Electrolysis					
Renewable electricity	kW	1 279	1 279	1 279	1 279
Deionized water	L h ⁻¹	118	113	115	114
Separation					
Electricity	kW	-	37	-	34
Cooling water	kg h ⁻¹	-	4 930	-	6 236
Reaction					
Electricity	kW	28	15	37	25
Cooling water	kg h ⁻¹	2 283	2 608	2 827	2 173
Steam	kg h ⁻¹	80	79	-	-
Boiler-feed water	kg h ⁻¹	242	238	-	-
Catalyst	kg y ⁻¹	12	15	197	114

Table H.6: Capital and operational costs, revenues and cash-flows for the four scenarios studied

		Cooled without membrane	Cooled with membrane	Adiabatic without membrane	Adiabatic with membrane
Capital Expenditures					
Equipment purchase cost	k€	1 840	1 935	1 839	1 990
Total Capital Investment	k€	2 576	2 709	2 574	2 786
CAPEX	k€ y ⁻¹	334	351	335	363
Operational Expenditures					
Utilities					
Electricity	k€ y ⁻¹	468	487	469	489
Cooling water	k€ y ⁻¹	10.7	10.8	9.09	10.8
Deionized water	k€ y ⁻¹	11.4	10.9	11.1	11.0
Catalyst	k€ y ⁻¹	0.10	0.12	1.60	0.93
Boiler feed water	k€ y ⁻¹	1.11	1.25	-	-
Steam	k€ y ⁻¹	11.1	12.2	-	-
O&M	k€ y ⁻¹	73.1	75.8	73.1	77.4
OPEX	k€ y ⁻¹	573	598	563	589
Revenues					
Biomethane	k€ y ⁻¹	825	822	823	835
Electricity	k€ y ⁻¹	13.2	14.9	-	-
Annual CF	k€ y ⁻¹	252	226	247	233
Cumulative CF at year 10	k€ y ⁻¹	2 515	2 262	2 464	2 332

Table H.7: Equipment costs, in k€, for the scenarios with adiabatic reactors both with and without membrane

Cooled without membrane			Cooled with membrane		
Equipment		Cost	Equipment		Cost
C-101	k€	36.2	C-201	k€	36.2
C-102	k€	22.5	C-202	k€	20.5
D-101	k€	6.57	C-203	k€	24.9
E-101	k€	7.03	D-201	k€	6.16
E-102	k€	5.02	E-201	k€	7.03
E-103	k€	6.82	E-202	k€	6.82
Electrolyzer	k€	1 404	E-203	k€	10.7
R-101	k€	3.61	E-204	k€	7.91
TK-101	k€	349	Electrolyzer	k€	1 404
-	-	-	Membrane	k€	47.5
-	-	-	R-201	k€	3.13
-	-	-	R-202		3.44
-	--	-	TK-201	k€	348
Total	k€	1 840	Total	k€	1 935

Table H.8: Equipment costs, in k€, for the scenarios with cooled reactors both with and without membrane

Adiabatic without membrane			Adiabatic with membrane		
Equipment		Cost	Equipment		Cost
C-301	k€	42.0	C-401	k€	50.3
C-302	k€	10.5	C-402	k€	42.0
D-301	k€	6.41	C-403	k€	10.5
E-301	k€	8.92	D-401	k€	6.14
E-302	k€	7.34	E-401	k€	7.67
E-303	k€	10.7	E-402	k€	7.97
Electrolyzer	k€	1 404	E-403	k€	10.4
R-301	k€	2.46	Electrolyzer	k€	1 404
R-302	k€	7.75	Membrane	k€	99.0
TK-301	k€	349	R-401	k€	2.28
-	-	-	R-402	k€	6.61
-	-	-	TK-401	k€	353
Total	k€	1 848	Total	k€	2 000