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Carbon dioxide removal in biomethane production

Bachelor thesis

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May 2023

NTNU
Norwegian University of
Science and Technology

Bachelor Thesis

NTNU
Norwegian University of Science and Technology
Faculty of Engineering
Department of Energy and Process Engineering

Institutt for energi- og prosessteknikk

Bacheloroppgave

Oppgavens tittel: **Project title (ENG): Carbon dioxide removal in biomethane production**	**Gitt dato: 22/05/2023**
	Innleveringsdato: 22.05.2023
	Antall sider rapport / sider vedlagt:
Gruppedeltakere: Chaymae El Hmidi Jebari	**Veileder: Bjørn Austbø**
	Prosjektnummer: 28
Oppdragsgiver:	**Kontaktperson hos oppdragsgiver:**

Fritt tilgjengelig: ☒

Tilgjengelig etter avtale med oppdragsgiver: ☐

Rapporten frigitt etter:

Gruppedeltakere signaturer:

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Abstract

The main objective of this project has been the preliminary design and optimization of the biogas upgrading stage as part of an LBM production process. An approach from the point of view of chemical engineering has been given to the process, carrying out the design of the basic and conceptual engineering, with the aim of obtaining as a result an efficient process and with adequate control of its operation and safety.

Moving forward, a preliminary optimization was carried out making use of the information obtained in the sensitivity analyses.

On the other hand, from an engineering point of view, it must be ensured that the plant satisfies the operating requirements, even in the presence of external influences. For this reason, a control solution has been successfully carried out, as well as its corresponding representation in a P&ID diagram.

Likewise, plant safety management is crucial in any industrial plant, and especially with the handling of toxic substances. For this reason, a study of the safety in the operation of the stripping column has been carried out using the HazOp methodology. The different sources of danger have been identified and actions or implementation of safeguards have been proposed to avoid and/or alleviate these situations.

The purge stream of CO2 and H2S resulting from the regeneration of the solvent was identified. This stream cannot be released into the atmosphere without being treated to comply with the imposed regulations. On the other hand, an alternative solution is to give it an economic output by applying a treatment process. The proposed treatment process consists of 4 stages; dehydration, separation of CO2 and H2S, conversion of H2S to S through the Claus process, and finally the liquefaction of CO2. In this way, both S and CO2 can be sold to different interested parties, usually to other chemical plants that can use these substances as raw materials to produce their products.

Sammendrag

Hovedmålet med dette prosjektet har vært den foreløpige designen og optimaliseringen av biogassoppgraderingsfasen som en del av en LBM-produksjonsprosess. En tilnærming fra et kjemiteknisk synspunkt er gitt til prosessen, gjennomføring av utformingen av den grunnleggende og konseptuelle konstruksjonen, med sikte på å oppnå som et resultat en effektiv prosess og med tilstrekkelig kontroll over dens drift og sikkerhet.

Fremover ble det foretatt en foreløpig optimalisering ved bruk av informasjonen innhentet i sensitivitetsanalysene.

På den annen side må det ingeniørmessig sikres at anlegget tilfredsstiller driftskravene, selv ved ytre påvirkninger. Av denne grunn er det vellykket gjennomført en kontrollløsning, samt dens tilsvarende representasjon i et P&ID-diagram.

På samme måte er styring av anleggssikkerhet avgjørende i ethvert industrianlegg, og spesielt ved håndtering av giftige stoffer. Av denne grunn er det utført en studie av sikkerheten ved driften av strippingsøylen ved bruk av HazOp-metodikken. De ulike kildene til fare er identifisert og tiltak eller implementering av sikkerhetstiltak er foreslått for å unngå og/eller lindre disse situasjonene.

Rensestrømmen av CO2 og H2S som følge av regenereringen av løsningsmidlet ble identifisert. Denne bekken kan ikke slippes ut i atmosfæren uten å bli behandlet for å overholde de pålagte forskriftene. På den annen side er en alternativ løsning å gi den et økonomisk resultat ved å bruke en behandlingsprosess. Den foreslåtte behandlingsprosessen består av 4 stadier; dehydrering, separering av CO2 og H2S, konvertering av H2S til S gjennom Claus-prosessen, og til slutt flytendegjøring av CO2. På denne måten kan både S og CO2 selges til ulike interessenter, vanligvis til andre kjemiske anlegg som kan bruke disse stoffene som råstoff for å produsere sine produkter.

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1. Introduction

1.1. Background

In the following decades, bioenergy obtained from biogas and biomethane has great potential to become an alternative to fossil fuels globally, given its environmental and economic appeal.

Until now, fossil fuels have led the use of energy in different sectors, such as transport and heating. However, the recent emphasis on the emission of greenhouse gases, for instance CO_2, and consequent global warming have gained relevance due to political and environmental reasons.

The rapid increase in greenhouse gas emissions, a consequence of the increase in energy demand, demonstrates the imperative need to find a suitable alternative to fossil fuels. In fact, the International Energy Agency (IEA) predicts a 57% increase in carbon dioxide emissions by 2030 due to economic and industrial growth.(International Energy Agency, 2022)

The release of CO_2 into the atmosphere must be reduced. Over time, many alternatives have been investigated, such as the use of biofuels and the capture of CO_2 emissions. However, in the medium term, renewable energies will continue to require the contribution of fossil fuels to meet energy needs.

In the process of industry and transport decarbonization, the use of both will continue to be necessary, given that renewable energies still do not provide a sufficiently mature solution. In fact, according to bibliographical sources, the demand for natural gas will remain practically constant until 2030, the year after which environmental policies will cause a reduction in demand for 2050.(Mete, 2020)

In an effort to provide a solution to the stated problematics, biofuels are gaining popularity over time given their ability to partially or totally replace traditional fuels. This is mainly because biofuels are considered an emission neutral energy source and they can play a key role in the energy transition. In fact, by 2030 the European Union intends to increase the contribution of renewable energy in transport to 14% of the total, with a minimum of 3,5% biofuels.

There are already many ongoing projects for the production and integration of biofuels. For example, the Biokraft AS plant, located in Skogn (Norway), which produces biogas from fish and manure waste, with a capacity to produce about 12,5 MCM of liquid fuel.(Norske Skog, 2021) Another project in an advanced state is the biomethane plant located in La Galera (Spain), which injects and distributes its production through the Enagás natural gas network.(La Vanguardia, 2023)

The use of biofuels has several advantages, such as its high flexibility as it can be stored and transported using cryogenic tanks when injection into the gas network is not possible.

Specifically, biogas is a gas mixture consisting primarily of methane and carbon dioxide, with smaller amounts of components such as hydrogen sulfide, water, and siloxanes, produced by anaerobic digestion. Biogas that goes through an upgrading process, where it is separated from carbon dioxide and other impurities, is called biomethane and can be a substitute for natural gas due to the similarity of its properties.

Additionally, a methanation process can also be carried out prior to upgrading, with which it is intended to convert part of the carbon dioxide into methane through the Sabatier reaction, which implies the additional feeding of hydrogen.

In any case, after this process it is vitally important to eliminate excess carbon dioxide by upgrading, to avoid possible freezing of it during the liquefaction process and therefore, possible breakdowns and malfunctions of the equipment.

Chemical absorption is often applied for upgrading, while alternative technologies include water scrubbing, physical absorption, adsorption, membrane separation, and cryogenic separation. The choice of the process to remove CO_2 must be made considering the most relevant criteria for the specific application, since this has a direct impact on the efficiency of this stage and, finally, of the biofuel production process in general.

The biogas upgrading process is a highly energy-demanding process, especially carried out on a large scale. In fact, one of the challenges that this technology presents is the energy efficiency. In upgrading by chemical absorption, the reduction in energy consumption is mainly linked to the energy consumption of the reboiler in the regeneration section. For this reason, it is vitally important to carry out the design of each stage of the process in such a way that the most integrated and energy efficient and economical result is obtained.

1.2. Objective

The main purpose of this Bachelor Thesis is to design the upgrading stage of the biomethane production process using Aspen HYSYS, specifically the carbon dioxide removal process. Additionally, it is also intended to propose solutions for the management of the potential residual streams of the process, as well as to carry out a preliminary design of the necessary processes.

In the design of the separation stage, it is intended to carry out a safety study using the HAZOP methodology, as well as the design of the control strategy necessary for a proper operation of the process.

1.3. Scope of Work

The tasks that are intended to be met in the realization of this project are listed below.

- Carry out a bibliographical study on biomethane and its production process, as well as the power-to-gas concept in general, and specifically on the carbon dioxide removal process in the upgrading stage.
- Design of the carbon dioxide removal process in a liquified biomethane plant (LBM) plant using HYSYS. Carry out a preliminary design using the solver Hyprotech SQP available in HYSYS.
- Provide solutions for the management of the residual streams and comply with current legislation when necessary. Preliminary design of the processes.
- Carry out a safety study of the operation of a piece of equipment applying the Hazard and Operability Analysis methodology.
- Carry out the design of the control strategy of the upgrading stage and prepare the corresponding P&ID.

1.4. Methodology

The results obtained in this Bachelor Thesis are based mainly on the data obtained using the software Aspen HYSYS V11 to carry out the simulations of the process and a bibliographical study carried out from resources provided by the NTNU.

The different unit operations have been used to establish the process flowsheet. Additionally, the Case Study tool has been used to perform sensitivity analysis of the variables, as well as the Optimizer tool in the optimization of previously established objective functions.

To carry out the different technical illustrations, such as the PFD and P&ID diagrams of the process under study, software Microsoft Visio has been used.

1.5. Thesis Outline

The thesis contains eight chapters, including the introduction.

- **Chapter 1**. Contains an explanation of the background, the objective, scope and methodology followed in the thesis.
- **Chapter 2**. A bibliographic study on biomethane is presented, starting from a global vision of the current state of the energy sector, as well as its future evolution with the availability of new technologies. More specifically, a theory on biomethane is presented, starting from biogas and its fermentation process, and continuing with existing technologies for its processing.
- **Chapter 3**. The different technologies available for the upgrading stage are presented, the object on which the thesis focuses. The choice of technology to be used in the design of the process is made.
- **Chapter 4**. The design process of the upgrading stage based on amine absorption technology is shown, starting from the base case in which the design objectives are presented, up to a sensitivity analysis of the main process variables.
- **Chapter 5**. The theory behind an engineering optimization process is briefly introduced and notions are given about the use of the Optimizer tool in Aspen HYSYS, specifically through the Hyprotech SQP solver. A preliminary optimization of the process is carried out.
- **Chapter 6**. The process is approached from a chemical engineering point of view, making a control proposal for the upgrading plant, as well as the safety study of a process unit using the HazOp methodology.
- **Chapter 7**. The residual streams of the process are identified, and a solution is proposed for their management and/or obtaining an economic benefit.
- **Chapter 8**. The conclusions reached after the completion of the thesis are presented. Proposals for future work are given in relation to the limitations in the scope of this thesis.

2. Literature Study on Biomethane

This section presents the bibliographic study carried out on biomethane, with the aim of founding the bases for subsequent tasks. Firstly, a brief context on the current situation of the energy sector and fossil fuels is given, as well as a presentation of alternative technologies. Next, it delves into biogas and more specifically into biomethane and its production process.

2.1. Consumption of Natural Gas in the EU and the Energy Transition

Currently, there is abundance of conflicting information regarding the supply and demand of natural gas in the markets, which can lead one to mistakenly think that there is a dramatic drop in its demand.

Contrary to what one might think, in the short and medium term, renewable energies will continue to need natural gas until a viable method for large-scale electricity storage is developed, despite advances in energy efficiency and the increase in the use of renewable energies.(Mete, 2020)

Natural gas and renewable energies are not necessarily enemies considering the uncertainty that the current energy transition entails. In the decarbonization of the electricity industry, the use of both is still necessary, and as regards the transport industry in general, renewable energies do not yet offer a mature solution.

On the other hand, the decarbonization plans of the EU, whose policy consists of three fundamental pillars, will also influence future demand; the increase in the use of renewable energies, the reduction of CO_2 emissions and other greenhouse gases, and an improvement in energy efficiency.

According to bibliographical sources, the demand for natural gas will remain practically constant until 2030, the year after which environmental policies will cause a reduction in demand for 2050.(Mete, 2020)

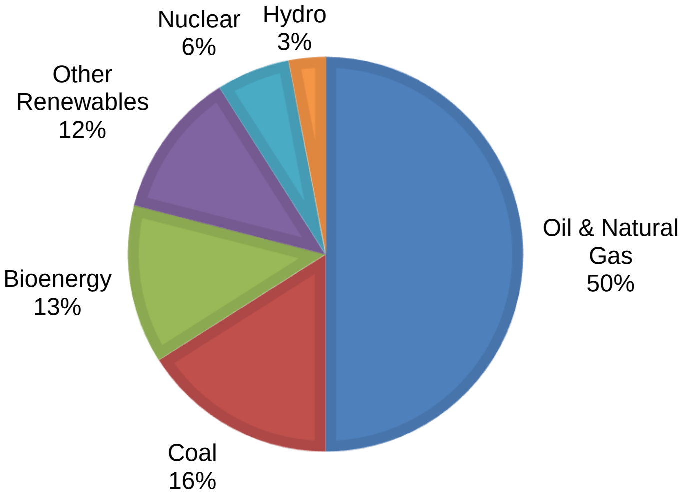


Figure 2.1 IEA prediction of energy sources in the year 2050.(International Energy Agency, 2022)

It should be noted, then, that natural gas plays an important role in conjunction with renewable energy. The fact that it presents a significant difference with other fossil fuels such as coal and oil in greenhouse gas emissions, as well as the advantages in storage and transportation flexibility that it offers (through pipelines and as LNG) make it a very valuable tool in an energy transition like the one that is being faced.

2.2. The Role of Renewable Energy and Other Low Carbon Gases

Despite the fact that, as previously mentioned, natural gas will continue to maintain demand in the near future, there is a need to reduce dependence on fossil fuels. Especially taking into account the fact that from the year 2030 natural gas will be considered high carbon, and the EU 2050 net zero carbon ambition.(Mete, 2020)

Some of the alternatives that currently exist to natural gas are presented below.

2.2.1. Hydrogen

Hydrogen is considered a fuel similar to gasoline due to its properties, and it can be obtained from coal and natural gas.(Gregorie et al., 2020)

There are different technologies with which it can be produced, for example carbon capture and storage (CCS), through the decarbonization of natural gas using steam forming processes. This practice is commonly known as Blue Hydrogen and could be especially useful in the heat sector, although CO_2 capture technology and adaptation of current distribution networks are currently very expensive.

Another method to produce hydrogen is through electrolysis using renewable energy, a method known as Green hydrogen. This is known as renewable gas and is mainly pollution-free.

Hydrogen can be used in various sectors, such as in the transport industry, in electric cars, buses, boats and other vehicles. Hydrogen can also contribute to the production of electricity and the heating system, through the use of fuel cells.

There are some challenges to the large-scale use of hydrogen in the mentioned applications; the production of hydrogen in sufficient quantities, the integration of hydrogen into the existing natural gas network and the competition with another interesting alternative, biogas.

2.2.2. Biogas

Another alternative to natural gas is biogas, which is obtained from biomass such as waste and other similar products. Historically it has been used in the production of electricity, heating and cooking, although more recently as a substitute for natural gas.(Ryckebosch et al., 2011)

For its integration into the natural gas network, biogas must go through an upgrading process (separation of certain substances and purification of methane) to become considered biomethane. This renewable gas can play a vital role in the energy transition due to the similarity of its properties with natural gas, as will be seen later.

Despite this, it is necessary to continue developing technologies for the safe integration of biomethane into the existing natural gas network.

2.2.3. Ammonia

Ammonia is produced from renewable energy sources such as wind, solar or hydro power, through the electrolysis of water to produce hydrogen and oxygen. The hydrogen then combines with nitrogen to form ammonia, which can be easily stored and transported.(Mete, 2020)

One of the main advantages of ammonia as a low emission fuel is its high energy density, similar to that of gasoline. It can be used in a variety of applications, including electric power generation, transportation, and heating. In fact, it has been used as fuel for ships and ferries in Japan and Norway, and as fuel for buses in China.

Another advantage of ammonia is that it does not emit greenhouse gases such as carbon dioxide when burned. Instead, it produces nitrogen and water vapor, which are harmless to the environment. However, ammonia production requires energy, and if that energy comes from fossil fuels, it could lead to greenhouse gas emissions.

There are also some challenges associated with using ammonia as a low emission fuel, including its toxicity and flammability. Safety measures and regulations must be established to ensure their safe handling and storage.

2.2.4. Carbon Capture Utilization and Storage

Carbon Capture Utilization and Storage (CCUS) is a practice that consists of the capture of CO_2 (either before or after its emission) to be used in the production of another product, or to be stored underground. Carbon dioxide is stored in aquifers and depleted hydrocarbon reservoirs.(Mete, 2020)

The existing technologies for this practice are classified into pre-combustion, oxy-fuel combustion, post-combustion and chemical looping, depending on the stage in which carbon is captured.

Currently, chemical absorption is the most widely used method due to its technological maturity for this practice.

Although CCUS technology has great potential to reduce greenhouse gas emissions, there are still challenges to overcome, such as high costs, lack of infrastructure, and the need for appropriate policies and regulations to drive its large-scale implementation.

2.3. Biogas

Biogas can be produced from different organic substrates, such as manure, sludge, organic waste and crops. This biogas is produced in equipment called digesters, although it can also be produced by anaerobic degradation in landfills, in which case this biogas is called landfill gas.(Asgari et al., 2011)

Biogas, which consists mainly of methane and carbon dioxide, can be used as a source of energy in generation plants, as fuel for vehicles, or as a substitute for natural gas by supplying it to the natural gas grid. The methane present in biogas can be used in various industrial processes or as raw material in industry.

Depending on the final use that the biogas will have, different treatments will be necessary. In the case of use as fuel or as a substitute for natural gas, where it is necessary to have a high energy power, the biogas must go through an upgrading process. Table 2.1 presents a comparison with fossil fuels of some fuel properties.

Table 2.1 Selected fuel properties.

Energy source	Density @STP (kg/m^3)	Fuel heating value (kJ/kg)	Ignition temperature (°C)	Air/fuel ratio (kg/kg)	Octane number
Methane	0,72	50000	650	17,2	100
Propane	2,02	46300	470	15,6	35
Petrol	750	43000	220	14,8	-
Diesel	850	42500	220	14,5	-
Natural gas	0,83	57500	600	17,0	80
Biogas (60% methane)	1,2	18000	650	10,2	130

2.3.1. Substrates

The main sources of organic matter from which it is possible to obtain biogas are landfills, animal waste, sewage and urban solid waste.

2.3.1.1. Landfills

In landfills, solid urban waste is buried under layers of ground, while microorganisms rapidly consume the oxygen contained in these layers, creating an anaerobic environment that allows anaerobic digestion to take place, through which the organic fraction of the waste is decomposed, and landfill gas is generated.(Ong et al., 2014)

The obtained landfill gas has a composition similar to that of biogas but may contain other gases from the decomposition of landfill waste. Landfills must have a system for the recovery of landfill gas. One of the objectives for which landfill gas is collected is for safety reasons, to avoid accidents that can be generated due to the formation of explosive gas mixtures, since methane has explosive limits at 5-15% concentration in the air.

It must also be guaranteed that methane emissions into the atmosphere and gases that cause bad odors are minimized. The most widely used system to control emissions in a landfill is the torch.

2.3.1.2. Wastewaters

Although the anaerobic digestion of wastewater is not as widespread as landfills, it is an interesting option to try to reduce the amount of sludge produced during wastewater treatment. This system works by pumping the solids from primary and secondary clarifiers to an anaerobic digester where the organic fraction is converted into biogas. Anaerobic digestion provides some energy savings by reducing the organic load that must be destroyed and can make the wastewater treatment plant a net energy producer.(Ong et al., 2014)

The sludge obtained as effluent from anaerobic digestion can be used as fertilizer or for the production of energy by incineration. It is also possible to deposit these effluents in specific landfills for this purpose. However, this practice can have negative effects on the environment due to greenhouse gas emissions into the atmosphere, which is why this use is prohibited in most European countries.

2.3.1.3. Agricultural and Livestock Waste

The anaerobic digestion of agricultural and livestock waste represents a good alternative to the dumping of these residues. A reduction in waste of up to 50-70% can be achieved, and a reduction in methane emissions of 60-70%. The nitrogenous compounds are converted into ammonia and the effluents can be used as fertilizers.(Ong et al., 2014)

The digesters that are used can have different arrangements, from perfect stirred tanks to piston flow pools. Different designs will affect the retention time, efficiency, and cost of the system. The choice of one or the other depends on several factors, such as the availability of land and volume requirements.

2.3.1.4. Solid Urban Waste

In many countries there is a common practice of collecting urban solid waste (USW) and mixing it with other streams in power generation plants or depositing it in landfills. This practice is not optimal from an energetic point of view, since the organic part could be separated and used as a substrate for anaerobic digestion.(Ong et al., 2014)

Due to this, it is currently being decided to separate the organic part of the USW to use it as raw material for anaerobic digestion. The goal is to recycle this organic waste instead of sending it to landfill or incineration.

The treatment of USW is similar to that carried out on agricultural and livestock residues, and in some cases some residues can be mixed with others. Digesters used to treat USW are more prone to performance changes and disturbances than other systems due to the unpredictable heterogeneity of the wastes fed to the digester.

2.3.2. Biogas Composition

Biogas consists mainly of methane and carbon dioxide. In addition to these compounds, in biogas there are other secondary compounds such as hydrogen sulphide or ammonia. During anaerobic digestion, while methane and carbon dioxide are produced, H_2S and NH_3 are also produced as a consequence of the transformation of compounds containing sulphur and nitrogen, respectively.

Landfill gas is produced during the anaerobic digestion of organic matter in the landfill and its composition is very similar to that of biogas. The methane content of landfill gas is generally lower than in biogas and it normally contains nitrogen due to air leaking into the landfill during recovery.

The composition of biogas depends on the source of organic matter used to obtain it, the technique used to generate it and how it has been collected. For example, gas produced in digestion tanks has a higher energy content than gas obtained from landfills. This is due to the fact that more controlled process can be achieved in the digestion tanks.

The different compounds that can form part of a biogas obtained by anaerobic digestion are described below, in addition to methane, the main compound that provides added value to the gas obtained.(Farghali et al., 2022)

- **Carbon dioxide**. CO_2 is the by-product of anaerobic digestion that is found in the highest proportion. The presence of CO_2 in the biogas reduces its energy, since it causes the concentration of methane in the biogas to decrease.
- **Sulfur compounds**. Sulfur is present in organic matter, especially in that which contains proteins in high concentration. Compounds such as H_2S or mercaptans are produced as a consequence of the biological degradation of organic matter. Sulfur compounds can be harmful to health and potentially toxic. Furthermore, H_2S in the presence of moisture is corrosive due to the formation of sulfuric acid.
- **Water**. Biogas is usually saturated with water vapor. Water not only decreases the energy content of biogas, but any presence of H_2S or CO_2 can dissolve and form corrosive acids.
- **Silicon compounds**. Siloxanes, used in industry and in consumer products, are present in biogas. On combustion, siloxanes are converted to SiO_2, a crystalline compound known as silica, with physical and chemical characteristics similar to those of glass. This means that its deposition on engines, heat exchangers, gas treatment systems, pipes and other equipment causes major problems during operation.
- **Nitrogen**. It is present in the air that is drawn into the system. Nitrogen dilutes the methane in biogas, reducing its energy content.
- **Oxygen**. It also gets into the system through the air. Oxygen promotes microbial growth, making the anaerobic conditions less than optimal and, therefore, the yield decreases. In addition, depending on the concentrations in which oxygen and methane are found, there is a risk that an explosive atmosphere can be generated.
- **Volatile organic compounds (VOCs)**. This includes aromatics, alkanes, and halocarbons. They are quite polluting and can form very toxic compounds in their combustion.
- **Particles**. Biogas can carry dust from the gas collection systems. These particles can erode the equipment used for biogas extraction.

As previously mentioned, the different types of microorganisms used, the source of organic matter, the environmental conditions and the operating parameters produce variations in the composition of the biogas generated. However, it is the source of organic matter that has a greater influence on the biogas composition.

Table 2.2 compares the composition and some properties of biogas and natural gas. CO_2 is a major component in biogas, while in natural gas it is an almost residual component. In addition, natural gas contains hydrocarbons other than methane, while biogas exclusively contains methane. This makes the energy content of biogas less than that of natural gas. This means that the biogas must undergo an upgrading process in order to remove the CO_2 from the biogas and, in this way, increase its calorific value to levels comparable to those of natural gas.

Table 2.2 Comparison of properties and composition of biogas and natural gas.(Ryckebosch et al., 2011)

	Biogas	Natural gas (Denmark)	Natural gas (Netherlands)

Heating value (kWh/Nm^3)	6,5	11	8,8
Other hydrocarbons (%)	0	9,4	3,5
CH_4 (%)	60-70	89	81
H_2 (%)	0	0	-
CO_2 (%)	30-40	0,67	1
N_2 (%)	0,2	0,28	14
O_2 (%)	0	0	0
H_2S (ppm)	0-4000	2,9	-
NH_3 (ppm)	100	0	-

2.3.3. Biological Production of Biogas

The process by which microorganisms degrade the complex molecules that make up substrates or organic matter in the absence of oxygen to produce biogas is called anaerobic digestion. Anaerobic digestion is a metabolic process that consists of four stages: hydrolysis, fermentative stage, acidogenic or acidogenesis, acetogenic stage or acetogenesis and methanogenic stage or methanogenesis. Figure 2.1 shows a diagram of the stages of anaerobic digestion of organic matter. Each of these stages is briefly explained below.(Asgari et al., 2011)

- **Hydrolysis**. During the first stage of anaerobic digestion, larger complex molecules are broken down into their simpler molecular components, which can be assimilated by microorganisms. Thus, proteins are broken down into amino acids, lipids into long-chain fatty acids and glycerol, carbohydrates into sugars, cellulose into cellobiose and glucose, and hemicellulose into pentose and hexose.
- **Fermentative stage**. The simpler organic molecules are broken down into short-chain fatty acids, such as butyric acid, propionic acid and acetic acid, the latter in greater proportion, in addition to also obtaining alcohols, hydrogen and carbon dioxide. Bacteria that carry out these reactions can grow under acidic conditions. To produce acetic acid, these bacteria need the oxygen and carbon present in the substrate, thus creating anaerobic conditions that are necessary for methane-producing microorganisms.
- **Acetogenic stage**. Organic acids are converted into acetic acid and other simple compounds such as hydrogen and carbon dioxide.
- **Methanogenic stage**. Some microorganisms convert the acetic acid generated in the acetogenic stage into methane (acetoclastic methanogenesis) and carbon dioxide, while others convert hydrogen into methane and carbon dioxide (hydrogenotrophic acetogenesis).

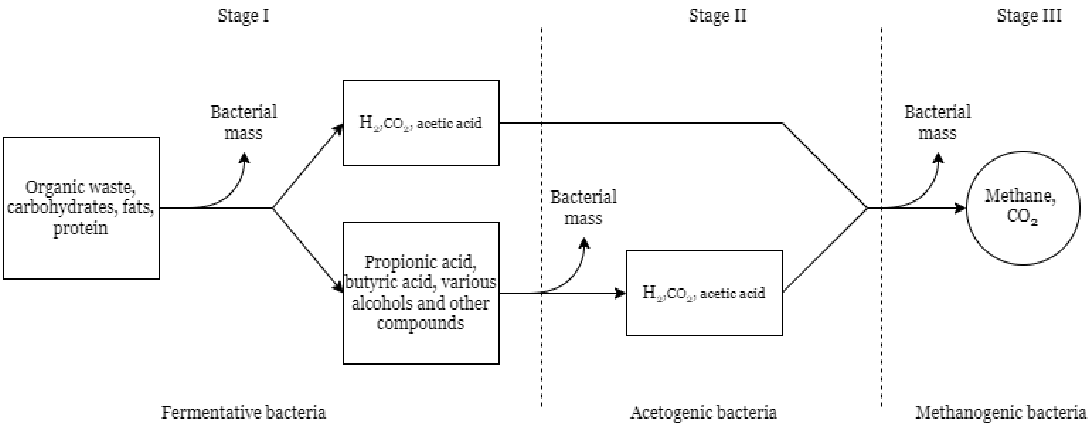


Figure 2.2 Diagram of the stages of anaerobic digestion of organic matter.

2.4. Biomethane

Biomethane is the gas resulting from biogas upgrading, with the reduction in the concentration of acid gases, moisture and other pollutants. When compressed for use as a vehicle fuel it is called Liquified Biomethane (LBM).

It has gained great popularity especially in European countries, where research and studies are carried out to develop new applications for biogas.

Biomethane has an LHV of around 36 MJ/m^3. It is indistinguishable from natural gas and so can be used without the need for any changes in transmission and distribution infrastructure or end-user equipment and is fully compatible for use in natural gas vehicles.(International Energy Agency, 2022)

2.4.1. Biomethane Production and Use in the World

The development of biogas has been uneven across the world, as it depends not only on the availability of feedstocks but also on policies that encourage its production and use. Europe, China and the United States account for 90% of global production, as can be seen in Figure 2.2.(International Energy Agency, 2022)

Currently Sweden, Germany and the US are the countries with the most developed and established biomethane industry. Although globally it is still a newborn industry, some European countries have several operational biogas plants.

The Intergovernmental Panel on Climate Change has stated that greenhouse gas emissions need to be reduced to less than half of the global levels seen in 1990. As a step towards this objective, European energy production from biogas reached 6 million tons of oil equivalents (Mtoe) in 2007. The European Union (EU) is responsible for approximately 60% of the world's biogas production and is expected to maintain its leading position. (Koonaphapdeelert et al., 2020)

While the biomethane market is still relatively new on a global scale, certain European countries have been actively involved in biomethane production for years and have multiple operational plants, as can be seen in Table 2.3. However, other countries within Europe have yet to initiate any biomethane projects.

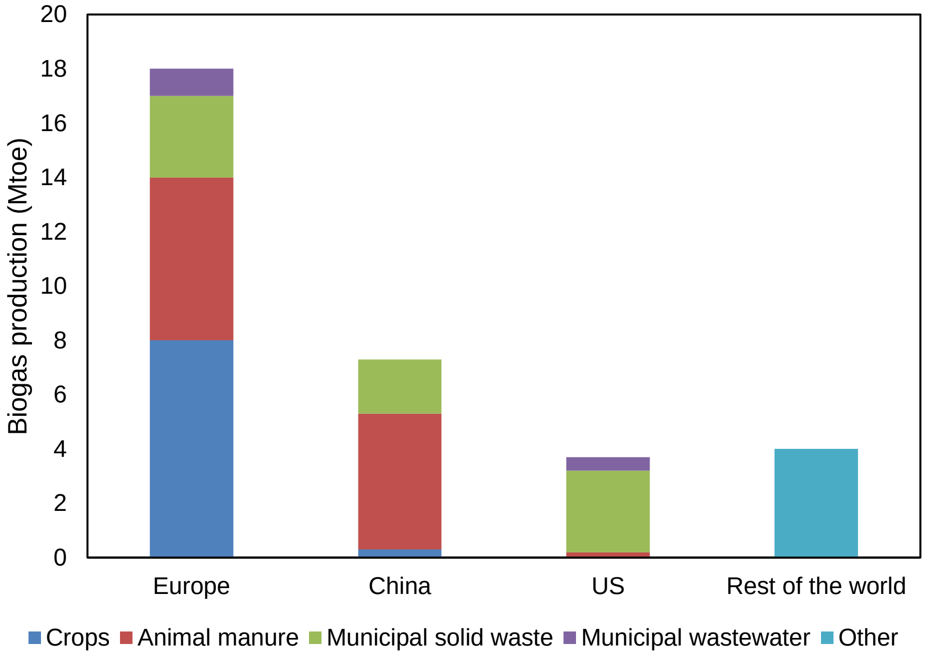


Figure 2.3 Biogas production by region and feedstock in 2018. (International Energy Agency, 2022)

Table 2.3 Production of biomethane in European countries.(Koonaphapdeelert et al., 2020)

Country	Number of feed-in plants	Total feed-in capacity (Nm³/h)	Main market drivers	Dominating feedstock
Germany	110	66830	Government support schemes for energy crops	Energy crops Organic waste Manure
Sweden	7	2610	Vehicle fuel	Sewage sludge Organic waste
UK	2	160	Heat market	Organic waste
France	2	715	Government support schemes Vehicle fuel	Sewage sludge Organic waste
Netherlands	17	7605	Green gas products Government support schemes	Sewage sludge Organic waste Landfill gas
Switzerland	13	1664	Government support schemes Vehicle fuel	Sewage sludge Organic waste Manure

2.4.1.1. Sweden

Sweden is one of the global leaders in biomethane production. In 2013, the use of renewable energies in its Energy Mix reached 52%, being the highest in the EU. Biomethane is distributed using its natural gas pipeline network.

In Sweden, biomethane is mainly used as a fuel for vehicles. In 2016 it had more than 55,000 vehicles capable of consuming biomethane. As if that were not enough, the Swedish government has set a goal for 2030 to have a fleet of vehicles completely independent of fossil fuels.(Koonaphapdeelert et al., 2020)

2.4.1.2. Germany

Germany is currently the largest producer of biogas worldwide due to the installation of plants on farms. The main uses of biomethane in Germany are transportation and as a substitute for natural gas.

The German government has set ambitious targets for 2030; produce 10 billion Nm3 of biomethane as a substitute for natural gas, and reduce emissions by at least 40% compared to 1990 emissions.(Koonaphapdeelert et al., 2020)

Thanks to the well-developed German natural gas pipeline networks distributed throughout the country, biomethane produced in one place can be used for multiple applications throughout the country.

2.4.1.3. USA

The USA has more than 2,000 biogas production plants, and has great long-term potential to continue developing its biogas production industry. In fact, after an estimate of this potential, it was determined that 18.5 billion m3 of biogas/year could be produced, generating approximately 41.2 TWh of electricity.(Koonaphapdeelert et al., 2020)

2.4.2. Advantages of the Use of Biomethane

The use of biomethane brings numerous benefits at different levels, and its potential for use worldwide has been demonstrated in different sectors including the biofuel industry, waste management and bioenergy. Listed below are some of the advantages provided by the use of biomethane.(Koonaphapdeelert et al., 2020)

- It is a renewable energy source.
- GHG emissions in its combustion are lower compared to diesel or gasoline.
- Biomethane can be obtained from locally produced biogas, unlike natural gas.
- The digestate, a by-product of the biogas production process, can be sold as a biofertilizer.
- Potential for reducing the contamination of aquifers due to livestock activity. It provides the possibility of processing this waste in the biogas plant.
- The increase in the use of biomethane in a country increases the reliability in the use of natural gas.

- Reduces fuel import costs and has the potential to increase employability at the local level. Also, rural areas especially benefit as most of the revenue is produced there.

2.4.3. Analysis of Strengths, Weaknesses, Opportunities and Threats

The use of biomethane has potential barriers that may interfere with its development and implementation in today's industry. To identify these barriers, an analysis of the strengths, weaknesses, opportunities and threats caused by the production and use of biomethane has been carried out, and is presented in Table 2.4. (Franco et al., 2021)

Table 2.4 SWOT Analysis of the potential impacts of producing and using biomethane.(Franco et al., 2021)

Internal origins (attributes of the organization)	
Strengths	**Weaknesses**
- Enabling a green transition - Contributing to waste management - Contributing to greater energy security - Generation of clean energy and reduction of GHG emissions in various sectors - Renewable source for the production of gas - Promoting recycling/reuse of bio-wastes - High-efficiency gas - Production of biofertilizer as a by-product - Use as an alternative source of energy in domestic networks - Combined heat and power production - Use of biomethane as motor fuel	- Little development of research on environmental impacts - High-cost technology - Use for environmental purposes is still limited - Might prove non-profitable without subsidies - Geographic restrictions might hinder production - Scarce qualified labor - High maintenance costs - CO_2 cost is rising, but it is insufficient to support the low carbon transition through biogas - Little incentive to use biomethane - Lack of stability in the regulatory environment and public policies to attract investors - Seasonal/annual price
External origin (attributes of the environment)	
Opportunities	**Threats**
- Support from government systems for energy policies - Potential as an alternative source of energy - Potential for sustainable growth - Reduction of greenhouse gas (GHG) emissions - Decentralization of energy generation	- Need for improvement in infrastructure - High storage costs - High taxes - Little competitiveness with natural gas - Few agreements to reduce environmental impacts - Need for energy efficient technologies

- High untapped potential - Promotes environmental awareness - Potential decrease in waste sent to landfills - Commercial opportunity for biomethane producers - Business diversification towards a green transition - Reduction of dependence on natural gas - Energy recovery might take place in landfills	- Lack of governmental support for the transition to a low carbon society - Lack of general awareness of the socioenvironmental benefits from the use of biomethane - Need for robust standards for social sustainability certification - Few partnerships between industries and - research institutions - Little incentive from the public system - Lack of adequate infrastructure

The diagram was elaborated from an analysis of the LCA and the results in the different indicators. Some of the most relevant points are highlighted below.

Strengths

The greatest strength of the use of biomethane is the ability to use waste while generating something as valuable today as energy. This fact provides both economic and environmental added value.

Weaknesses

The main weakness of biomethane is the large investment required and the high operating costs associated with its production. In centralized generation there is a need to transport the substrate to the plants, while in decentralized generation, the implementation of small plants may not be as efficient.

Opportunities

The same concept for the greatest strength has been identified as the greatest opportunity. Instead of generating waste that must be treated for disposal, a highly valuable product such as energy is obtained. As a by-product, digestate is obtained, which can be used as a biofertilizer.

Another relevant opportunity is the GHG emission reduction potential that comes from using biomethane instead of other fossil fuels.

Threats

The biggest threat facing biomethane production is the pre-existing fossil fuel industry. Being an industry that is fully established, it has received incentives for decades and therefore, thanks to lower operating prices, is able to offer a more competitive price. The biomethane industry has a long way to go to reach the same level.

2.4.4. Applications of Biogas and Biomethane

Both biomethane and biogas contain chemical energy that can be used for different purposes, such as the production of electricity, heat, be used as fuel for vehicles or to be injected into the natural gas network as a substitute, when the specifications established in the legislation of each country for such use are met. Figure 2.3 shows the biogas consumption by end use.

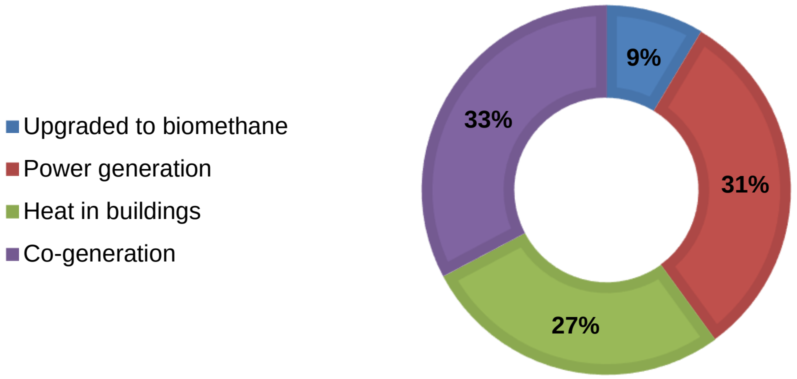


Figure 2.4 Biogas consumption by end use, 2018.(International Energy Agency, 2022)

2.4.4.1. Heat and Energy Production

Combustion of biogas to produce heat is the most common and easiest way to use this gas. Normally, no prior conditioning of the gas is necessary, except for the separation of the water, which is done by draining the piping system or even by drying, which would be the most appropriate way to do it. The H_2S emission is reduced by separating the H_2S from the gas prior to the combustion process, which is beneficial from an environmental point of view. An alternative to combustion is the combined production of power and heat. Before the biogas is used for power and heat production, water must be removed from the biogas stream. In addition, dust and corrosive components must also be removed.(Petersson & Wellinger, 2006)

2.4.4.2. Vehicle Fuel

The biomethane obtained after subjecting the biogas to the recovery process can be used as fuel for vehicles in the form of Compressed Natural Gas (CNG) or Liquified Natural Gas (LNG). When the biogas undergoes the upgrading process, the CO_2 is separated to increase its calorific value. Subsequently, the gas is dried to avoid condensation when in the following compression process, since the condensed water could cause corrosion.

Biogas used in vehicles can be an interesting alternative to power generation since the emissions are transferred to the vehicle, so the necessary authorizations and permits are simplified, as well as being more economically profitable. (Persson et al., 2006)

Normally light vehicles are designed to run on gasoline and CNG (in separate tanks), while heavy vehicles are designed for only one type of fuel, diesel or CNG. When natural gas is used instead of diesel, emission reductions of 60-85% for NO_x, 10-70% for CO, and 60-80% for particles are achieved. (Petersson & Wellinger, 2006)

To obtain CNG or LNG, the biogas must undergo a cleaning and upgrading process with the aim of obtaining biomethane. In cleaning, moisture is removed, mainly siloxanes and H_2S, and later

CO_2 is removed in the upgrading process to obtain biomethane, with a methane percentage greater than 88%. Oxygen is also removed to prevent the formation of gas accumulations that could cause explosions.

2.4.4.3. Gas Grid Injection

Another option for the application of biogas is to submit it to upgrading to obtain biomethane and inject it into the natural gas network. The use of biogas for its supply to the network has the advantage that the infrastructure for this supply network already exists and that it allows efficient use of biogas. Since the infrastructure already exists, it is possible to connect production centers with densely populated areas. In addition, the contribution of biogas to the gas supply network contributes to ensuring the gas supply in all areas. This is a relevant advantage since most countries consume more gas than they produce.

The high investment and operating costs, as well as the regulatory barriers imposed by governments and companies (permits, quality standards, gas testing and monitoring, etc.), have limited the injection of the pipeline to large generators of biogas with large biomass yields that have the necessary resources to achieve it.(Petersson & Wellinger, 2006)

One issue to keep in mind is that the capacity of the lines may not be enough, especially in rural areas. Even if there is a supply line, not all sites can have it because they may not be close enough to it. And even if there is a line quite close, it may not be possible to supply the necessary biogas capacity.

2.5. Liquified Biomethane

The production of liquid biomethane (LBM) consists of several processes; firstly, the cleaning of the biogas, followed by the elimination of CO_2 or upgrading, and finally the liquefaction of the biomethane obtained.

2.5.1. Biogas Cleaning and Pretreatment

Whatever the purpose of the biomethane that is going to be produced (as fuel for vehicles or as a contribution to the natural gas supply network), the biogas can go through two stages, one for cleaning and one for recovery, in order to obtain a biomethane with the specifications required by the use for which it is intended. The cleaning stage consists of removing water, H_2S, ammonia, VOCs and solid particles from the biogas stream. It is important to remove H_2S and particles, as it can cause equipment corrosion and mechanical components wear, respectively. The following subsections will describe the different components that can be part of biogas and the most typical way to separate it.

2.5.1.1. Sulphuric Acid

H_2S must be separated since it is the source of corrosion of the equipment used in the plant. Additionally, it interferes with the subsequent removal of carbon dioxide and can cause odor problems, in addition to the fact that it forms sulfur dioxide when burned. There are different ways to remove H_2S from biogas:

- **Adsorption with activated carbon**. Adsorption is a separation operation based on the ability of some adsorbent solids to selectively adhere molecules of a gas mixture to their surface. When the gas flows through the adsorption bed, the molecules of the unwanted compounds are attached to the surface of the adsorbent, which is a very porous material, and therefore has a large internal surface per unit of mass.(Paglini et al., 2022) Activated carbon is currently the most widely used adsorbent, due to its low cost, wide availability, large specific surface area and high affinity for undesirable biogas compounds (H_2S, CO_2, water...). Hydrogen sulfide adsorbs on the inner surface of the coal, where in the presence of oxygen it can be oxidized to sulfur. The H_2S removal capacity of activated carbon is relatively low, so to effectively and economically remove hydrogen sulfide, removal capacities and rates are enhanced by impregnating the activated carbon with appropriate chemicals, such as potassium iodide (KI), potassium carbonate (K_2CO_3) or zinc oxide (ZnO).(Wasajja et al., 2020)
- **Precipitation**.This technique is mainly used to eliminate sulfurous compounds formed from sludge with high concentrations of sulfides or when H_2S is found in high concentrations in the biogas, normally greater than 1000 ppm. The addition of Fe_2^+ and Fe_3^+ ions in the form of $FeCl_2$ or $FeSO^4$ in the digester causes the sulfides to precipitate in the form of iron sulfides, which are subsequently removed together with the digestate.(Paglini et al., 2022)
- **Chemical absorption**.One of the oldest techniques is washing with sodium hydroxide. Due to the high technical requirements to deal with the caustic solution, its application is rarely used except when dealing with large volumes of gas or high concentrations of H_2S.(Paglini et al., 2022)H_2S can also be absorbed using iron oxides. In this treatment the biogas passes through the bed with the iron oxides.This process operates with two columns, one of them in operation eliminating the H_2S from the biogas, while the other is regenerating the ferrous solution by adding oxygen and water. This technique is used in plants that treat sludge and is not applicable to biogas plants.
- **Biofiltration**. H_2S can be removed from biogas by air oxidation in a biological filter containing microorganisms that are capable of oxidizing H_2S. Biofiltration equipment is designed so that the greatest possible number of microorganisms can develop and so that the contact between them and the gas is as great as possible.This technology is not usually used for biogas that is going to be sent to the supply network or used as fuel.(Wasajja et al., 2020) Since biofiltration is a biological process, it is highly dependent on environmental conditions for good operation.

2.5.1.2. Water

When it is extracted, the biogas is saturated with water that must be eliminated. The most common way to do this is by refrigeration. Having water in the gas can be dangerous because it can condense with the H_2S, and H_2SO_4 can be formed and therefore corrosion in process piping and equipment.(Paglini et al., 2022)

When the gas cools or the pressure increases, the water vapor condenses, and the water can be withdrawn. As the solubility of ammonia in water is high, a part of the ammonia is also removed from the biogas stream. At -73ºC VOCs will condense, hence if cooled down to these temperatures these compounds can also be removed from the mainstream. It is also possible to remove water from the biogas stream by adsorption with activated carbon, molecular sieves or SiO_2.

2.5.1.3. Oxygen and Nitrogen

Oxygen and nitrogen, which are not natural components of biogas, can appear if the biogas obtained is at a pressure below atmospheric, which can cause air to contact it. These gases can be separated by adsorption with activated carbon, membranes or molecular sieves. It can also be eliminated to some extent in desulphurization processes or upgrading processes, although its presence should be avoided as much as possible, since they are difficult to eliminate.(Paglini et al., 2022)

2.5.1.4. Siloxanes

Siloxanes are compounds derived from silicon. When siloxanes burn, silicon oxide is formed, which is the source of many engine problems. Siloxane can be removed by cooling the gas, by adsorption with activated carbon, activated aluminum, or silica gel, or by absorption with liquid hydrocarbon mixtures. It is also possible to separate the siloxanes while removing the H_2S.(Paglini et al., 2022)

2.5.1.5. Particles

The particles present in the biogas are separated with filters. The removal of the particles can be done before the biogas recovery process or before the biomethane compression stage. It is important to remove the particles as these can cause mechanical wear on engines and turbines.(Paglini et al., 2022)

2.5.1.6. Comparison of Technologies for the Removal of Contaminants

The main contaminants that appear in biogas are hydrogen sulfide, oxygen, nitrogen, volatile organic compounds, moisture, and siloxanes. As mentioned in the previous sections, the most common methods to remove these contaminants are adsorption, washing with water, biofiltration and humidity. Table 2.5 shows the contaminants that each technique can remove.

Table 2.5 Contaminant removal capacity of biogas cleaning technologies.(Ong et al., 2014)

Technology	H_2S	O_2	N_2	VOCs	NH_3	Siloxanes	Water
Adsorption	Yes	Partially	No	Yes	Yes	Yes	Yes
Washing with water	Yes	No	No	Yes	Yes	Yes	No
Biofiltration	Yes	No	No	Yes	Partially	Partially	No
Refrigeration	Partially	No	No	Partially	Yes	Yes	Yes

As can be seen, adsorption tends to be the technique with which the largest amount of pollutants can be removed from biogas, with the exception of nitrogen and a part of oxygen. On the other hand, biofiltration is the least useful technology, since it is the technique with which the least amount of compounds can be removed, only being able to completely remove H_2S and VOCs.

2.5.2. Upgrading of Biogas

As previously mentioned, the elimination of CO_2 is a fundamental part of the purification process to obtain a gas with a high energy value. In industry, several technologies have been used throughout history for washing acid gases such as carbon dioxide, some more mature and perfected than others.

Depending on the use that is going to be given to the biomethane, a lower percentage of CO_2 will be necessary, being the use as fuel for vehicles the most restrictive application.

There are several technologies for upgrading biogas, among which stand out the water scrubbing, organic scrubbing, pressure swing absorption, chemical absorption, cryogenic separation and membrane separation.

Section 3 deals specifically with this stage and the technologies available to carry out this process, which is the main purpose of this thesis.

2.5.3. Liquefaction of Biomethane

Biomethane can be transported in the gas state through pipelines or in the liquid state (LBM) through cargo ships, this being the most common way.

Biomethane can either be liquefied using conventional liquefaction cycles (SMR, N2 expander, etc.) or by coupling the small liquefaction plant with low-temperature upgrading technologies. This last option can present advantages over conventional liquefaction, by combining two processes that take place at low temperatures. However, the integration of both processes results in a process that operates at very low temperatures and therefore highly demanding of energy.

The first natural liquefaction plants and some currently operating are based on the classic cascade processes with pure compounds such as methane, ethylene and propane as refrigerant. However, today most existing gas liquefaction plants operate with at least one mixed refrigerant cycle. In recent years, other processes have been used, such as the cascade system with mixed refrigerants and processes with double cycles with mixed refrigerants. On the other hand, expander-based cycles operating with nitrogen as the working fluid are used in a number of small-scale gas liquefaction plants.(Qyyum et al., 2020)

2.6. Power-to-Gas Process

In the future, the Power-to-Gas (PtG) process can play a significant role in energy systems, particularly in countries with abundant renewable sources like solar and wind. Excess electricity generated during periods of low demand can be used to power electrolysis units, producing hydrogen that is then converted into methane. Two options can be given for the conversion and use of electrical energy in a PtG system(Perez Gil & Belsue Etxebarria, 2017):

- Production of H_2 and injection into the natural gas (NG) network.

The production of hydrogen using electrical energy is carried out through the electrolysis of water with electrolysers. The generated hydrogen can be injected directly into the NG network for its distribution and use. However, the amount of hydrogen that the gas network can admit is limited by the specific rules and regulations of each country.

- Production of H_2, conversion to biomethane and injection into the NG network.

  The use and distribution of hydrogen as an energy vector is associated with problems of lack of infrastructure for its distribution and consumption, low volumetric density and lack of safety guarantee. Therefore, the conversion of hydrogen into methane and its direct injection into the existing natural gas network can play a key role in making use of surplus renewable energy. Hydrogen can be converted into methane through the methanation process and be injected and distributed unlimitedly through the natural gas network, as long as the methane generated meets the quality requirements. Thus, hydrogen and methane can serve as a link between the electricity grid and the gas grid. The methanation process produces methane from hydrogen and CO_2, and is also called the Sabatier reaction. Through this process, CO_2 from thermal processes or biogas generation plants can be recovered, which is a great environmental benefit, and biomethane can be generated without technical or safety restrictions, as is the case with the hydrogen distribution.

A brief description of the different technologies necessary to be able to carry out the different options of the PtG systems will be presented.

2.6.1. Electrolysis

The electrolysis of water is the method by which electrical energy is converted into chemical energy (hydrogen and oxygen) and is the main element of the PtG concept. The necessary equipment to be able to achieve this conversion is the electrolyser, which must have adequate efficiency, flexibility and lifetime so that the conversion performance is maximum. In the electrochemical cell, hydrogen and oxygen are generated independently and in a gaseous state, by applying a continuous electric current through metallic electrodes, depending on the reaction.(Perez Gil & Belsue Etxebarria, 2017)

$$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g) \qquad \Delta H_R(25ºC, 1atm) = 286{,}43\ kJ/mol \qquad (2.1)$$

The metallic electrodes are immersed in a solution of the water to be decomposed and an electrolyte. The electrolyte is essential for the reaction to take place, since it increases the conductivity of the medium, and it can be made up of a salt, an acid or a base. Depending on the electrolyte used, different types of electrolysers are distinguished.(Schiebahn et al., 2015)

- **Alkaline electrolysis (AEL).** Alkaline electrolysis is the most mature and developed electrolytic hydrogen production technology to date, with commercially available modules offering hydrogen production capacities of up to 760 Nm^3/h.
- **Electrolysis by solid polymeric electrolyte (PEMEL).** In PEM cells, a solid polymeric membrane acts as both the electrolyte and the separation system. This membrane is directly connected to the electrodes and allows the transit of protons from one electrode to the other. They are less developed systems than alkaline systems and are only commercially available for small-scale applications. The efficiency of these systems is in the range of 70% and its operating limit temperature is 80ºC, due to the limitation of the material that makes up the polymeric membrane.
- **Solid Oxide Electrolysis (SOEL).** It is the least mature and developed electrolysis technology of all, although it is more efficient because part of the energy is provided as heat. The electrolyte is an oxidized solid, which presents high conductivities at high temperatures and good thermal and chemical stability.

Table 2.6 Advantages and disadvantages of the presented electrolyser alternatives.(Hashemi, 2022)

	AEL	PEMEL	SOEL
Advantages	High reliability Low cost Long lifetime	Dynamic operation High current density Short start-up	High efficiency Co-electrolysis possibility Possibility of heat integration
Disadvantages	Low current density High manteinance cost Large cell area	Expensive materials Short lifetime	Heat management High investment cost

2.6.2. Methanation

The methanation reaction is a hydrogenation reaction that is commercially implemented to obtain methane from CO or CO_2. This reaction is carried out in the ranges of 250-450°C and 1-30 bar. Ni or Ru catalysts supported on alumina are usually used(Liu et al., 2012), achieving conversion yields close to thermodynamic and obtaining a biomethane with 95-97% methane, which means that it can be directly injected into the existing natural gas network.

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O(g) \qquad \Delta H_R(298K) = -165{,}1\ kJ/mol \qquad (2.2)$$

The main characteristics of this reaction are:

- Highly exotermic. It is necessary to remove the heat generated to avoid the formation of hot spots.

- The reduction of approximately 40% of the volume of reaction gases due to the formation of water.
- Catalyzed. It is necessary to use a catalyst, since the reduction of CO_2 has strong kinetic limitations.

This process has been carried out using fixed or fluidized bed reactors. The biggest differences between the fixed bed and fluidized bed methane reactors are the temperature level at which the generated heat is evacuated and the operating pressure, with the fixed bed usually following an adiabatic regime and the fluidized one isothermal. But, because the aforementioned reactors present certain difficulties in terms of process efficiency and heat removal, in recent years other types of reactors have also been used, such as slurry or microstructured. The design of new reactors focuses, above all, on temperature control, since if it is not controlled properly, its increase can cause sintering of the catalyst and the decomposition of methane to carbon.(Perez Gil & Belsue Etxebarria, 2017)

3. Upgrading: Carbon Dioxide Removal from Biogas

In the upgrading process to obtain biomethane, biogas from the cleaning process is used. The elimination of CO_2 is the core of biogas recovery and the techniques to separate this component will be the focus of this section.

Additionally, in this section the selection of the technology used in the design of the upgrading stage of the base case is carried out, and the theoretical basis of this technology is presented, as well as the industrial process that derives from it.

3.1. Available Technologies

In practice, there are different methods used industrially for the separation of CO_2, which are based on the unit operations of chemical engineering: physical and chemical absorption, adsorption, gas permeation, and other methods such as cryogenics. The most widespread techniques in Europe are physical absorption, adsorption using PSA (Pressure Swing Adsorption) systems, chemical absorption and membrane separation.

3.1.1. Pressure Swing Adsorption

With PSA systems, CO_2, O_2 and N_2 are separated by adsorption on zeolites or activated carbon, at different pressure levels. The adsorption material also adsorbs H_2S, but unlike CO_2 adsorption, this is irreversible.(Ryckebosch et al., 2011)

The separation process consists of a series of adsorption columns that work in parallel and in which, in each of them, a cycle of four operating stages is carried out to make sure that at at least one of them is producing adsorption, and on the other hand, the regeneration of the adsorbent.(Petersson & Wellinger, 2006)

- **Adsorption**. The biogas from a previous stage of desulphurization and drying is fed to the column at a pressure of 6-8 bars, selectively adsorbing CO_2, N_2 and O_2.
- **Depressurization**. The column is first operated at atmospheric pressure and then at vacuum pressure.
- **Regeneration/purge**. A fraction of the purified biogas is processed under vacuum conditions, producing the desorption of CO_2. The resulting CO_2-rich stream is recycled if it contains a significant amount of methane, or treated and released to the atmosphere if it contains little methane.
- **Increased pressure**. Once the regeneration process ends, the column is brought back to adsorption conditions, that is, 6-8 bar.

Using PSA, a cleaner recovered gas is obtained than with other methods. However, a more sophisticated process and greater control of it are required, including the recirculation of part of the gas to avoid excessive methane losses.

3.1.2. Water Scrubbing

This technology is widely spread and is based on the principle of physical absorption of CO_2 and H_2S in water.

In the first place, the compression of the biogas occurs at pressures between 8-20 bar. Subsequently, it is injected through the base of an absorption column, to which a stream of water is fed through the top. The column is randomly packed in order to provide a longer contact time with the absorbent and favor mass transfer. Finally, the purified biogas leaves the column at the top to be sent to a drying process that leaves with a methane content of up to 98%. The water stream with the absorbed compounds does so at the bottom and is subsequently subjected to a regeneration process.

This technology requires a large flow of water in the process. According to the bibliography, two water scrubbing methods are currently on the market: with absorbent recovery, which allows reducing water consumption, and without recovery, when the water flow comes from water treatment plants.

If there is absorbent recovery, the resulting liquid stream is sent to a flash separator at lower pressure (2,5-3,5 bar), from which a gaseous stream rich in CO_2 and CH_4 is obtained that is recirculated to the inlet of the compressor, and a liquid stream that goes to a desorption column and is subsequently recirculated to the absorption column.(Petersson & Wellinger, 2006)

The main energy requirements of this technology are mainly due to the compression of the biogas and the pumping of the flow of water present in the process. The biomethane produced contains between 96 and 98% methane, with losses of around 2%.

3.1.3. Organic Scrubbing

It is an absorption process similar to water scrubbing in which instead of using water as an absorbent, organic compounds are used. The most commonly used absorbents are mixtures of methanol and polyethylene glycol dimethyl ethers. This technology has several advantages compared to water scrubbing.(Petersson & Wellinger, 2006)

- Organic absorbents have a higher CO_2 solubility than water, so in this case lower solvent flow rates are required.
- Organic absorbents have anticorrosive properties, which is advantageous when choosing the material for the column.
- In the event that the absorbent presents low vapor pressures, its losses will be less in the column.

However, CO_2 and, above all, H_2S, have a high solubility in organic solvents, so the absorbent regeneration costs are higher in this case.

In the regeneration process, the solvent is depressurized and heated to temperatures around 80°C. Subsequently, it is necessary to cool it down again to inject it through the top of the scrubber. Given its high solubility, a greater amount of H_2S in the biogas will mean a higher operating temperature in the solvent regeneration unit. To reduce costs, desulfurization units are used prior to the absorption column.(Ryckebosch et al., 2011)

The required energy contribution comes from the heat necessary to heat the stream to be regenerated, and the electricity necessary in compression.

3.1.4. Chemical Absorption

In this technology the separation is produced by absorption through a chemical reaction. Some of the most common solvents are monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), and methyldiethanolamine (MDEA).(Arachchige, 2019)

The process consists of introducing the biogas through the bottom of an absorption column into which the solvent is injected from the top. The reaction is exothermic, so the temperature increases depending on the feeding conditions, forming intermediate compounds, such as CO_3^{2-} and HCO^{3-}, which favors the transfer of CO_2. As a result, the absorption units used are smaller and the flow rate of absorbent in the process is lower.

The solution obtained at the bottom, rich in CO_2 and H_2S, is pumped to a stripping column to regenerate the solvent at low pressures and high temperatures. Usually, an energy integration is carried out between the bottom stream of the absorption column and the stream of regenerated absorbent from the stripping column.

The resulting biomethane has a very high purity, greater than 99%, methane losses can be less than 0.1%, and the process is faster than physical absorption.(Arachchige, 2019)

However, energy consumption is higher than in other absorption technologies. In addition, the toxicity of the absorbents used, the degradation of amines, and possible corrosion problems must be considered.

3.1.5. Cryogenic Separation

This technique consists of separating the methane present in the biogas from the rest of the components, taking advantage of the difference in boiling points. At 1 atmosphere, the boiling point of methane is -161,5ºC, while that of CO_2 is -78,2ºC.(Petersson & Wellinger, 2006)

The process begins with a series of alternating cooling and compression stages to reach operating conditions in the separation column of 80 bars and -110ºC.

Cryogenic separation allows purities of around 97-98% methane to be achieved with losses of less than 2%. However, it is complex and requires a high cost of capital. On the other hand, there is a high energy consumption in the operation, which is why this new technology is barely used and is still under development.

3.1.6. Membrane Separation

Membranes for biogas recovery are made of materials permeable to CO_2, water or ammonia. Part of the H_2S and O_2 pass through the membranes, while N_2 and CH_4 pass in a very low proportion, so separation is possible.

There are wet and dry techniques. The dry technique is based on the fact that certain substances pass more easily through membranes than others. The rate of passage of each substance depends on the difference in partial pressure of each substance on one side and the other of the membrane. The partial pressure is dependent on the permeability, which is a function of the chemical solubility of the substance in the membrane. To achieve good CO_2 separation, the membrane must be selective for this compound and the difference in permeability between CO_2 and CH_4 must be high.

The membranes for this type of operation are hollow fiber type to achieve the largest possible surface area. These hollow fibers can be made of different polymers, which have 20 to 60 times higher permeability for CO_2 and H_2S than for CH_4. To prevent corrosion, H_2S is removed before passing the biogas through the membrane.

The separation is achieved at high pressure, normally between 25 and 40 bar. CH_4 remains on the high-pressure side, while CO_2 passes through the membrane. This decreases the compression that the gas needs when it is distributed to the natural gas network or to fuel vehicles.

The design of the membranes means that obtaining a high CH_4 concentration conflicts with low CH_4 losses. Increasing the size or the number of membranes can increase the CH_4 concentration, but at the same time the CH_4 losses become greater. To achieve a high concentration of CH_4 with low losses, the CO_2-rich gas obtained in the permeate must be recirculated.

There are few biogas recovery plants using dry membranes, since the high pressure in combination with recirculation means high energy consumption. Unlike dry membranes, wet separation is not selective for some gases. The operation of this technique is carried out by an entrainment fluid on one side of the membrane that selectively absorbs certain components. The CO_2 molecules diffuse through the pores of the membrane and are absorbed by the entrainment fluid, which is regenerated by heating. These membranes work at atmospheric pressure, which means lower costs compared to other types of membranes.(Ryckebosch et al., 2011)

3.1.7. Comparison of Upgrading Technologies

In this section, a comparison of the advantages and disadvantages of the different techniques described in previous sections will be made, as well as a comparison of the characteristics of the biogas obtained through the use of each of the aforementioned techniques.

Table 3.1 summarizes all the advantages and disadvantages of each of the techniques used for biogas recovery.

Table 3.1 Advantages and disadvantages of biogas upgrading technologies.(Farghali et al., 2022; Ong et al., 2014)

Technology	Advantages	Disadvantages
Pressure Swing Absorption	No chemicals or heat requirements Compact	High methane loss Complex process Pre-treatment required High investment cost
Water Scrubbing	High methane purity and low loss Inexpensive Removal of H_2S Pre-treatment not required Special chemical or equipment not needed	High pressures and cooling units needed Foaming formation Biomethane must be dried Operating problems with H2S

		Environmental problems of acidification, global warming and human toxicity High water demand
Organic Scrubbing	High carbon dioxide solubility Low operating and capital costs Removal of H_2S Low methane loss Low regeneration temperature	High investment and operation cost Complex process Requirement of chemicals Regeneration requires heating
Chemical Absorption	Highest biomethane purity Lowest methane loss High CO_2 removal efficiency Low pressure required in absorber, thus lower capital costs	High operation cost High energy requirement for regeneration Corrosion problems Foaming Salt precipitation
Cryogenic Separation	High methane purity Removal of all impurities	Highest energy consumption (10% of generated methane) High losses of methane Operational problems (p.e. clogging) Requires multiple processes for high methane purity
Membrane Separation	Compact and simple Easy maintenance and operation Does not require chemicals or heat	High methane losses High pressure requirements Physical ageing (replacement every 1-5y) Fouling and clogging of membranes Pre-treatment required Energy and capital intensive

Table 3.2 shows the characteristics listed above in more detail, where the purity of the biomethane obtained by each technique can be seen, as well as the methane losses, some operating conditions, the need for pretreatment and the resources needed for each process.

Table 3.2 Operational requirements of biogas upgrading methods.(Farghali et al., 2022)

Technology	**Operating pressure (bar)**	**Operating temperature (°C)**	**Biomethane purity (%)**	**Methane losses (%)**	**H_2S cleaning requirement**	**Solvent or adsorbent agent**
Pressure Swing Absorption	2-11	5-30	95-98	1-3,5	Required	Adsorbent

Water Scrubbing	8-21	20-40	93-98	1-3	No	Water, drying agents, Anti-fouling agents
Organic Scrubbing	5-9	10-20	95-98	1,5-4	No	Organic solvent
Chemical Absorption	<15	35-50	99	0,04-0,1	Recommended	Amine solvent, anti-fouling agents, drying agents
Cryogenic Separation	19-31	-59-(-45)	96-98	0,5-3	Required	Coolant
Membrane Separation	8-42	25-60	85-99	0,5-20	Recommended	Membranes

3.1.8. Process Selection

After carrying out the comparison of the different upgrading technologies presented, and based on the base case, a chemical absorption system with amines has been selected.

The main disadvantage of this system is the investment cost, since auxiliary equipment is needed, increasing the cost. Another of its disadvantages is the possible degradation of the amine if its limit temperature is exceeded, as well as possible corrosion problems depending on the amine used.

Faced with these disadvantages, a system with high efficiency (<99%) and very few methane losses predominates, in addition to having greater selectivity for carbon dioxide, which is a primary factor in achieving biomethane with sufficient quality. to cope with the subsequent liquefaction process.

On the other hand, this system has a relatively low operating cost, and has been widely used in the industry, which is why it is considered a reliable and easy-to-operate system.

3.2. Chemical absorption using amines

A more detailed description of the chemical absorption process with amines is given in this section. In the first place, the available solvents are introduced, as well as the chemical reactions on which the absorption process is based. The different unitary operations used are presented below, as well as the relevant parameters and operating ranges. Table 3.3 presents a summary of the most relevant amines presented.

3.2.1. Available Solvents

There are different types of amines that can be used in the acid gas absorption process. A typical classification of these solvents is according to chemical structure; Some of them are categorized as primary amines (MEA, DGA), secondary amines (DEA), tertiary amines (MDEA, TEA), hindered amines (AMP) and cyclic amines (Piperazine). The amines are categorized as primary, secondary and tertiary according to the number of organic groups attached to the alkaline nitrogen atom.

The use of one or another will depend on different factors such as the composition and conditions of the gas to be treated. Some of the most used industrial solvents are presented in more detail below.

3.2.1.1. MEA (Monoethanolamine)

It is the most reactive ethanolamine. It is preferably used in non-selective processes to remove CO_2 and H_2S. It is a stable compound that, in the absence of other chemicals, does not have degradation up to its normal boiling point. However, in the presence of CO_2 and at temperatures above 118ºC, a secondary reaction with CO_2 occurs, forming a stable salt, consuming solvent. Therefore, it is necessary to purge 1 to 3% of the solvent from the bottom of the stripping column.

Very low concentrations of CO_2 and H_2S can be reached, although it commonly presents operational problems in terms of corrosion and foaming. For this reason, the amine concentration is normally limited to 15% by mass, requiring a relatively high energy input in the process.

The vapor pressure of MEA is higher than for the other amines at the same temperature, which can lead to higher vaporization losses. According to experience of use in the industry, an adequate load ranges from 0,3 to 0,4 mol of acid gas/mol MEA.(Arachchige, 2019)

3.2.1.2. DEA (Diethanolamine)

It is a less corrosive amine than MEA, although the solution can become very viscous at high concentrations. Being a secondary amine, the reaction with CO_2 and H_2S occurs more slowly than with MEA, and different products are also obtained. Solvent losses by evaporation are usually less due to its lower vapor pressure.

DEA is used to sweeten streams containing a total of 10% or more acid gases (H_2S plus CO_2) at operating pressures of about 34,5 bar or higher. DEA concentrations that are commonly used in industry to prevent corrosion range from 25 to 35% mass. The mol acid gas/mole amine loading usually ranges from 0,35 to 0,65 without unsustainable corrosion.(Arachchige, 2019)

3.2.1.3. MDEA (Methyldiethanolamine)

Methyldiethanolamine is a tertiary amine that reacts slowly with CO_2, therefore, to remove it, a greater number of equilibrium steps are required in absorption. Its best application is in the selective removal of H_2S when both gases are present (CO_2 and H_2S).

With a high CO_2/H_2S ratio, MDEA can be used to improve the quality of the acid gas feed stream to a Claus Sulfur Recovery Plant. Solutions of 30 to 50% weight of amine are used.

In the case of offshore installations, the biggest disadvantage is the need to use very high absorbers.(Arachchige, 2019)

3.2.1.4. Amine blends

The use of blended amines is useful to eliminate several of the operating problems or limitations that occur when using a specific amine, improving system performance. In the case of MEA, one of the problems it presents is that when it is regenerated, it retains a relatively high amount of acid gases. This means that when it returns to the absorber it has a more limited retention capacity. For this reason, the use of methyldiethanolamine (MDEA), a tertiary amine, is common.

With the use of these two amines together it is possible to reduce the amount of solvent required as well as the energy consumption of the process. This solvent blend is produced by mixing a MDEA/MEA ratio of 4:1 by mass.(Arachchige, 2019)

Table 3.3 Summary of the main characteristics of some solvents.(Arachchige, 2019)

Amine	MEA	DEA	MDEA	Blended amines (MEA+MDEA)
Type	Primary	Secondary	Tertiary	Primary and tertiary
Molecular weight (g/mol)	61,08	105,14	119,16	MEA: 61,08 MDEA: 119,16
Concentration (wt%)	Up to 15	25-35	30-50	MEA: 10 MDEA: 40
Acid gas loading (mol acid gas/mol amine)	0,3-0,4	0,35-0,65	Up to 0,4	Up to 0,35
Energy requirement	Moderate	Lower than MEA	Moderate	Low
Losses	Moderate	Lower than MEA	Moderate	Low
Corrosion	Moderate	Low	Moderate	Low
Operational problems	Foaming Heat stable salt formation	High viscosity at high concentrations	Foaming	
Removal capacity	Higher than DEA	High	High	Higher than MEA

3.2.2. Process Description and Unitary Operations

The absorption of carbon dioxide with amines is a method that has been widely used in the petrochemical and natural gas industry, which is why it is a very well-studied method, and it is relatively easy to adapt it for biogas treatment. With this method it is also possible to remove the commonly present hydrogen sulphide.

In this process, the mentioned acids react with an active component (amines) to form unstable compounds in a solvent that circulates in the plant. The rich and unstable solvent is separated into its original components by reducing pressure and adding heat, separating the acid gases and thus regenerating the solvent.

The different stages of the process are described below and relevant information is provided.

3.2.2.1. Inlet Scrubber

The gas to be treated is fed to an initial separator, in which solids are removed, as well as moisture and hydrocarbons that are dissolved in the gas. The need for the presence of this stage will be determined by the characteristics of the gas to be treated and its impurity content.

3.2.2.2. Compression Stage

In this stage, the aim is to bring the biogas to the operating conditions of the absorption column. These are one or more compressors with coolers to lower the temperature of the gas before it is fed to the absorber. The use of more than one compressor with intercooling can be a way to reduce the energy requirements of this stage.(Arachchige, 2019)

3.2.2.3. Absorption Column

The gas to be treated, free of impurities, is fed into the absorber. This tower works at high pressure and low temperature. The amine solution is usually fed counter currently through trays or packing (random or structured), which provides good mixability.

When the gas flow to be treated is small, the absorption column normally includes a scrubber in which impurities, moisture and liquid hydrocarbons are removed. In this way, the quality of the amine solution is preserved. However, when the gas flow rate is higher, the previously mentioned inlet scrubber is used, which performs the same function, but helps to reduce the height of the column.

The treated gas leaving the column at the top is saturated with water and may contain entrained amine. Therefore, a dehydration process is normally carried out.

The acid-rich amine solution leaves the column at the bottom and is taken to the flash tank.

The mass flow rate of lean amine to be used can be determined from the amount of acids present, choosing an amine concentration and the amount of acids to be absorbed. It is appropriate to choose values recommended in the bibliography and adapt them to the current case.

For an effective system and to minimize corrosion, 35 wt% DEA and an acid gas loading of 0,5 mol acid gas/mol DEA are typically used.It is common to add an excess of 10-15% to the required flow rate of amine to provide a safety margin.(Arachchige, 2019)

Both MEA and DEA are basic solutions that form salts when reacting with H_2S and CO_2. Below are the reactions that take place in the use of DEA.(Arachchige, 2019)

$$DEACOO^- + H_2O \leftrightarrow DEA + HCO_3^- \tag{3.1}$$

$$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+ \tag{3.2}$$

$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O \tag{3.3}$$

$$DEAH^+ + H_2O \leftrightarrow DEA + H_3O^+ \tag{3.4}$$

$$2H_2O \leftrightarrow OH^- + H_3O^+ \tag{3.5}$$

The heat of reaction is produced in the first contact between the acid gas and the amine, therefore the lower part of the absorber is the place where the most heat of reaction is produced.

As the gas goes towards the top of the column, an energetic exchange with the amine solution takes place, leaving the column at a temperature slightly higher than the inlet temperature.

3.2.2.4. Flash Tank

The acid-rich amine stream from the absorber is fed to a flash separator, in which it is intended to eliminate entrained liquid hydrocarbons. However, a small fraction of the absorbed acids also flashes with the mentioned hydrocarbons due to the drop in pressure.

If the sour gas to be treated contains a high amount of liquid hydrocarbons, the use of a three-phase separator may be necessary.

Again, like in the inlet scrubber, the need for this tank will be determined by the composition of the rich amine and therefore the biogas.

3.2.2.5. Lean-rich Amine Heat Exchanger

After the separation in the flash tank, the rich amine is taken to a heat exchanger in which it is intended to recover sensible heat as energy integration of the process. The exchange takes place between the lean and rich amine streams and the heat exchanged can represent up to 50% of the heat required in the stripper reboiler.

The preheated rich amine is taken to the stripper, while the cooled lean amine is taken to an additional cooler, in which the temperature reached is about 5,5ºC above the temperature of the sour gas to be treated.(Arachchige, 2019)

It is important to take into account that the temperature of the rich amine does not reach such a point that the acid gases are released prematurely, since this could cause excessive corrosion to the pipes. For this reason it is important to use materials such as stainless steel for the pipes.

The most common heat exchanger is of the U-shaped shell and tube type. The rich solution normally flows through the tubes and the lean solution flows through the shell of the exchanger, bathing the tubes on the outside.(Stewart & Arnold, 2011)

3.2.2.6. Stripping Column

The regenerator is the tower in which the amine solution is separated from the acid gases. Works at low pressure and high temperature.

In an amine plant, the stripping column typically has between 18 and 24 trays.(Stewart & Arnold, 2011)

The reboiler provides the necessary energy to reverse the absorption reactions of the acids in the amine, in order to regenerate the solvent to be used again. Usually the reboiler can be using indirect heat as a heat source or a kettle-type reboiler using steam.(Stewart & Arnold, 2011)

The power required varies depending on the system. A higher energy requirement in the reboiler requires higher refrigeration in the condenser and a higher reflux ratio, although it allows columns of fewer trays. However, a lower energy requirement in the reboiler requires less refrigeration in the condenser and a lower reflux ratio, obtaining columns with more trays.

The operating temperature in the reboiler is given by the operating pressure and the concentration of the amine solution.

A typical range of operating temperatures for a 35% DEA solution is 110-121°C. Typical operating pressures range from 60 to 170kPa.(Stewart & Arnold, 2011)

The generated steam acts as stripping gas for the acids, dragging them up the column. The rich amine is normally fed into the 3rd or 4th tray from the top.

Typically, the stripper condenser can be of the Shell and tube type or also an air-cooled fin-fan heat exchanger. Once the energy consumption of the reboiler has been determined, the consumption in the condenser can be easily determined with an energy balance in the stripper.

In the condenser, the vapors leaving the top of the stripper are cooled, condensing a fraction of the generated vapor as reflux. The accumulator is used to separate acids and steam from condensed water.

Finally, the acid gases are obtained at the top of the column, and the lean-amine at the bottom of the column, which is taken to the lean-rich amine heat exchanger.

3.2.2.7. Surge Tank

Due to the effects of daily work, part of the DEA solution is lost in the contactor and in the regenerator. There will also be small leaks in the pump and other places. As the solution level in the supply tank drops, it is necessary to add fresh solution. Care must be taken to ensure that the water/amine ratio in the original design is maintained when adding solution to the system.

If the amine solution comes into contact with air, it will react with oxygen and lose its ability to remove acidic components from natural gas. As a consequence, it is essential that air does not come into contact with the solution. To prevent this effect, an inert gas atmosphere can be used in the supply tank.

4. Simulation of the Upgrading Process in Aspen HYSYS

This section shows the process of simulation of the chemical absorption with amines. First, the base case is introduced; a stream of biogas with a given composition, which must be treated to comply with the specifications that will be presented.

The design decisions that are made and their implementation in the Aspen HYSYS model are shown.

Once the simulation is completed, a sensitivity analysis of the most relevant process variables is carried out, in order to obtain useful information for the preliminary optimization of the model.

4.1. Base Case

As a base case for the modeling that concerns the project, the treatment of a biogas stream from a relatively large plant located in Skogn (Norway), has been chosen. The plant has a production capacity of 12,5 MCM/year of LBM from waste from fish and the forest industry, abundant in the area.(Norske Skog, 2021)

The upgrading stage, the main focus of this project, constitutes an intermediate stage for obtaining the LBM, and therefore, the biogas must be treated in such a way that it is suitable for the subsequent stages of processing, taking into account the quality of the final product. As previously mentioned, the production of LBM imposes restrictive product specifications.

Table 4.1 shows the feeding conditions, as well as the specifications of the final product.

Table 4.1 Feed and product conditions/specifications of the considered base case.

Feed (biogas)		
Molar flow rate (kmol/h)		200
Temperature (°C)		35
Pressure (bar)		1,013
Composition (%)	CH_4	60
	CO_2	39,9
	H_2S	0,01
Product (biomethane)		
Composition	CH_4	> 99,7 %
	CO_2	< 50 ppm
	H_2S	< 5 ppm

4.2. Model Implementation

4.2.1. Assumptions

In simulating the upgrade process, the following assumptions have been made:

- The biogas fed to the plant does not contain impurities. This allows to avoid the inlet scrubber and/or a cleaning process.
- There are no losses of methane and/or another component, which is common in real processes.
- The pressure drop in the equipment (especially heat exchangers and columns) is negligible.
- The isentropic efficiency is 80% in compressors and expanders, and 85% in pumps.

4.2.2. Initial Guess

The method followed to obtain an initial estimation has been derived from the book "Gas Sweetening and Processing Field Manual" by the reference (Stewart & Arnold, 2011). A summary of the method can be found in appendix A.

This method allows for determining the most suitable gas sweetening method for a given stream, depending on its flow rate and composition, using selection charts. Once the method is determined, design variables are defined based on ranges commonly used and validated in the industry, and simplified calculations are performed to determine the required solvent flow rate, energy consumption, and other relevant data for the simulation.

Convergence has been greatly facilitated by having estimations of the different parameters important in the process simulation.

Table 4.2 Summary of the variables and results used as an initial guess for the absorber.

Absorber		
	Temperature (ºC)	Mass flow rate (kg/h)
Lean DEA	40,0	52167
Rich DEA	64,3	55652
Biogas	35,0	5438
Purified biogas	43,0	1953

Table 4.3 Summary of the variables and results used as an initial guess for the lean/rich heat exchanger.

Lean/rich DEA Heat Exchanger		
	Temperature (ºC)	Duty (kW)
Lean DEA inlet	120	2292

Lean DEA outlet	78,7
Rich DEA inlet	64,3
Rich DEA outlet	103

Table 4.4 Summary of the variables and results used as an initial guess for the stripper.

Stripper	
Top tray temperature (°C)	104
Condenser operation temperature (°C)	55
Condenser water loss (kg/h)	146
Reflux mass flow rate (kg/h)	4108
Accumulator operational temperature (°C)	55
Accumulator operational pressure (kPa)	170
Reflux rate	2,7

4.2.3. Thermodynamic Package

According to recommendations from HYSYS, the Acid gas - Chemical Solvents method has been used. The thermodynamic package technology is based on the NRTL electrolyte model for electrolyte thermodynamics and the Peng-Robinson equation of state for vapor phase properties. This method is specifically designed for systems that involve water, ethanolamines, hydrogen sulfide, carbon dioxide, and/or other components typically present in gas sweetening. It is important to review the validity ranges of the method in terms of temperature, maximum H_2S or CO_2 loading, and concentration of the amine solution.

4.2.4. Trayed/Packed Absorption Column

The choice between packing and trays in biogas amine absorption columns depends on several factors, including the specific process requirements, gas composition, operating conditions, and economics. Both packing and trays have its advantages and disadvantages.

The main advantages for the use of packing are the following:

- Mass transfer: packing provides a large surface area for gas-liquid contact, which can promote efficient mass transfer and absorption of acid gases.
- Low pressure drop: a lower pressure drop takes place, hence lower pressure is needed.
- Easier to handle fouling: easy to clean and replace.

The main advantages for the use of trays are the following:

- Liquid distribution: the liquid can be better distributed which is helpful with a uniform gas-liquid contact.

- Operational flexibility: trays can handle a wider range of gas flow rates compared to packing, which may be beneficial when flow rates can vary significantly.
- Control: trays can provide more straightforward measurement and control of the liquid level in the column, which can be important for controlling the absorption process.

Moreover, as a rule of thumb in the industry, when a smaller diameter (< 50cm) is required, stainless steel packing is normally used, while if a larger diameter (> 50cm) is required, stainless steel trays are used. For normal amine concentrations, columns of around 20 trays are normally used.(Stewart & Arnold, 2011)

In the base case of this simulation, it has been chosen to work with a trayed column since the required diameter is significantly greater than 50cm.

4.2.5. Process Flowsheet

Based on the results obtained with the short-cut calculation method, these results were used as initial estimates to define the different operating variables and the solvent flow rate necessary to treat the biogas feed.

The logic behind the development of the model was to first implement a simple and functional model, and gradually increase the complexity, based on a functional model.

In a first iteration of the simulation, the biogas was fed directly to the absorption column (skipping the initial compression stage) and defining a pressure of 10 bars. The Absorber model was used for the absorption column, in which the connections (inputs, outputs) and the number of stages are defined first, followed by the bottom and head pressures, and finally estimates of the operating temperature in bottoms and head. Next, the VLV-100 expansion valve and provisionally a heater were added to increase the temperature of the feed stream to the stripper.

The stripper simulation is assimilated and performed by distillation column models. The Short-cut Column model was used in this first iteration, through which it is possible to define the separation to be achieved (components and purities of the bottom and top products), obtaining as a result the number of necessary stages and the reflux rate. This information obtained could be used in the configuration of the rigorous Distillation Column model.

At this time, the process stream heat exchanger could be implemented using the Heat Exchanger model, defining the temperature of the feed stream to the stripper as a specification.

Next, after the stream of regenerated solvent from the E-103 heat exchanger, the Makeup model was added to model the surge tank, in which the solvent is purged and fresh solvent is fed. The information required is the total outlet flow rate, the purge flow rate and the corresponding final amine concentration.

Finally, the P100 pump, the cooler prior to the absorber, and the Recycle model, which allows recirculation of the regenerated solvent, were added.

In order to prepare the model for the optimization that will be carried out, the Set model and the spreadsheet integrated in HYSYS were used to define some variables and prevent Aspen HYSYS from presenting errors caused by possible inconsistencies arising from the variability of the operating variables. The following was specified:

- The temperature variation of the solvent feed stream to the absorber can be affected by the recycle temperature input, creating an interference in the variation of this value during optimization. For this reason, a Set is established, through which it is ensured that the temperature of the Lean DEA to Abs stream is the same as in Lean DEA, avoiding these interferences.
- The pressure at the top of the Absorption column must be lower or equal to that at the bottom, to avoid reverse flow problems. The variation of the bottom pressure of the Absorption column can lead to cases where this is not fulfilled, giving rise to errors. Using the Spreadsheet, the bottom pressure value is taken as a reference, calculating a slightly lower pressure and exporting this result to the head of the column.
- The solvent feed pressure to the absorber must be equal to the operating pressure of the stage in which it is fed. This is achieved by using a Set and taking the pressure of the product at the top of the column as a reference.
- The biogas feeding pressure to the absorber must be equal to the operating pressure of the stage in which it is fed. In this case, the spreadsheet is used to import the pressure value of this stage and export it to the desired stream.
- In the same way as in the Absorption column, in the Stripper it must also be ensured that the pressure at the top of the column is lower than at the bottom. This is achieved in the same way, by using the spreadsheet and exporting these variables.

Figure 4.1 shows the flowsheet of the final result of the simulation.

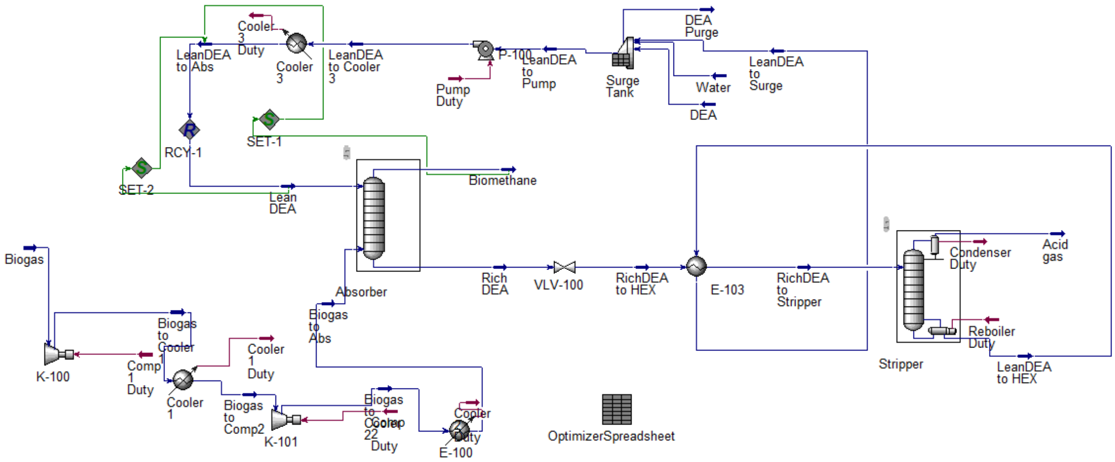


Figure 4.1 Flowsheet of the simulation of the chemical absorption process in Aspen HYSYS.

4.3. Sensitivity Analysis

As a step prior to optimization, a parametric sensitivity analysis has been carried out to identify the key variables of the process, as well as to study their influence on removal efficiency and energy consumption.

4.3.1. Effect of Type of Amine

There are different types of amine that can be used for the acid gas absorption process. The use of one or another will depend on different factors such as the composition and conditions of the gas to be treated.

The different existing types are classified according to the chemical structure in primary, secondary, tertiary amines, hindered amines and cyclic amines. This study has been limited to the amines most widely used in this application.

In order to compare the performance of the mentioned amines, a 98% removal efficiency value has been set to be achieved with the three amines. The flow is varied to obtain the desired efficiency. The results obtained are shown in the following figures.

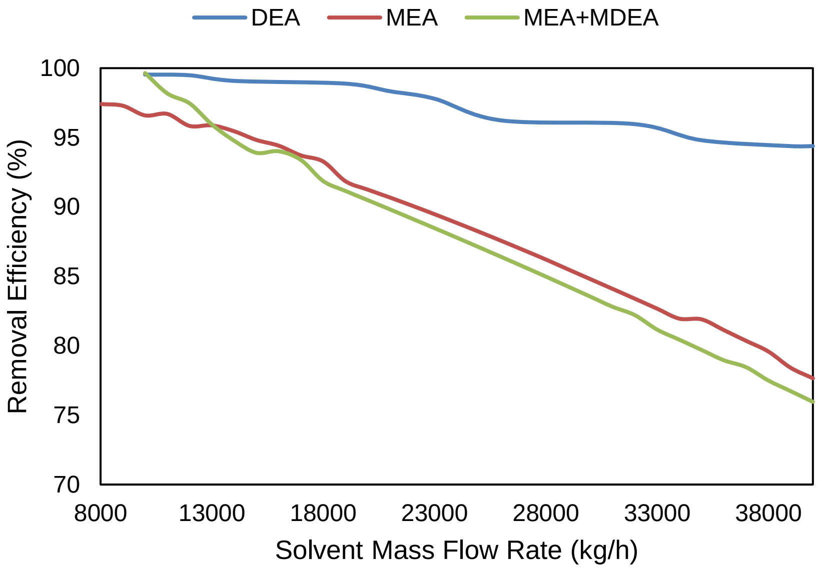


Figure 4.2 Variation of removal efficiency with respect to the solvent mass flow rate for different solvents.

The removal efficiency is calculated considering the total amount of acidic gases entering the plant and the total amount exiting.

$$Removal\ efficiency\ (\%) = \frac{Total\ acids\ inlet - Total\ acids\ outlet}{Total\ acids\ inlet} \cdot 100 \qquad (4.1)$$

It can be observed that the removal efficiency of DEA is higher and remains higher with increasing mass flow rate, unlike MEA and MEA+MDEA.

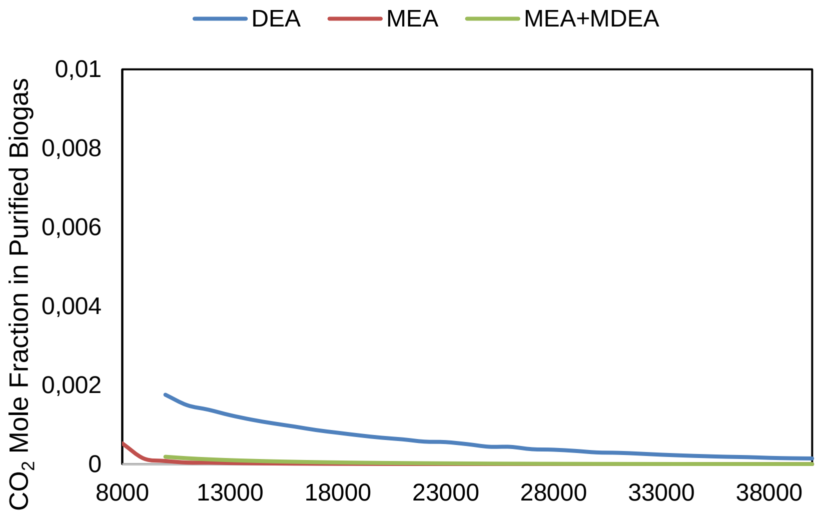


Figure 4.3 Variation of CO_2 mole fraction in purified biogas with respect to the solvent mass flow rate for different solvents.

According to the information provided previously, a lower molar fraction of carbon dioxide is obtained with MEA and MEA+MDEA. This is due to the presence of primary amine, which is highly reactive with the acid.

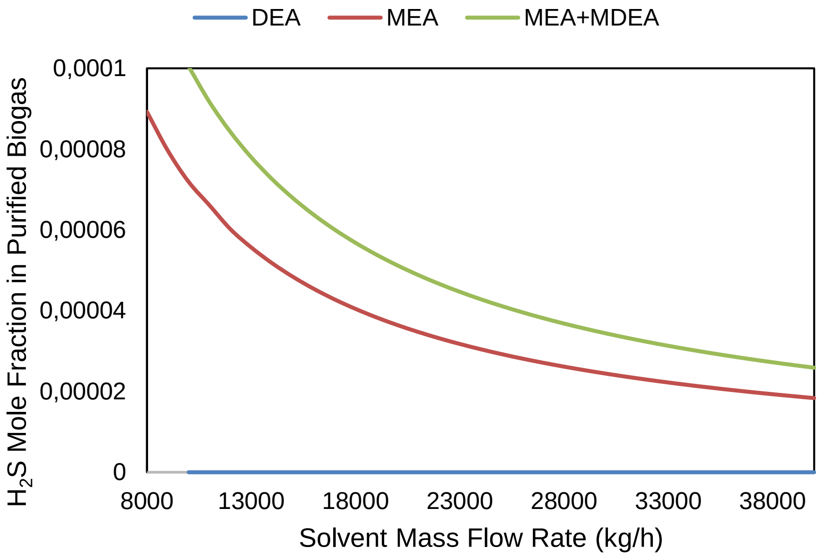


Figure 4.4 Variation of H_2S mole fraction in purified biogas with respect to the solvent mass flow rate for different solvents.

In the case of hydrogen sulfide removal, DEA allows for significantly better results, almost completely eliminating the substance.

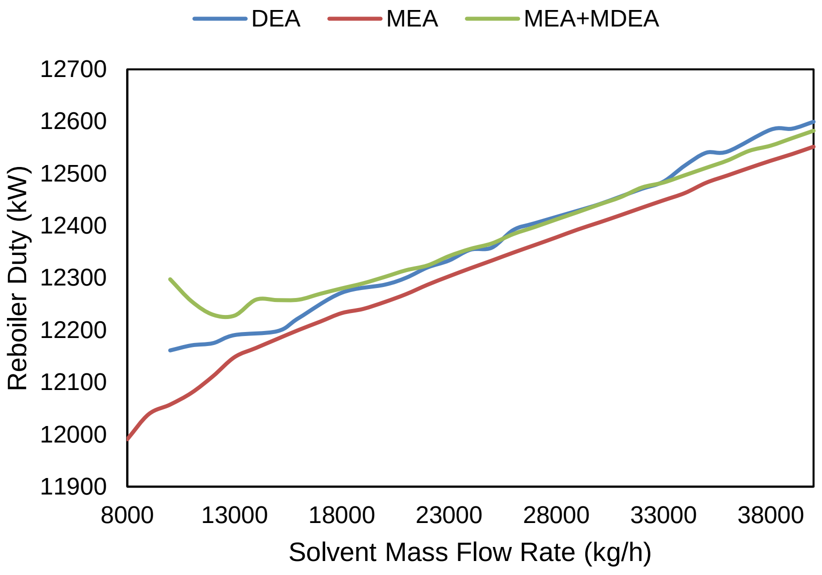


Figure 4.5 Variation of reboiler duty with respect to the solvent mass flow rate for different solvents.

The reboiler duty for MEA+DEA is the highest followed by DEA and MEA. One of the reasons for this is the concentration of amine in each solvent. The solvent with the highest concentration (MEA+MDEA) has the highest energy consumption in order to be processed in the stripper.

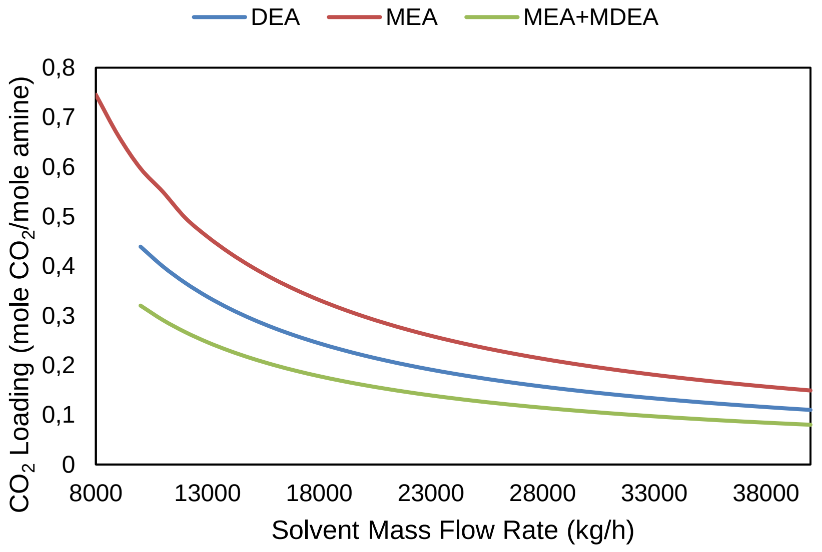


Figure 4.6 Variation of CO_2 loading with respect to the solvent mass flow rate for different solvents.

The high reactivity of MEA allows for a high loading of carbon dioxide in the solvent. However, it is crucial to adhere to the permitted ranges due to corrosion and equipment integrity concerns. The loading is related to the amount of energy required in the reboiler to reverse the reactions, as higher loading results in a lower flow rate to be treated by the stripper.

In the following table, the results obtained from the simulation with different amines to achieve a 98% efficiency in acid gas removal are shown.

Table 4.5 Results obtained with different solvents for a removal efficiency of 98%.

Solvent	**DEA**	**MEA**	**MEA+MDEA**
Amine concentration (%wt)	35	15	MEA: 10 MDEA: 35
Mass flow rate (MT/h)	11	8	11
Reboiler duty (MW)	12,17	11,99	12,26
CO_2 loading (mole CO_2/mole amine)	0,399	0,746	0,291

Once again, the superiority of MEA in CO_2 removal with lower mass flow rate is demonstrated, while no significant difference in the required flow rate is observed for both DEA and the solvent blend.

The energy consumption in the reboiler is the lowest for MEA, followed by DEA and MEA+MDEA. One of the reasons for this lower consumption is the higher acid loading in the solvent, which means that a smaller volume of solvent needs to be processed in the stripper. However, working with such high acid loadings is not allowed due to severe corrosion issues in the system. As mentioned earlier, the maximum allowed acid loading for MEA is 0,4.

The use of DEA will significantly reduce the corrosive effect even though it requires a slightly higher reboiler duty.

For these reasons and based on the results presented in the previous figures, DEA has been considered as the best option in this case.

4.3.2. Effect of Solvent Temperature

Another variable with a relatively high influence on the absorption process is the temperature at which the lean amine is fed. The following figures show how the molar fractions of methane and carbon dioxide vary with respect to temperature in purified biogas and rich amine streams.

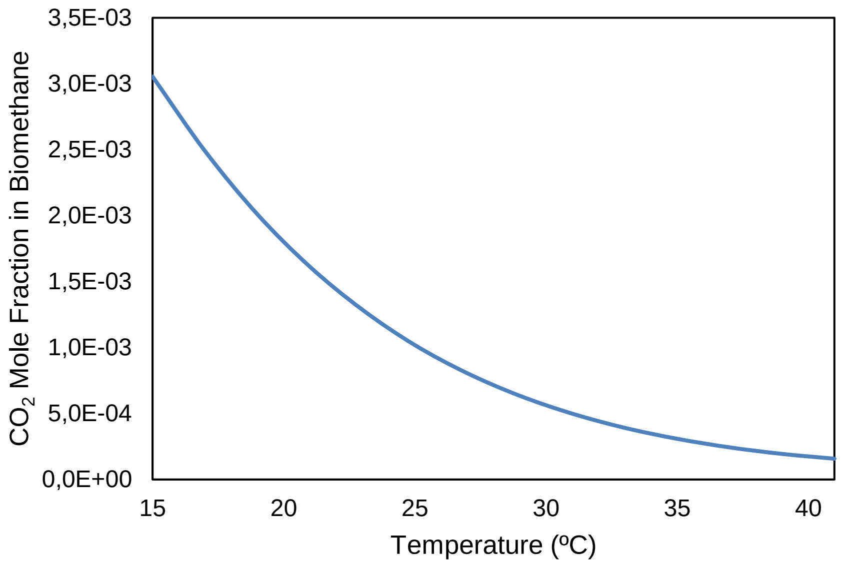


Figure 4.7 Variation of CO_2 mole fraction in the upgraded gas with respect to lean DEA feed temperature.

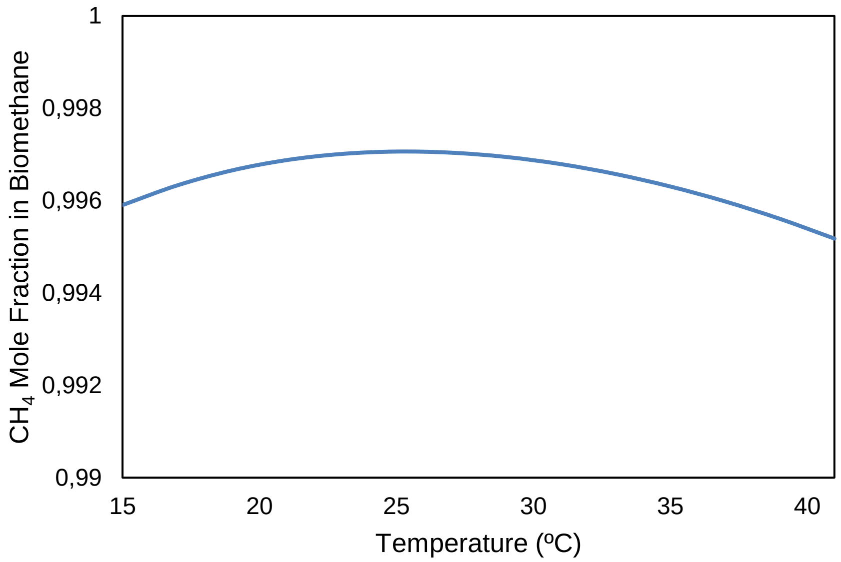


Figure 4.8 Variation of CH_4 mole fraction in the upgraded gas with respect to lean DEA feed temperature.

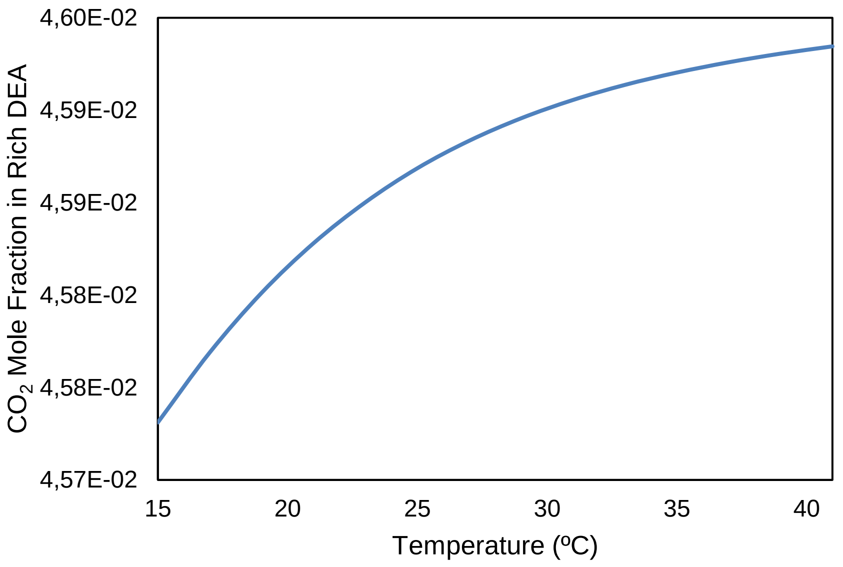


Figure 4.9 Variation of CO_2 mole fraction in the rich DEA with respect to lean DEA feed temperature.

The temperature range used for the study is based on bibliographic data on typical operating temperatures. It can be seen in the figures how the mole fraction in biogas and in rich DEA decreases and increases respectively with temperature, although this increase is smaller as temperature increases.

The reaction speed and diffusivity are enhanced with the increase in temperature, and therefore also the absorption process.

On the other hand, a temperature that is too high translates into a higher vapor pressure of the liquid, favoring solvent losses by vaporization.

Therefore, based on the results obtained with the base case, it is recommended to work in a temperature range of 35 to 40 ºC.

4.3.3. Effect of Solvent Concentration

The concentration of amine in the solvent used in the process has significant effects on the overall performance, cost and environmental impact of the process.

When a higher concentration of amines is used more reactive sites are available for acid gas molecules to be absorbed, resulting in higher removal efficiency. The reaction rate can also be increased, reducing the contact time necessary between the amine solution and the gas, and thus resulting in a smaller size of the equipment.

On the other hand, a high concentration of amine increases operating costs as it needs to be constantly replenished due to degradation and losses that occur. Additionally, corrosion is also higher, as well as foam generation, which impacts process efficiency.

Therefore, below is the study conducted to verify the effect of this variable in the base case.

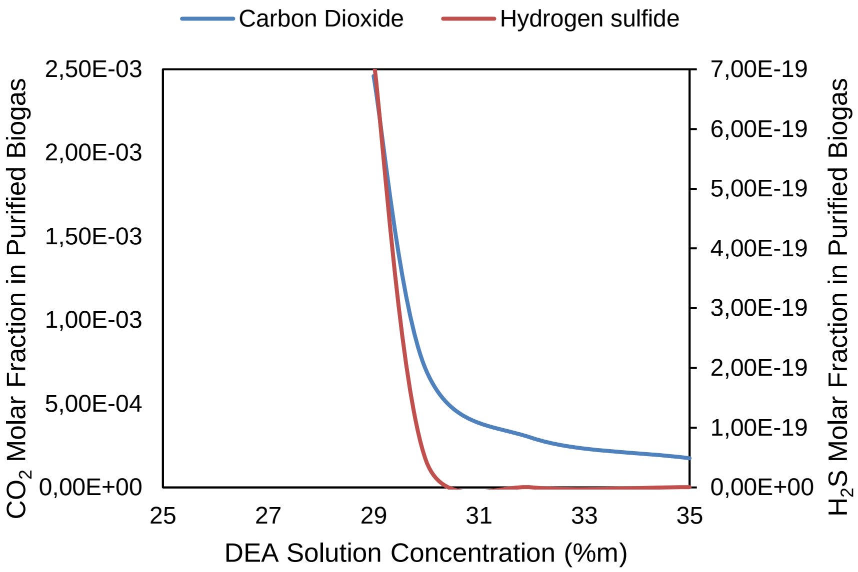


Figure 4.10 Variation of acid gases molar fractions in the purified biogas with respect to the DEA solution concentration.

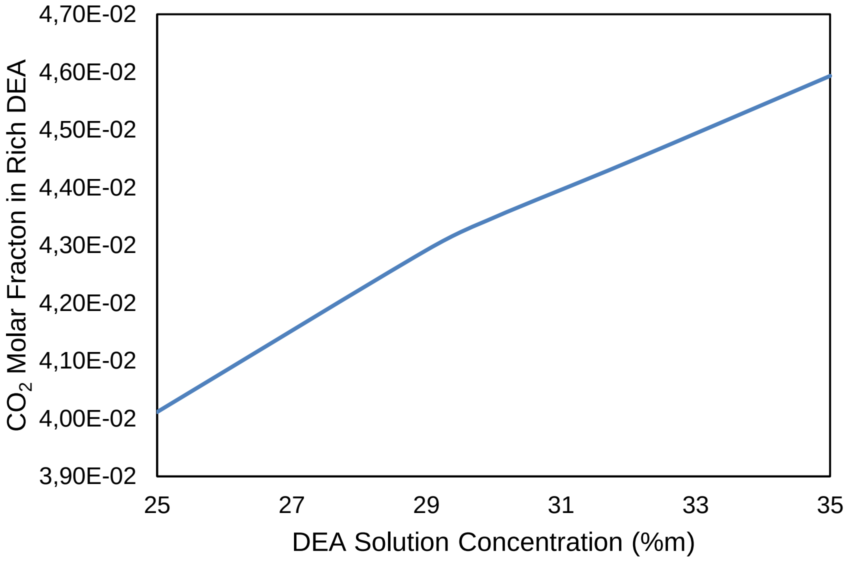


Figure 4.11 Variation of CO_2 molar fraction in rich DEA with respect to the DEA solution concentration.

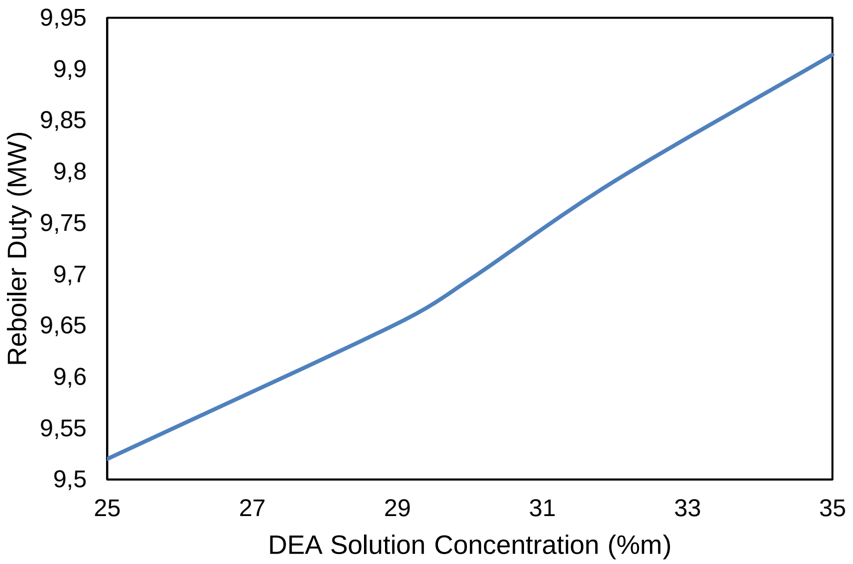


Figure 4.12 Variation of reboiler duty with respect to the DEA solution concentration.

The concentration range considered for the study is from 25% to 35% by mass, as these are commonly used values in the industry and cause moderate corrosion.

Figure 4.10 shows how the molar fraction of acid gases decreases linearly up to 30%, beyond which no significant variations in molar fractions are observed. Therefore, it is recommended to work with concentrations around 30% by mass in this case.

4.3.4. Effect of Absorber Pressure

The operating pressure of the absorber is a variable that can significantly impact the process at many levels.

The solubility of gases in a liquid is often influenced by pressure. In cases such as amine-based processes, higher pressures can increase the solubility of the acid gases in the solvent, leading to a higher absorption capacity.

In another hand, the driving force for mass transfer is the difference in concentration between the gas phase and the liquid phase. A higher pressure can increase the partial pressure of gases in the gas phase, resulting in a larger driving force for mass transfer and potentially a higher absorption rate, leading to a more efficient gas removal in the sweetening process.

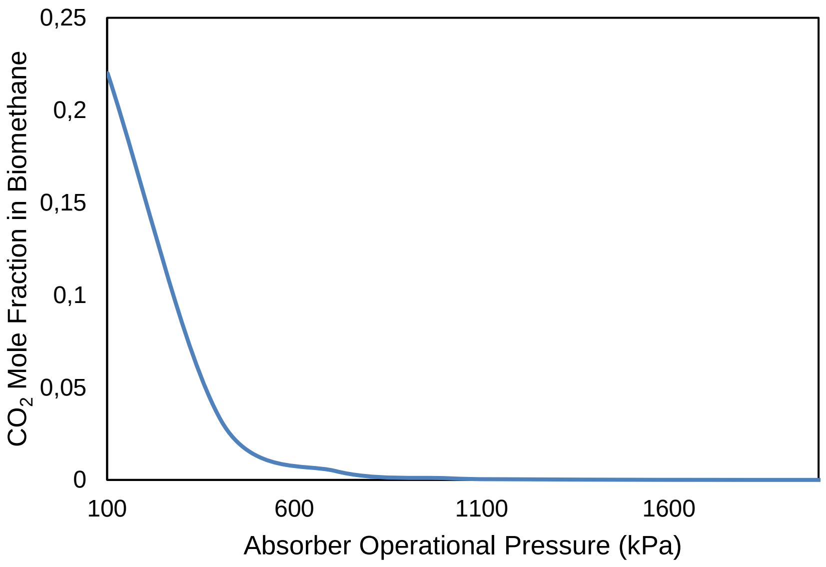


Figure 4.13 Variation of CO_2 mole fraction in the upgraded gas with respect to pressure in the absorber.

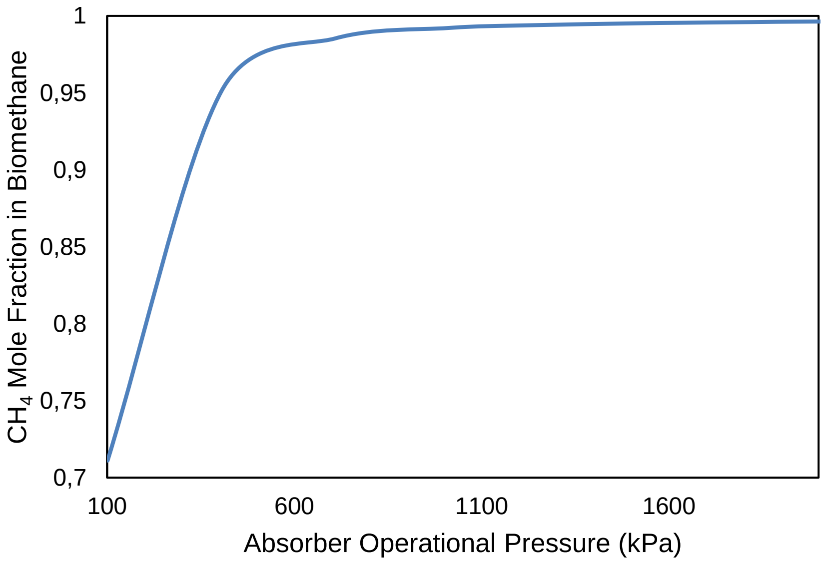


Figure 4.14 Variation of CH_4 mole fraction in the upgraded gas with respect to pressure in the absorber.

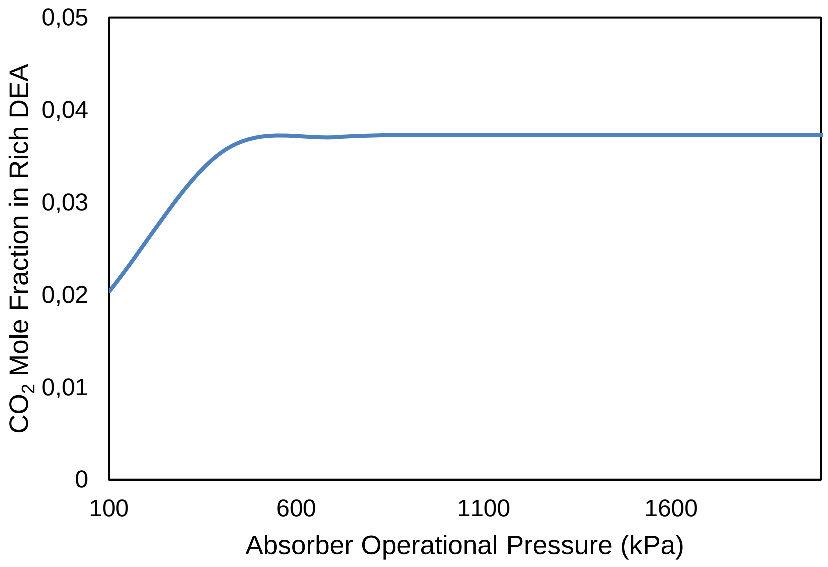


Figure 4.15 Variation of CO_2 mole fraction in the rich DEA with respect to pressure in the absorber.

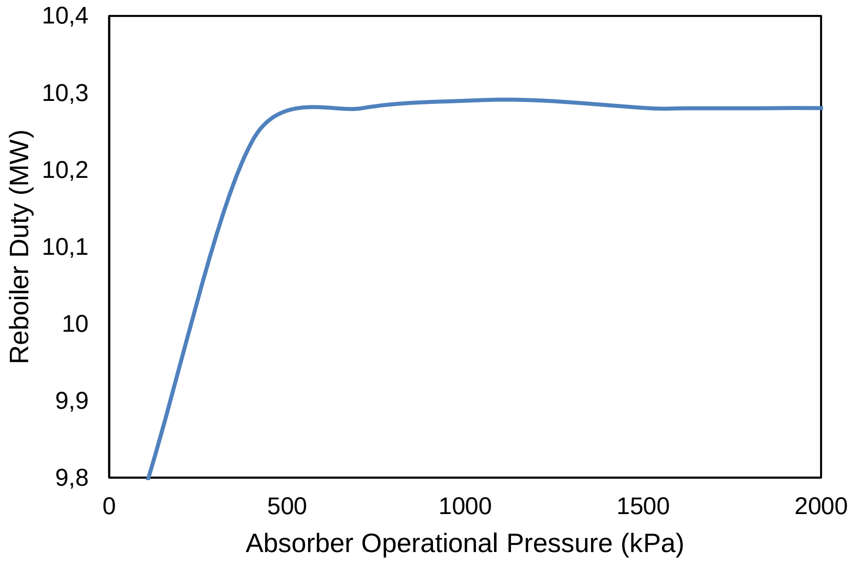


Figure 4.16 Variation of reboiler duty with respect to pressure in the absorber.

According to the results shown in the previous figures, a pronounced and continuous decrease in the biogas CO_2 mole fraction can be observed, especially at pressures up to 1500 kPa, from which the variation is not very notable in this case since, by maintaining a constant amine flow rate, the maximum load of acid gas is reached.

The specification of maximum CO_2 content (50 ppm) is met at a pressure of 1621,2 kPa (16,21 bar).

Considering these results, it is determined that the recommended operating pressure for the absorption column is 15-20 bar.

4.3.5. Effect of Reboiler Pressure

Bearing in mind that the reboiler of the regenerating tower is responsible for the energy compensation of the plant and given that the necessary heat is produced in this equipment to vaporize the regenerated solution, the pressure variation of the reboiler is then considered as a case study.

The pressure variation range is from 200 to 450 kPa. Given this variation, the behaviour of two fundamental variables of the regeneration process is studied: the temperature of the amine stream and the concentration of CO_2 in the regenerated amine.

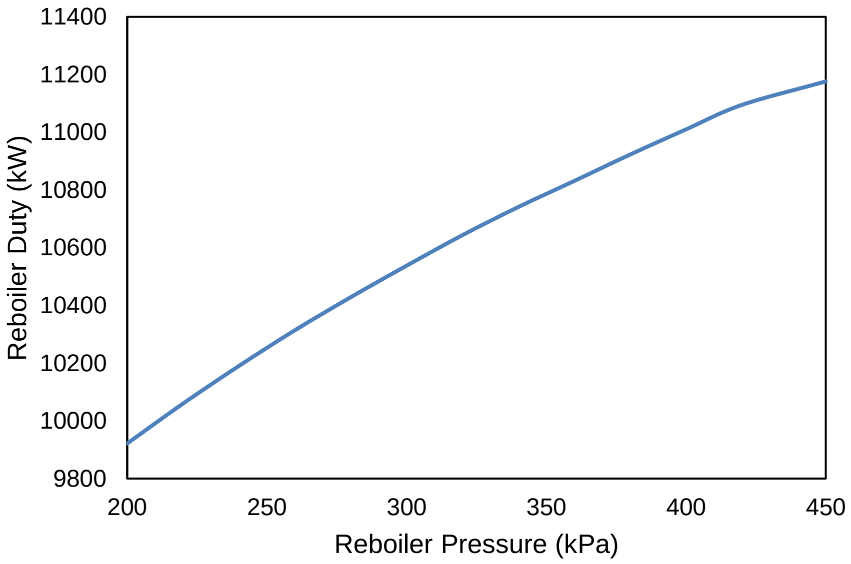


Figure 4.17 Variation of reboiler duty with respect to reboiler pressure.

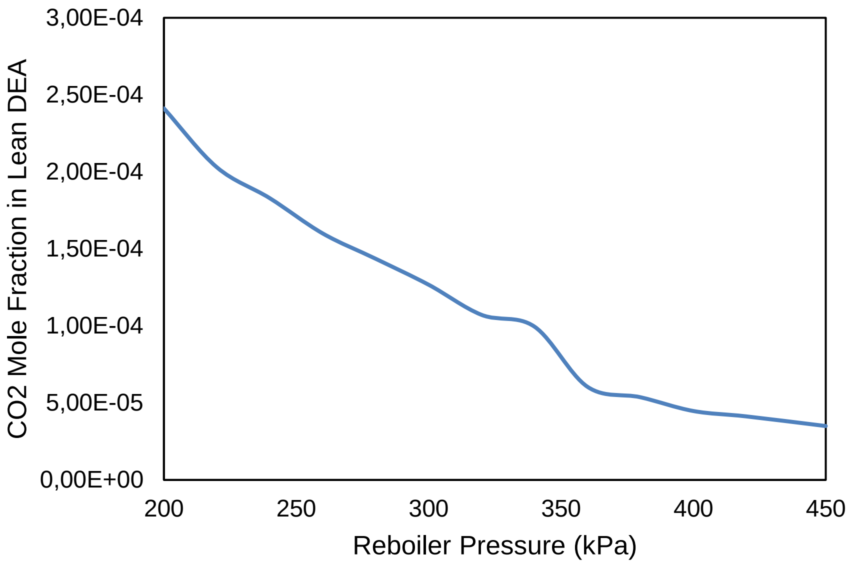


Figure 4.18 Variation of CO_2 mole fraction in lean DEA with respect to reboiler pressure.

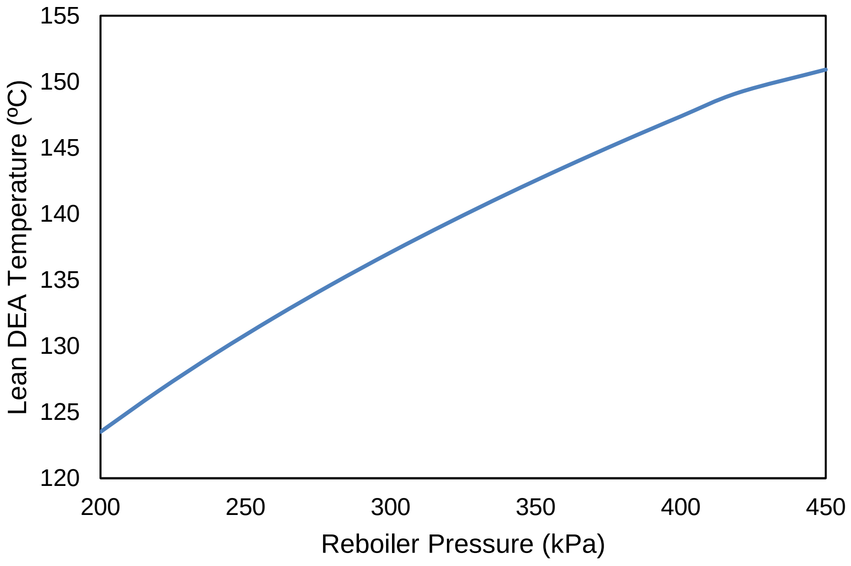


Figure 4.19 Variation of lean DEA temperature with respect to reboiler pressure.

As can be seen in the figures, the reboiler operating pressure has a linear relationship with higher regeneration. A higher pressure allows reaching higher temperatures that enhance the depletion of the amine.

Higher stripper pressure however increases the bottom temperature and can cause excessive corrosion and chemical degradation of the amine. Typical pressures in amine units range from 60 to 170 kPa with a maximum temperature of up to 126 ºC.

On the other hand, a too low temperature can cause poor separation of acid gases and therefore cause additional corrosion.

In this work, the temperature in the regenerating tower reaches a maximum value of 124 °C, not exceeding the maximum of 126 °C nor reaching the minimum of 110 °C, values in which corrosion is possible.

4.4. Process Flow Diagram (PFD)

The PFD diagram of the process will be presented in appendix A.

5. Preliminary Optimization

The optimization is a tool that consists of several processes in which mathematical methods are used to determine the optimal operating conditions of a given system, complying with the specifications and restrictions specified by the user. (Tapias García & Palacio Santos, 2013)

Aspen HYSYS has a multi-variable steady state optimizer which has a dedicated spreadsheet in which any mathematical expression can be specified for the objective function, variables and/or constraints.

As previously mentioned, the upgrading stage is highly demanding in energy terms.(Arachchige, 2019) For this reason, it is of vital importance to carry out an optimal design so that the process operates in operating conditions that allow the lowest energy consumption, and in turn respecting the product specifications and the safety of plant operation.

Applied to the upgrading process that has been modelled, it is intended to find the operating conditions that make it more efficient, based on the objective functions and restrictions that are shown later.

5.1. Theoretical Framework

In an optimization problem, the main elements are the objective function, the variables, and the constraints. The goal is to find the optimal values of the variables that maximize or minimize the objective function, complying with all the restrictions.

Optimization problems can be classified into two main categories(Vecchietti, 2000):

- Linear optimization problem. Both the objective function and the constraints are linear. These problems can be solved efficiently using linear programming methods.
- Nonlinear optimization problem. These are the most common in chemical engineering. The objective function or some of the constraints are nonlinear. These problems are more complex and require numerical methods and nonlinear optimization algorithms to find the optimal solution.

In an optimization problem, linear or nonlinear, several local minima can exist, but there can only be one global minimum. Unlike linear optimization, where there are few minima, nonlinear optimization often has multiple local minima and only one global minimum.(Rødstøl, 2015)

Due to the nature of nonlinear optimization, there can be several feasible regions that result in different local minima. If the starting point is in a feasible region where the local minimum is not the global minimum, the resulting minimum point may have a poorer value. Also, equality constraints are easy to violate in nonlinear optimization when the solver tries to move to another point to reach a lower minimum.

Optimization algorithms search for solutions through iteration. The process begins with an initial assumption of the model variables, which generates a starting point. The optimizer uses this starting point to generate a sequence of best estimates until a solution is reached. The way the algorithm iterates varies depending on the type of optimization algorithm. However, all algorithms must possess the following properties: efficiency, precision, and robustness. (Rødstøl, 2015)

- Efficiency. The problem must be solved without using too much computing and storage time.
- Accuracy. Involves finding an accurate solution without being overly sensitive to rounding and data errors that occur during solving.
- Robustness. The algorithm should perform well on a variety of problems within its class, for all reasonable choices of initial variables.

Mathematically, an optimization problem can be represented as follows (Vecchietti, 2000):

$$Minimize\ f(x) \qquad subject\ to \begin{cases} g_i(x) \geq 0,\ i = 1, \ldots, m \\ h_i(x) = 0,\ i = 1, \ldots, l \end{cases} \tag{5.1}$$

Where x is the vector of variables and f(x) is the objective function to be optimized. The functions g(x) and h(x) are functions that represent the inequality and equality constraints, respectively.

5.2. Method

Any optimization problem contains at least one objective function to be optimized (minimized/maximized), equality or inequality constraints, and optimization variables with their respective limits. (Vecchietti, 2000)

Therefore, the process followed to carry out the optimization consists of the following steps:

1. Selection of the variables that are degrees of freedom. These can be defined during the optimization runs by changing the specifications to optimized or independent variables. Typically, these variables correspond to the operating conditions that can be manipulated and are targets of the control system.
2. Setting limits on the variables. By setting upper and lower limits on the variables, the movement of the Aspen solver during optimization is restricted by these limits. Limits can be placed on any variable, whether it is a degree of freedom or not. Sensitivity analysis results are useful to define these limits.
3. Definition of an objective function and its constraints. The objective function is the equation that is to be optimized by manipulating the degrees of freedom in the problem. There can be more than one objective function in a problem, but the solver uses only one during execution.
4. Execution of the problem in optimization mode. The problem is executed by selecting the optimization mode.

One of the key points to increase the chances of finding an optimal solution to the problem is its proper definition. In this case, for the definition of the optimization problem, the data obtained in the sensitivity analysis previously presented have been used as a basis. In these analysis, the best operating ranges of the most relevant process variables were determined, according to bibliographic sources.

Once the model is defined, the optimization algorithm must be chosen. The selection strongly depends on the nature of the process, and it can make the difference between solving the problem or not, as well as the time needed to do so.

The task does not end here, since after applying the algorithm and obtaining the results, these must be analysed to ensure that it is an adequate solution. If it is not, the optimization parameters or the problem specifications must be modified. (Vecchietti, 2000)

5.3. Optimization Problem

As previously mentioned, the upgrading process is one of the biomethane processing stages with the highest energy consumption. During this process, the impurities present in the biogas, CO_2 for instance, are removed by absorption with an amine solution. The amine solution is then heated to release the impurities, leaving behind a purified biogas. However, heating the amine solution requires a significant amount of energy, which can make the process energy-intensive and increase its overall cost. (Arachchige, 2019)

Several factors can influence the energy requirements of biogas upgrading through amine absorption, including the composition of the biogas, the type and concentration of the amine solution, and the desired purity of the final biogas product. (Arachchige, 2019)

The optimization of these and/or other variables is crucial to obtain an efficient design that meets the product specifications and ensures safe operation.

After carrying out the sensitivity analysis, useful information was obtained to determine which are the most interesting variables to be used as degrees of freedom and to which it is more interesting to give a fixed value.

It is proposed to carry out the optimization in two stages; the first focused on minimizing energy consumption in biogas compression, and the second stage focused on minimizing the reboiler consumption of the solvent regeneration stage.

Below are the defined objective functions for the process optimization, as well as the constraints and variables that have been chosen as degrees of freedom.

5.3.1. Objective Function 1

The objective function 1 (Table 5.1) must be minimized, and it is the sum of the power consumption of the compressors of the biogas compression stage.

Table 5.1 Objective function 1.

Objective Function 1	$\min \dot{W}_{comp\ 1} + \dot{W}_{comp\ 2}$		
		Condition	**Value**
Constraints	CO_2 concentration in purified biogas	<	50 ppm
	H_2S concentration in purified biogas	<	5 ppm
	Removal efficiency	>	98%
Degrees of freedom		**Lower Bound**	**Upper Bound**

	Lean DEA flow rate	40000 kg/h	55000 kg/h
	Absorber pressure	15 bar	20 bar
	Solvent temperature	35°C	40°C

As can be seen, the defined restrictions refer to the specifications of the product and the removal efficiency of the plant. Respecting the maximum threshold in acid concentrations in the final product is essential for the purified biogas to be suitable for subsequent processing stages. (Rødstøl, 2015)

The degrees of freedom affect the process and the objective functions in the following ways:

- Lean DEA flow rate. An increase in this variable can lead to a decrease in energy consumption since a higher contact surface and loading are achieved, making the process more efficient. However, beyond a certain point, the increase in flow rate can also increase the energy consumption due to the regeneration in the stripper and pumping costs. Therefore, this variable has effect in both objective functions.
- Absorber pressure. This variable affects the solubility of gases in the solvent. A higher pressure will increase the solubility and the partial pressure of gases, leading to a larger driving force for mass transference and potentially a higher absorption rate until a certain point. This variable has a directly proportional relation with the consumption in the compression stage.
- Solvent temperature. The reaction speed and diffusivity are enhanced with the increase in temperature, and therefore also the absorption process, increasing its efficiency. A higher temperature can allow a reduction of the pressure needed in the absorber.

5.3.2. Objective Function 2

The objective function 2 (Table 5.2) must also be minimized and it is the energy consumption of the reboiler.

Table 5.2 Objective function 2.

Objective Function 2		$\min \dot{Q}_{reb}$	
		Condition	**Value**
Constraints	Temperature in reboiler	<	126,7°C
	CO_2 concentration in regenerated solvent	<	500 ppm
	H_2S concentration in purified biogas	<	5 ppm
		Lower Bound	**Upper Bound**
Degrees of freedom	Reboiler pressure	60 kPa	200 kPa
	Reflux ratio	2	5

As already mentioned, high operating temperatures in the reboiler can lead to the degradation of the amine present in the solvent. (Stewart & Arnold, 2011) Due to that, a restriction regarding the maximum operating temperature in the reboiler has been established.

The maximum composition of acids in the solvent has also been established as a restriction since it will be recirculated to the absorption stage to absorb acids again.

The degrees of freedom affect the process and the objective functions in the following ways:

- Reboiler pressure. A higher value allows to reach a higher temperature and has a linear relation with higher regeneration, enhancing the depletion of the amine. This variable has a directly proportional relation with the reboiler energy consumption.
- Reflux ratio. A higher value improves the CO_2 removal efficiency, but it will also require more energy to pump the solvent back and to operate the reboiler, since more energy is needed to reheat.

5.4. Hyprotech SQP Solver

Aspen HYSYS has several optimization solvers for nonlinear problems, including derivative free algorithms and an SQP solver among others.(Rødstøl, 2015) The solver chosen in this optimization problem is Hyprotech SQP since it has been used before in the same type of problem and has shown to be capable of providing good results.(Hashemi Sayed Ebrahim et al., 2019)

5.4.1. SQP Optimization

The SQP (Sequential Quadratic Programming) algorithm is based on the sequential quadratic optimization technique, which is an iterative method used to solve nonlinear optimization problems. This method focuses on solving a series of sequential quadratic programming problems, which are local approximations of the original nonlinear optimization problem.

The basic idea of sequential quadratic programming is to solve the necessary Karush-Kuhn-Tucker optimality conditions using Newton's method (or quasi-Newton methods). (Rødstøl, 2015)

The Hyprotech SQP solver uses a combination of gradient methods and sequential quadratic programming to find optimal solutions. At each iteration, the algorithm calculates a quadratic approximation of the original problem and then solves this approximation using a sequential quadratic programming method. The algorithm then uses the gradient of the objective function to compute a search direction and makes adjustments to the current solution in that direction. (AspenTech, 2004)

The Hyprotech SQP solver can find optimal solutions for a wide variety of nonlinear optimization problems in Aspen HYSYS. Furthermore, this solver is very efficient and accurate in solving nonlinear optimization problems, which makes it a valuable tool for process optimization in the chemical industry.

5.4.2. Derivative Utility Set Up

For the use of the solver Hyprotech SQP, a derivative utility must be defined. There are three main components: variables, constraints, and the objective function. The variables are the independent properties that are changed to satisfy the dependent variables or constraints. This is done simultaneously to achieve an optimized objective function within the feasible boundaries of the problem. (Rødstøl, 2015)

- Objective function. It is the function to be optimized. It can be defined as a single variable or as a combination of several variables into one expression, that can be specified in the dedicated spreadsheet.
- Variables. These are the degrees of freedom, and they are imported directly from the flowsheet. These parameters are varied to optimize the objective function. The upper and lower bounds must be specified, providing a search range to the optimizer to find a solution. Therefore, these bounds should be set in a proper way, based on the knowledge of the process. The status of a variable can be shown as:
  - Inactive. The optimizer has succeeded in finding a variable value in between the upper and lower bound, meaning that the variable does not prevent the optimizer in its search for the best value.
  - Active low. The value equals the lower bound. The search region is limited by the lower boundary.
  - Active high. The value equals the higher bound. The search region is limited by the higher boundary.
- Constraints. The constraints of the problem. These can be equality or inequality. Unlike variables, they can be one-sided, assuming a maximum or minimum value of a parameter. A scale value can be specified, which translates into the tolerance towards the constraint. Increasing this value simplifies the task of the optimizer in finding an optimum.

Initially, the information in tables 5.3 and 5.4 was entered. As the optimizer has run, variations can be made to the bounds of the variables and/or the constraints to find a suitable solution to the problem and to solve problems that may appear in the optimization. These variations are discussed later, in the Running results section.

Table 5.3 Derivative utility values for variables in Objective function 1.

Variables	**Lower bound**	**Starting value**	**Upper bound**
Lean DEA flow rate (kg/h)	20000	50000	55000
Absorber pressure (kPa)	1500	1600	2000
Solvent temperature (°C)	35	40	40
Constraints	**Minimum**	**Starting value**	**Maximum**
CO_2 mole frac. in purified biomethane	-	$4{,}76\cdot10^{-5}$	$5\cdot10^{-5}$

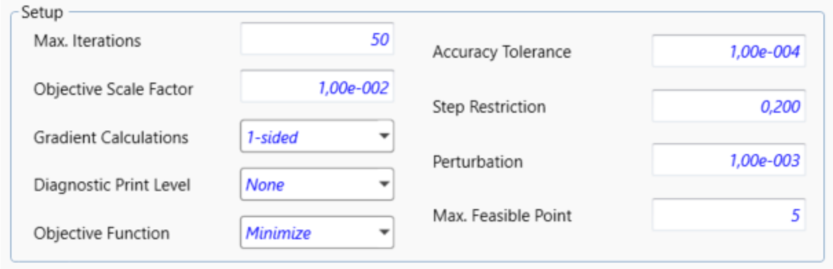
H_2S mole frac. in purified biomethane	-	$1{,}39\cdot10^{-10}$	$5\cdot10^{-6}$
Removal efficiency	0,98	0,999	-

Table 5.4 Derivative utility values for variables in Objective function 2.

Variables	**Lower bound**	**Starting value**	**Upper bound**
Reflux ratio	2	2,6	5
Reboiler pressure (kPa)	60	200	200
Constraints	**Minimum**	**Starting value**	**Maximum**
Temperature in reboiler (°C)	-	123,5	126,7
CO_2 mole frac. in lean DEA	-	$2{,}37\cdot10^{-4}$	$5\cdot10^{-4}$
H_2S mole frac. in lean DEA	-	$2{,}17\cdot10^{-8}$	$5\cdot10^{-6}$

5.4.3. Optimizer Set Up

The second part to be configured is the Optimizer. In this interface the solver can be chosen, Hyprotech SQP in this case. Once the solver is selected, a series of parameters with default values are displayed. The values of these parameters can be modified to facilitate the search for the solution. The default values are shown in Figure 5.1.



Setup

Max. Iterations 50

Objective Scale Factor 1,00e-002

Gradient Calculations 1-sided

Diagnostic Print Level None

Objective Function Minimize

Accuracy Tolerance 1,00e-004

Step Restriction 0,200

Perturbation 1,00e-003

Max. Feasible Point 5

Figure 5.1 Default values of Optimizer parameters.

A brief description of their effect on the process is given below. (AspenTech, 2004)

- Maximum iterations. Number of maximum iterations that the optimizer will do to achieve a desired objective value. Each major iteration consists of several minor iterations.

- Objective scale factor. Used for scaling the objective function. The specified factor is multiplied by the objective function, giving the optimizer a relative weight between the objective function and feasible search region. Low values can help in solving non-linear optimization problems.
- Diagnostic print level. Selects the amount of information to be included in the Optimizer diagnostic file.
- Objective function. Specifies if the objective function must be minimized or maximized.
- Gradient calculations. Specifies if one-sided (forward) or two-sided (central) differences are to be used for gradient calculations. Two-sided calculations perform twice as many function evaluations as one-sided calculations.
- Accuracy tolerance. Factor of the relative accuracy tolerance of the objective function improvement and is used as a convergence test for the optimizer. It is a weighted sum of possible objective function improvement and constraint violations. A very low value will make the objective function more accurate, but possibly resulting in step convergence, meaning that the accuracy could not be met in the given number of iterations.
- Step restriction. A line search step-size restriction factor used during the first 3 iterations. A value greater that 1 result in no step restriction.
- Perturbation. The perturbation can be viewed as a change in the scaled variables during gradient evaluation. A lower value results in faster gradient calculations, however, by setting a lower value, the gradient is limited and therefore it may not give an accurate gradient in cases where there is significant noise in the simulation.
- Max. feasible points. This parameter decides the maximum number of iterations that the optimizer can utilize in the line search procedure.

Following the recommendations provided in bibliographic sources, some of these initial parameters have been modified with the objective of facilitating the optimization and obtaining better results for the objective functions. The time required for optimization has not been a relevant factor in this case.(Rødstøl, 2015)

As for the Maximum iterations, Feasible points, Accuracy value, Gradient calculations and Step restriction parameters, it is recommended to provide a fixed value and not make further adjustments later.

To avoid limiting the search for the solution, it is recommended to give high values to the Maximum iterations and Feasible points parameters. In this case, 500 and 10 were defined respectively, based on data provided in bibliographic sources. (Rødstøl, 2015)

A value of 1 was given to the Step restriction parameter, meaning that there is no step restriction.

The Accuracy tolerance parameter should be set to a low value so that a result with high accuracy is obtained. Typical values are between 10^{-4} and 10^{-5}. For this parameter, the default value was kept.

The two-sided option was selected in the Gradient calculations parameter, due to the advantage of performing twice as many mathematical operations in the search for the optimal value of the objective function, which is highly recommended in highly nonlinear or noisy processes.

The Objective scale factor and Perturbation parameters must be modified after each execution of the Optimizer, to correct different errors that may arise. According to bibliographical sources, small changes in the Perturbation parameter may solve small modifications in the processes, while modifications that are more extensive may require adjustments in the Objective Scale Factor parameter.

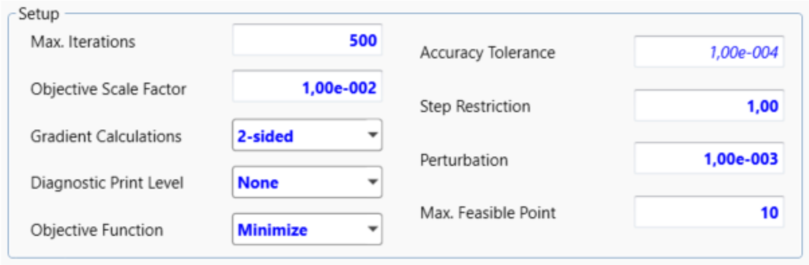

Setup
Max. Iterations 500
Objective Scale Factor 1,00e-002
Gradient Calculations 2-sided
Diagnostic Print Level None
Objective Function Minimize
Accuracy Tolerance 1,00e-004
Step Restriction 1,00
Perturbation 1,00e-003
Max. Feasible Point 10

Figure 5.2 Optimizer parameter set-up based on bibliographic recommendations.

5.4.4. Running Results

This section shows the process followed in the optimization as well as the relevant results obtained during it. As already mentioned, objective function 1 was optimized first, followed by objective function 2. The variables were added to the derivative utility one by one to facilitate the detection of possible sources of error in the convergence.

5.4.4.1. Objective function 1

In the optimization of the objective function 1, modifications had to be made to the definition of some variables of the unitary operations of the flowsheet.

The biogas feed pressure should be the same as the absorber stage it is fed into. Likewise, for correct operation, the pressure at the head of the column must be lower or equal to the pressure at the bottom of the column. To ensure that these conditions were met, the spreadsheet integrated in the Optimizer was used, defining the pressure of stage 20 as the base and exporting this pressure to the biogas feed and to the head of the column.

Regarding the temperature of the solvent, it must be ensured that it is the same before and after the recycling unit implemented in the flowsheet. Due to that, the SET unit was used. Not making this modification resulted in the inability for the Optimizer to make changes to the temperature.

- Addition of the absorber pressure

First, the absorber operating pressure variable was activated. The Optimizer operation did not show any problems or errors with the initially defined limits. The initial value of the variable was varied, indistinctly obtaining the same optimum point.

Table 5.5 Running results of Objective function 1 with the absorber pressure as active variable and a start value of 1600 kPa.

		Initial value	Final value
All constraints within boundaries?		No	Yes
Variable	Abs. pressure (kPa)	1600	1681,8

Objective functions	1 (kW)	590,35	603,82
	2 (kW)	$5,78\cdot 10^{3}$	$5,78\cdot 10^{3}$
Constraints	CO_2 mole frac. in biomethane	$7,06\cdot 10^{-5}$	$5,00\cdot 10^{-5}$
	H_2S mole frac. in biomethane	$1,24\cdot 10^{-10}$	$1,02\cdot 10^{-10}$
	Removal efficiency	0,999	0,999

Table 5.6 Running results of Objective function 1 with the absorber pressure as active variable and a start value of 2000 kPa.

		Initial value	**Final value**
All constraints within boundaries?		Yes	Yes
Variable	Abs. pressure (kPa)	2000	1682,3
Objective functions	1 (kW)	651,61	603,91
	2 (kW)	$5,78\cdot 10^{3}$	$5,78\cdot 10^{3}$
Constraints	CO_2 mole frac. in biomethane	$1,49\cdot 10^{-5}$	$5,00\cdot 10^{-5}$
	H_2S mole frac. in biomethane	$1,24\cdot 10^{-10}$	$1,19\cdot 10^{-10}$
	Removal efficiency	0,999	0,999

In both situations, a better value of the objective function is reached, either for which all the restrictions are fulfilled and/or to minimize its value. It can be seen that in the case of starting with a pressure further from the optimum, more iterations are necessary to reach it.

The H_2S concentration and removal efficiency restrictions are always within the limits, with the CO_2 concentration being the restriction that most limits the objective function.

As can be seen in the results tables, the value of the objective function 2 is not significantly affected by the variation in the absorber pressure in these ranges.

- Addition of lean DEA mass flow rate

Next, the solvent mass flow variable was activated. The first error that was obtained was "Unbounded", which was solved by changing the limits on the mass flow variable to a lower limit of 40 MT/h and an upper limit of 60 MT/h.

On the other hand, the pressure variable showed the "active low" status, which leading to the result not respecting the CO_2 concentration restriction. This issue was fixed by changing the lower limit from 1500 kPa to 1000 kPa.

The initial value of the variables did not show any effect on the final results obtained.

Table 5.7 Running results of Objective function 1 with the absorber pressure and lean DEA mass flow rate as active variables.

		Initial value	Final value
All constraints within boundaries?		No	Yes
Variable	Abs. pressure (kPa)	1600	1521,48
	Lean DEA mass flow rate (MT/h)	50	60
Objective functions	1 (kW)	590,35	576,87
	2 (kW)	$5{,}78 \cdot 10^3$	$6{,}04 \cdot 10^3$
Constraints	CO_2 mole frac. in biomethane	$7{,}03 \cdot 10^{-5}$	$5{,}02 \cdot 10^{-5}$
	H_2S mole frac. in biomethane	$1{,}63 \cdot 10^{-10}$	$1{,}61 \cdot 10^{-10}$
	Removal efficiency	0,999	0,999

It can be seen in the final results that the solvent mass flow variable reached the established upper limit, giving pressure room to be minimized with respect to the optimizations shown in tables 1.4.3. and 1.4.4. Likewise, it is observed that the increase in solvent significantly affected objective function 2, since more amount of solvent must be processed in the stripper.

- Addition of lean DEA temperature

Finally, the solvent inlet temperature variable was activated. By having the three variables active, some errors occurred during the optimization that could be solved by modifying the limits of the variables and the parameters of the Optimizer.

The initial pressure affected the operation of the Optimizer, presenting the Step convergence error with an initial value of 1600 kPa. This was fixed by increasing the initial pressure.

Likewise, beginning the optimization with the constraints within the specifications facilitated subsequent convergences.

Table 5.8 Running results of Objective function 1 with all variables active.

		Initial value	Final value
All constraints within boundaries?		Yes	Yes
Variable	Abs. pressure (kPa)	2000	1342,11
	Lean DEA mass flow rate (MT/h)	50	60
	Lean DEA temperature (°C)	40	45

Objective functions	1 (kW)	651,61	543,8
	2 (kW)	$5{,}78\cdot10^{3}$	$6{,}04\cdot10^{3}$
Constraints	CO_2 mole frac. in biomethane	$1{,}40\cdot10^{-5}$	$5{,}00\cdot10^{-5}$
	H_2S mole frac. in biomethane	$7{,}48\cdot10^{-11}$	$2{,}29\cdot10^{-10}$
	Removal efficiency	0,999	0,999

As can be observed in the results, the variation of the solvent temperature did not significantly affect the value of the objective function 2, being the mass of the solvent the variable with the greatest effect on it.

The addition of this variable allowed to improve the value of the objective function 1.

5.4.4.2. Objective Function 2

In the same way as for objective function 1, the execution of objective function 2 implied making changes to the flowsheet. The pressure in the condenser (and in the upper stages) must be lower than the pressure in the reboiler. The flowsheet was used again to properly define and export these variables.

In this case, no problems or errors were obtained during optimization. The initial value of the variables had no effect on the final value of the objective function.

Table 5.9 Running results of Objective function 2 with all variables active.

		Initial value	Final value
All constraints within boundaries?		No	Yes
Variable	Reboiler pressure (kPa)	200	198
	Reflux ratio	2,6	3
Objective functions	1 (kW)	543,8	543,8
	2 (kW)	$6{,}04\cdot10^{3}$	$6{,}45\cdot10^{3}$
Constraints	CO_2 mole frac. in reg. DEA	$5{,}27\cdot10^{-4}$	$5{,}03\cdot10^{-4}$
	H_2S mole frac. in reg. DEA	$4{,}87\cdot10^{-8}$	$4{,}43\cdot10^{-8}$
	Removal efficiency	123,2 ºC	122,9

Initially, the restrictions were not within the specifications. Therefore, the final value of the objective function has turned out to be greater than the initial one to comply with the restrictions.

The pressure has decreased slightly but the reflux ratio has increased, which increases the energy that the reboiler must provide.

It can be seen that there is no effect on objective function 2, since the absorber operating pressure is not modified at any time. However, slight variations were observed in the concentration of acids present in the biomethane. This is due to the modification of the concentration of the solvent regenerated in the optimization, which is recirculated to the absorption stage.

5.5. Final Result

The optimization of the process is carried out with the objective of obtaining the lowest energy consumption in the biogas compression and stripping stages, and ensuring the compliance with the established restrictions, both for reasons of operation and product quality.

The final results obtained after performing the optimization are shown below.

Table 5.10 Final results of the optimization.

		Initial value	**Final value**
All constraints within boundaries?		No	Yes
Variable	Abs. pressure (kPa)	1600	1349
	Lean DEA mass flow rate (MT/h)	50	60
	Lean DEA temperature (°C)	40	45
	Reboiler pressure (kPa)	200	198
	Reflux ratio	2,6	3
Objective functions	1 (kW)	590,35	545,1
	2 (kW)	$5{,}78 \cdot 10^{3}$	$6{,}45 \cdot 10^{3}$
Constraints	CO_2 mole frac. in biomethane	$7{,}06 \cdot 10^{-5}$	$4{,}98 \cdot 10^{-5}$
	H_2S mole frac. in biomethane	$1{,}24 \cdot 10^{-10}$	$6{,}28 \cdot 10^{-10}$
	Removal efficiency	0,999	0,999
	CO_2 mole frac. in reg. DEA	$4{,}56 \cdot 10^{-4}$	$5{,}02 \cdot 10^{-4}$
	H_2S mole frac. in reg. DEA	$4{,}26 \cdot 10^{-8}$	$4{,}43 \cdot 10^{-8}$
	Reboiler temperature (°C)	123,3	122,9

In carrying out the optimization, it was necessary to make changes in the flowsheet and in the way some variables were defined. Likewise, based on bibliographic recommendations, some of the Optimizer parameters were also modified, as explained in section 5.4.3.

It was possible to comply with the restrictions with the lowest value for energy consumption in the biogas compression stage (OF 1), achieving a reduction of 7,66%.

Regarding the consumption of the reboiler, the restrictions were met, although it meant an increase in energy consumption of 11,59%.

The interaction between both objective functions was monitored at all times. It was observed that the OF 1 variable that has the greatest effect is the mass flow of solvent, since it implies an increase in the flow that must be processed in the stripper. The rest of the OF 1 variables did not show an appreciable effect on OF 2.

On the other hand, the optimization of OF 2 had no direct effect on the value of OF 1, since it does not influence the operating pressure. However, the concentrations of acids in the biomethane were affected, since changes in the composition of the solvent have a direct effect on the absorption stage. Therefore, adjustments were made in the optimization of the absorption stage.

It should be noted that in this optimization some of the variables involved in the process were considered. Therefore, as future work it is of interest to add more variables that also have a relevant effect on the optimization. In that case, the interaction between objective functions could give different results.

6. Control and Safety of the Plant

For a proper functioning of the plant, operating at all times within safety ranges and imposed specifications, the control of all equipment in the biogas upgrading process has been designed. A safety study of the plant has also been carried out using the HazOp methodology. It should be noted that this study was conducted on a preliminary design of the plant, and the results in later design stages may vary slightly.

6.1. Theoretical Basis

Any chemical plant is an arrangement of systematically integrated processing units, with the objective of converting a raw material into a desired product using available resources. During the operation, the plant must satisfy requirements imposed by the designers and, in addition, technical, economic and social conditions, in the presence of changing external influences (disturbances), as represented in Figure 6.1.(Stephanopoulos, 1984)

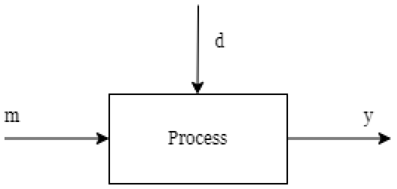


Figure 6.1 Representation of a generalized process with an input (m), an output (y) and a disturbance (d).(Stephanopoulos, 1984)

All the mentioned requirements show a need for continuous monitoring of the operation of the chemical plant and external intervention (through control) to make sure the process satisfies the operational objectives. This is accomplished using equipment (measuring devices, controllers, computers, valves) and human intervention.

The control of a process has the following objectives(Stephanopoulos, 1984):

- Supress the influence of disturbances.
- Ensure the stability of the process.
- Optimize the performance.

To achieve this, control strategies are used, which involve the implementation of control loops.

A control loop is a system that continuously measures process variables, compares measured values with desired values, and takes corrective action to keep the process in its optimal state. These control loops are represented by a P&ID diagram (Piping and Instrumentation Diagram), which shows the graphical representation of the equipment, pipes and instruments involved in the process.

The P&ID diagram is an essential tool for understanding and designing control loops, as it shows how measuring instruments, controllers, and final control elements are connected in the system. With this information, appropriate control strategies can be established, and controller parameters configured to achieve desired process objectives.

6.2. Unit Operations Control Model

In the preparation of the P&ID diagram of the upgrading process, first of all, the objective of each stage or unitary operation has been defined. Next, the variables to be controlled at each stage have been determined, based on the previously mentioned objectives, as well as the operating limits of these variables.

In most cases the final control element is a valve. For the control of each unitary operation, all possible degrees of freedom have been used, which has led to the elimination of some of the proposed control elements.

A brief description of the control strategies carried out in each of the stages and/or equipment of the process will be presented.

6.2.1. Nomenclature Used

An important part of process control is to use a formal and understandable nomenclature. The different formalisms and other aspects that have been followed are explained.

The basic hardware components of a feedback loop are(Stephanopoulos, 1984):

- Process equipment. Unit operations (reactors, separators) or auxiliary equipment (pressure and heat exchange).
- Measuring instruments. They can be diverse, depending on the variable to be measured.
- Transmission lines. Used to carry the measurement signal from the measuring instrument to the controlled, and from the controller to the final control element (usually a valve).
- Controller. Logic unit that compares the measured value with the set point and does the appropriate changes in the final control element.

Figure 6.2 is a representation of the presented elements. In order to differentiate the process lines from the plant control information exchange lines, two parallel lines of reduced length have been added to the control lines.

Secondly, the nomenclature in Table 6.1 has been used when naming the different meters and controllers. An arrow has also been added that indicates the set point to the controllers to which the process variable has to be set.

Finally, all the control elements have been listed through a number according to the stage they are in. In this case, the upgrading process is considered a single stage, therefore the first number will remain constant, being 1, and the following two numbers correspond to the numbering of each type of measuring device.

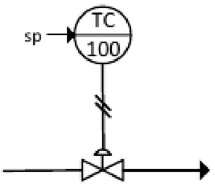


Figure 6.2 Example of nomenclature used.

Table 6.1 Nomenclature of different controllers.

Controlled Process Variable	Nomenclature
Flow	FC
Pressure	PC
Liquid level	LC
Temperature	TC
Composition	CC

6.2.2. Control in Heat Exchangers

The heat exchangers are a very important part of the process, and their control is essential in order to adjust at all times possible disturbances and temperature variations.

The control system used consists of a feedback control where the temperature at the exit of the heat exchanger is measured, in such a way that the water flow of the heat exchanger can be modified, by opening or closing the valve. In this way, the temperature of the desired output stream is reached, which is normally fixed by the next process unit.

A cascade loop has been considered: the temperature is measured in the process stream (master) and in the coolant (slave).

In figure 6.3 the approach to its control can be observed.

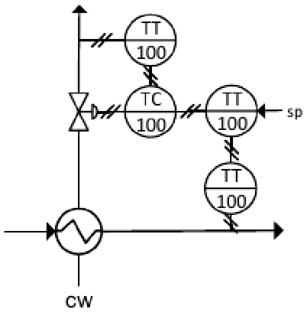


Figure 6.3 Heat exchanger control scheme.

6.2.2.1. Lean DEA/rich DEA Heat Exchanger

Unit E-102 involves two process streams in the heat exchange. In this case, the temperature to be controlled is that of the feed to the stripper. Since the flow of the hot stream (13) is manipulated to control the level inside the stripper, it cannot also be used in this control strategy. However, the output flow of the hot stream (14) can be manipulated. The valve that regulates this flow will tend to open or close, flooding more or less the heat exchanger to counteract the disturbances in the controlled variable.

In essence, the control loop is identical to the one used in the rest of the heat exchangers.

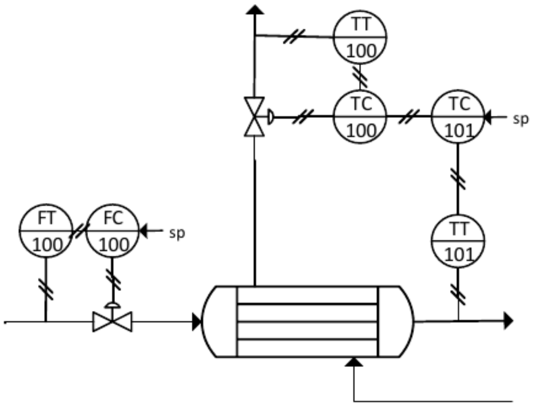


Figure 6.4 Heat exchanger E-102 control scheme.

6.2.3. Control in Pressure Change Equipment

For equipment such as compressors, turbines and pumps, a similar control has been carried out for each, to regulate the pressure of the stream that is intended to be controlled.

In the case of compressors (figure 6.5) and turbines (figure 6.6), the control system consists of a pressure gauge in the output stream. This sends a signal to the motor/rotor of the equipment through a cascade loop, regulating its rotation speed.

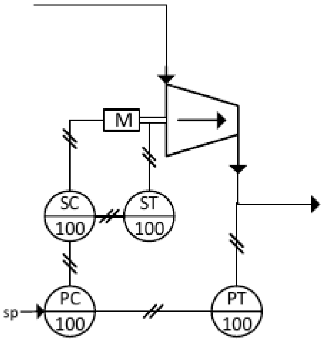


Figure 6.5 Compressor control scheme.

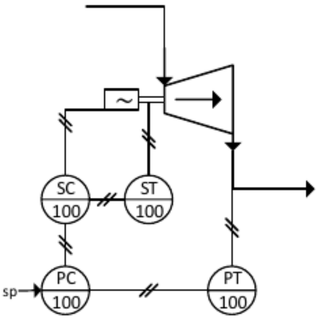


Figure 6.6 Turbine control scheme.

In the case of the P-101 pump, the objective is to increase the output pressure of the process stream. An LSS override loop has been proposed, with which the integrity of the pump is protected, while fulfilling its primary function.

The generally operative loop is 1, in which the valve is manipulated by controlling the output flow. At all times, the inlet pressure to the pump is measured, with loop 2. If in any case this pressure is less than the minimum, the operating loop is 2. The utility of this model prevents a pressure lower than the minimum allowed by the pump's performance, thus avoiding cavitation.

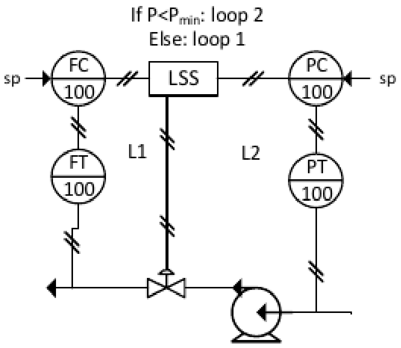


Figure 6.7 Pump P-101 control scheme.

6.2.4. Inlet Scrubber Control Strategy

The control strategy consisted first of all in the control of the presence of pollutants in the output of the equipment (by measuring their concentration) and the pressure of the equipment. This is done with an override loop, in which loop 1 is generally operative, with which the mentioned concentration is measured and controlled. At all times, the pressure inside the equipment is measured, and in the event that this pressure exceeds the maximum pressure (possible structural damage), the operating loop becomes 2, opening the valve with the aim of releasing biogas and reducing pressure.

The level inside the equipment is also controlled, manipulating the output flow of the waste stream.

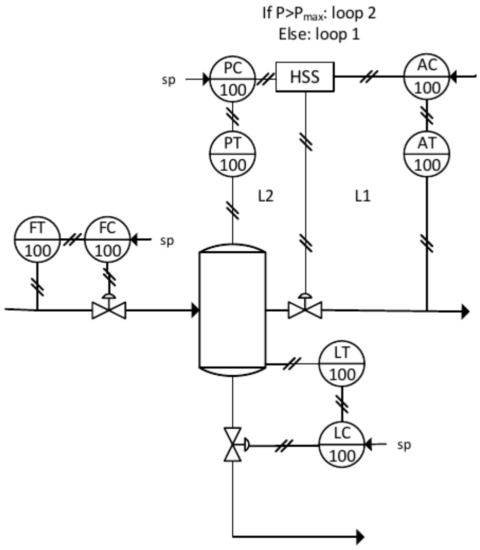


Figure 6.8 Inlet scrubber V-100 control scheme.

6.2.5. Absorber Column Control Strategy

In the absorption column, the aim is to obtain the upgraded biomethane that meets the composition specifications.

First of all, the feeding of solvent and biogas must be done in a known proportion and obtained in the design of the process. The maintenance of this ratio is crucial to comply with the product specifications. For this reason, a relationship of proportion between these flow rates is proposed.

The control of the composition is carried out with a loop identical to the one used in the scrubber inlet; an override loop, in which loop 1 is generally operative, with which the mentioned concentration is measured and controlled. In the same way, the pressure inside the equipment is measured, and in the event that this pressure exceeds the maximum pressure, the operating loop becomes 2, opening the valve with the aim of releasing biomethane and reducing pressure.

The level of solvent inside the column must be kept constant in the lower part to avoid flooding the column and in turn favor the contact between the solvent and the gas. The level is controlled by manipulating the solvent output flow.

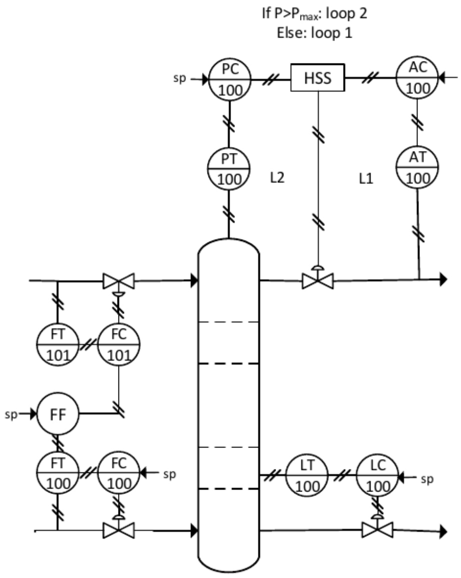


Figure 6.9 Absorber column T-100 control scheme.

6.2.6. Stripper Column Control Strategy

6.2.6.1. Inventory Control

The inventory control refers to the operating pressure, the feed flow rate, and the levels, both at the bottom of the column and at the accumulator.

The operating pressure is controlled by measuring the vapor pressure at the exit through the head of the column, and by adjusting the acid gas outlet valve.

The feed rate is also controlled, since it is important to be able to control the amount of product that has to be obtained.

On the other hand, the level of the bottom of the column is controlled so that the plates do not flood, and is regulated with the bottom outlet flow through a valve.

The level in the accumulator is also controlled so that the condenser is not flooded. In this case, since it is a column with total reflux, the level control valve has been placed in the reflux flow.

6.2.6.2. Product Control

Product control refers to the head and bottom product specifications of column, regulating the temperature.

If it is necessary to obtain a purer bottom product, in accordance with the imposed specifications, the steam inlet flow to the reboiler is manipulated. In this way, the steam feedback to the column is increased, depending on the temperature measured in the bottom plates.

Next is the representation of the control model of the stripping column.

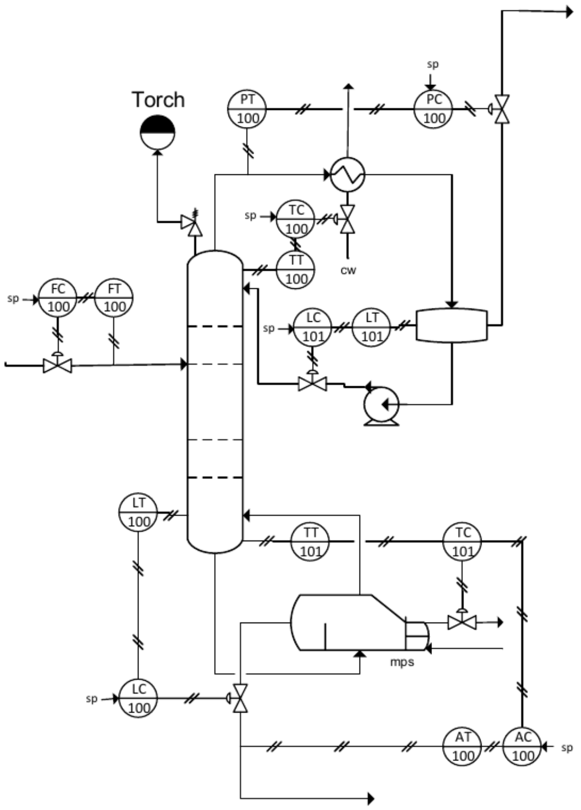


Figure 6.10 Control strategy of the stripping column T-101.

6.2.7. Surge Tank Control Strategy

In the surge tank, a small part of the solvent is purged, and this purge is replaced with pure water and solvent, so that the solvent concentration established by the design is obtained in the output stream.

The output concentration is controlled at all times with a cascade control loop linked to a ratio loop, which maintains a correct ratio between the water and the pure solvent that are fed.

The level inside the tank must also be controlled, and this is done by means of the solvent output flow.

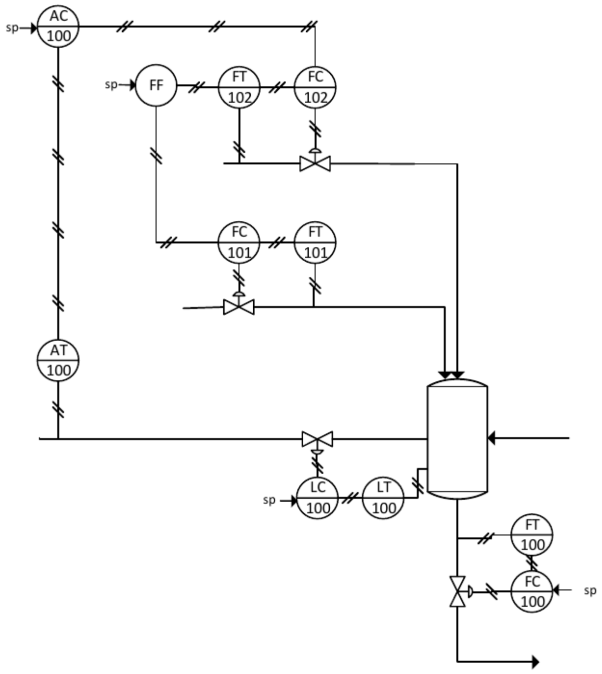


Figure 6.11 Control strategy of the surge tank V-101.

6.3. P&ID and Plant Control

The full P&ID of the upgrading process is presented in appendix B.

6.4. Safety Analysis

Safety is a fundamental aspect in any industrial plant, and particularly in those that handle flammable or toxic substances. In the case of a biogas upgrading plant, where biogas is processed to obtain biomethane, there are multiple potential risks that need to be identified and managed effectively.

A commonly used tool to analyse risks in an industrial plant is the HazOp analysis (Hazard and Operability Study). This analysis focuses on identifying possible dangerous scenarios in the operation of a plant and evaluating the security and contingency measures that must be implemented to minimize risks.

It is intended to carry out the safety study through the HazOp methodology for the T-101 stripping column. To do this, possible risk scenarios will be identified, such as gas leaks, explosions, fires, environmental contamination, and risks for workers. Additionally, the necessary security measures will be defined to prevent and mitigate these risks, including the use of detection and alarm systems, emergency cut-off systems, personal protection equipment and emergency procedures.

6.4.1. Hazard and Operability Study (HazOp) Methodology

The HazOp method focuses on studying specific parts of the process (stages, equipment, etc.), also called nodes. Each node (including all incoming or outgoing pipelines as well as utilities) is independently examined for potential hazards caused by deviations from normal or desired operation. These deviations come from the guide word applied to the process parameters.(Crowl & Louvar, 2011)

Guide words apply to both general (react, mix) and specific (pressure, temperature) parameters. In the next table can be found the guide words originally proposed by the ICI.

Table 6.2 Original HazOp guide words and meaning.(Crowl & Louvar, 2011)

Guide word	Meaning
No	Negation of the design intent
Less	Quantitative decrease
More	Quantitative increase
Part of	Qualitative decrease
As well as	Qualitative increase
Reverse	Logical opposite of the intent
Other than	Complete substitution

The HazOp methodology is put into practice in the following steps: preparing for the review, performing the review, documenting results. Next figure illustrates the concept of the HazOp analysis technique.

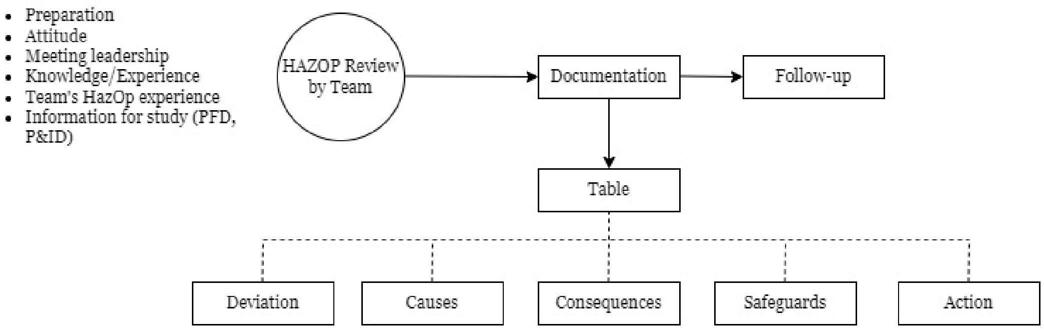


Figure 6.12 HazOp analysis technique.(Crowl & Louvar, 2011)

6.4.2. HazOp of Stripping Column

For a proper assessment and management of industrial risk, the different accidents that can occur in the T-101 stripping column have been identified through the application of hazard identification techniques, such as the HazOp analysis. This stripping column separates the acid gases previously absorbed in the solvent.

The HazOp analysis methodology takes into account the following hypotheses(Crowl & Louvar, 2011):

- The facility is well designed, in relation to the experience, the knowledge of the processes involved and the application of the relevant standards and codes.
- The construction materials have been adequate, and the building has been done correctly.
- The analyses are a "snapshot" where events of immediate effect are mixed with events of high temporal inertia.

Column T-101, requires obtaining a good separation of the acid gases present in the solvent, in order to be able to reuse the regenerated solvent.

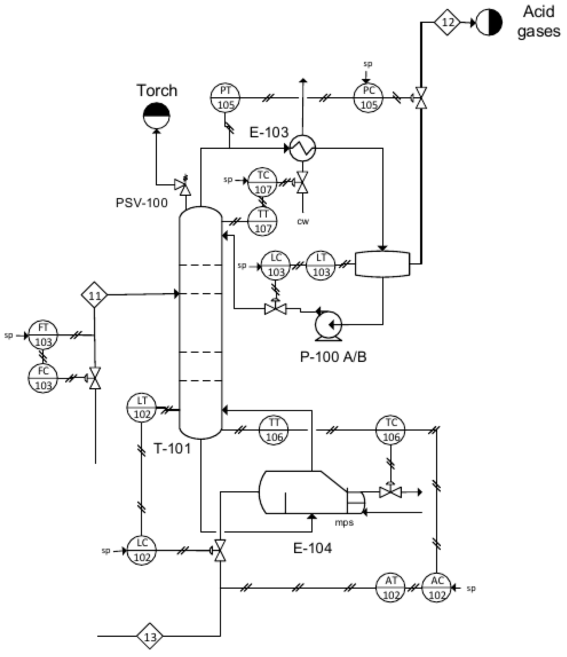


Figure 6.13 Stripping column T-101.

As can be seen in figure 6.14, the control loops involved are FC103, PC105, TC107, LC102, LC103, TC106 and AC102.

Table 6.3

Guide word	**Deviation**	**Possible causes**	**Consequences**	**Safeguards**	**Actions**
More	More level in bottom of T-101	LC102 controller failure (measures less level than the actual one)	Column flooding. No safety consequences		Set high level alarm on LC102
	More level in TK-100	LC103 controller failure (measures less level than the actual one) Failure pump P-100	Possibility of flooding of TK-100. If PC105 and TC107 are not able to release all the product, the pressure increases above the design and catastrophic rupture of the column. Possibility of explosion	Loops PC105 and TC107 valves will open Safety valve PSV-100 will open	Set high level alarm on LC103 Set high pressure alarm on PC105 Design safety valve PSV-100 for this case
Less	Less level in bottom of T-101	LC102 controller failure (measures more level than the actual one)	Product out of specifications. No safety consequences		Set low level alarm on LC102
	Less level in TK-100	LC103 controller failure (measures more level than the actual one)	No safety consequences		Set low level alarm on LC103
No	No feed flow rate to T-101	Lack of feed FC103 controller failure (closure)	Column instability with possibility of coning in the trays. No safety consequences		Set low flow rate alarm on FC103
	No reflux flow rate to T-101	LC103 controller failure (closure)	Higher temperature at the top of the column and product out of		

			specifications. No safety consequences	
	No top product flow rate	PC105 controller failure (closure)	Idem more level in TK-100	
	No steam flow rate to E-104	LC102 controller failure (closure)	Lower temperature at column bottom and product out of specifications. No safety consequences	
	No coolant flow rate to E-103	TC107 controller failure (closure)	No condensation in E-103. Higher pressure. Possibility of catastrophic rupture	Design safety valve PSV-100 for this case
	No bottom product flow rate	LC102 controller failure (closure)	Idem more level in bottom of T-101	Place restriction orifice for minimum flow
Less	Less feed flow rate to T-101	Lack of feed	Idem no feed flow rate to T-101	
	Less reflux flow rate to T-101	LC103 controller failure	Idem no reflux flow rate to T-101	
	Less top product flow rate	PC105 controller failure	Idem no top product flow rate	
	Less steam flow rate to E-104	LC102 controller failure	Idem no steam flow rate	
	Less coolant flow rate to E-103	TC107 controller failure	Idem no coolant flow rate to E-103	
	Less bottom product flow rate	LC102 controller failure	Idem no bottom product flow rate	
More	More feed flow rate to T-101	Feed excess	Column flooding and dripping. No	

			safety consequences		
	More reflux flow rate to T-101	Valve LC103 fully open	Top temperature decrease. Possibility of flooding and dripping. No safety consequences		
	More top product flow rate	Valve PC105 fully open	No safety consequences		Set high pressure alarm on PC105
	More steam flow rate to E-104	Valve TC106 fully open	Possibility of entrainment and flooding of the column T-101. No safety consequences		
	More coolant flow rate to E-103	Valve TC107 fully open	Top pressure decrease. No safety consequences.		
	More bottom product flow rate	Valve LC102 fully open	Emptying of the bottom of the column. Bottom product out of specifications. No safety consequences		
Reverse	Reverse flow rate	Not applicable			
More	More pressure on column T-101	External fire	Evaporation of liquid phase. Catastrophic rupture of T-101 and TK-100 with possibility of explosion		Design PSV-100 for this case
		Failure of coolant in E-103	Idem no coolant flow rate in E-103		

		LC103 controller failure (closure)	Idem no reflux flow rate to T-101	
		TC107 controller failure	Idem failure of coolant in E-103	
Less	Less pressure	Valve TC107 fully open	Idem more coolant flow rate in E-103	
		Valve PC105 fully open	Idem more top product flow rate	
		Valve LC102 fully open	Idem more bottom product flow rate	
More	More temperature in T-101 and TK-100	Valve TC106 fully open	Idem more steam flow rate to E-104	
		Failure of coolant in E-103	Idem no coolant flow rate in E-103	
Less	Less temperature in T-101 and TK-100	Valve TC107 fully open	Idem more coolant flow rate in E-103	
Other	Other composition in T-101 feed		Higher amount of top or bottom product. No safety consequences	
	Other phase in column bottom to tank		E-104 breakdown. Idem no bottom product flow rate	
	Other phase in TK-100		E-103 breakdown. Idem more pressure on T-101	
As well as	As well as corrosion/erosion in T-101 and TK-100	Corrosion under insulation	Leakage to the outside	Current inspection program

	Erosion in E-104 pipes due to direct contact with steam	Pipe breakdown. Idem more pressure on column T-101
	Failure of coolant in E-103	Idem more pressure on column T-101
	Failure of steam in E-104	Idem less pressure on column T-101
	Failure on instrument air	All valves will open
No restraint	No relevant cases	

7. Treatment of waste acid gas stream

In the upgrading process, regardless of the technology used, the acids present in the biogas are eliminated, but these acid gases are released in the regeneration of the solvent (mainly H_2S and CO_2), giving rise to a residual stream.

7.1. Waste Stream Conditions

Table 7.1 shows the main conditions of this stream.

Table 7.1 Conditions of the acid gas waste stream.

Variable		**Value**
Mass Flow rate (kmol/h)		85
Temperature (ºC)		43,47
Pressure (bar)		1,68
Composition (%)	CO_2	0,938
	H_2S	0,002
	Water	0,054

7.2. Release Regulations

The release of H_2S is limited by environmental regulations.(Comisión Europea, 2003) In fact, according to the BREF regulations, the emission limit of this substance is a maximum of 50 g/h in mass flow with a concentration limit of 5 mg/m^3. These limits are widely exceeded in the design presented in this project, as shown in Table 7.2.

Table 7.2 Limits imposed by BREF regulations for the release of H_2S to the atmosphere.(Comisión Europea, 2003)

	BREF limit	**Design**
Mass Flow (g/h)	50	6808,9
Concentration (mg/m^3)	5	$1{,}54 \cdot 10^6$

Another option is that acid gases could be sent to a torch, converting H_2S to SO_2, but environmental regulations also restrict the amount of these chemicals that can be released.

On the other hand, an adequate treatment of this residual stream could allow obtaining an economic benefit, by obtaining substances that can be potentially attractive to other industries.

In conclusion, this residual stream must be treated before it is released into the environment, in order to comply with environmental and safety requirements and/or obtain economic returns. In this section a solution for the treatment is presented.

7.3. Uses of CO_2

CO_2 has many uses in the industry.

- Coolant in industry. Solid state carbon dioxide can be used as a coolant in the transportation of frozen food products. On the other hand, liquid carbon dioxide, from this point of view, is the one with the greatest utility. Take R744 as an example, which is a carbon dioxide-based refrigerant widely used in many industries since it is characterized by not being toxic or flammable. It can be used as a refrigerant in air conditioning systems, water heat pumps or for industrial refrigeration.
- Food Industry. It is common to use CO_2 for the production of soft drinks and soda water, but it is also widely used in vacuum packaging. The main drawback in these cases is that a very high purity is required, close to 99,9%.
- Greenhouses. In some plants carbon dioxide is necessary to allow faster growth. This happens in most greenhouses where the aim is to increase the growth rate of plants for higher productivity and one way to do this is to increase carbon dioxide levels. Normally there is a unit of CO_2 stored in tanks outside the greenhouses and through the use of a vaporization unit it is distributed throughout the interior of the greenhouse.
- Storage. Empty reservoir carbon dioxide storage, also known as carbon capture and storage (CCS), is a technique used to reduce CO_2 emissions into the atmosphere and mitigate climate change. It consists of capturing CO_2 and then injecting it safely and permanently into underground oil or natural gas fields that have been depleted or are in decline.
- Enhanced Oil Recovery (EOR). Technique used in the oil industry to increase oil production from reservoirs that have reached their natural production capacity. This technique involves injecting CO_2 into the reservoir, which helps move oil toward producing wells and makes it easier to extract.

7.4. Uses of S

Sulphur is used as a raw material in various applications, such as sulfuric acid, solvents, reducing agents, water treatment products, pharmaceuticals, and dyes.

7.5. Proposed Solution

Based on the composition and conditions of the stream, H_2S separation is first carried out by chemical absorption with MDEA. The H_2S is then taken to a conversion unit to obtain solid sulphur. On the other hand, the CO_2 stream, which is saturated with water, undergoes a dehydration process with TEG. Once dehydrated and as the last processing step, liquefaction is carried out to be able to be transported for its final use.

Best Available Techniques (BAT) is a concept used in the field of environmental protection and pollution prevention.

BATs are defined within the framework of environmental legislation and their objective is to guarantee that companies apply the most appropriate techniques to prevent or reduce the emission of pollutants into the environment. These techniques must be feasible from a technical and economic point of view and must take environmental aspects into account at all stages of the production process.(Comisión Europea, 2003)

The determination of the BAT is based on the evaluation of various technical options available on the market and factors such as energy efficiency, consumption of natural resources, waste generation, atmospheric emissions, wastewater management, among others.

Based on the BAT and the literature, the following processes are proposed for the treatment of this residual current.

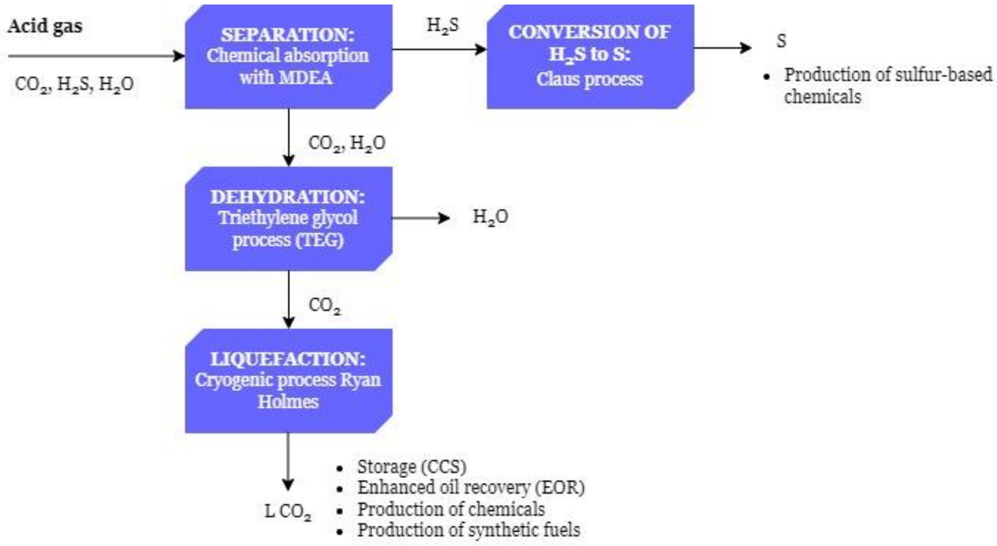


Figure 7.1 Scheme of the treatment process of the acid gas waste stream.

7.5.1. Separation: Chemical Absorption with MDEA

This process is essentially the same as that modeled for upgrading. It is done first, before dehydration, since the solvent contains water. A detailed description of the process is found in section 3.2. The solvent to be used is MDEA, since it is selective to eliminate H_2S from the stream.

7.5.2. Dehydration: TEG process

A typical TEG absorption plant is shown in figure 7.2. The wet gas is fed into the bottom of the absorber (or glycol contactor) through a scrubber section in order to remove liquids and solids which can contaminate the glycol. The lean glycol is fed at the top of the contactor and runs down the contactor at the same time as the gas is flowing upwards. A mass transfer process is taking place due to the affinity glycol have to water molecules and the water content is reduced upwards in the contactor. (Gámez, 2018)

A demisting section is normally put in the top of the contactor in order to reduce the carry-over of TEG into the rest of the process. As the glycols flows down in the contactor the water concentration in the glycol is increased. The rich glycol solution (rich in water) is sent to a stripper section where the water is removed from the glycol again by reducing pressure and adding heat to the system.

Heat integration is used in order to increase thermal efficiency. The lean glycol where the water is removed is pumped back to the absorber. The glycol circulation rate will depend on operational parameters like temperature and pressure, and amount of water in the feed gas and specification for water content in the gas outlet.

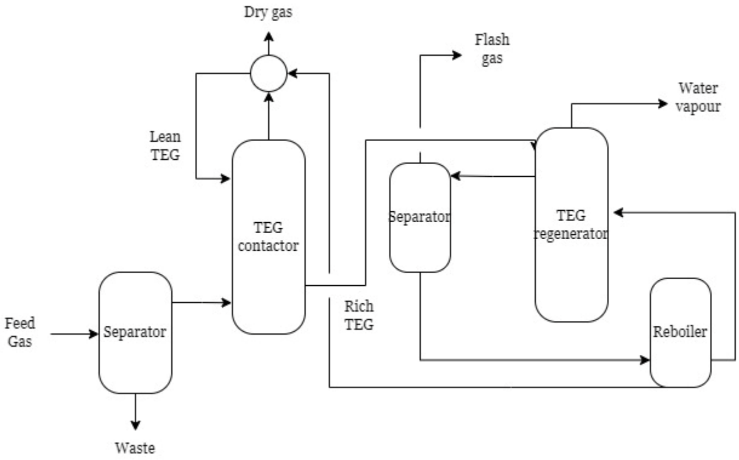


Figure 7.2 Flow diagram of the TEG absorption process.(Gámez, 2018)

7.5.3. Liquefaction of CO_2: Ryan Holmes Cryogenic Process

This process uses cryogenic distillation to remove acid gases. It is usually applied to obtain liquid CO_2. The process consists of one or more fractionating columns (depending on the composition).

The dry gas enters at high pressure and free of water. The gas undergoes a pressure drop and goes through the heat exchanger, where the temperature drops to -40ºC. After this, it is fed to the fractionation tower, where it is separated from the methane present in the stream. The CO_2 leaves through the bottom of the column in a liquid state.(Gámez, 2018)

7.5.4. Conversion of H_2S to S: Claus Process

This process is used to treat gas streams with a high H_2S content. On a chemical level, there is a partial oxidation of H_2S to SO_2, and a catalytic reaction between H_2S and SO_2 to produce sulfur, as can be seen in the following reactions.(Stewart & Arnold, 2011)

$$H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + H_2O \qquad (7.1)$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \qquad (7.2)$$

SO_2 is obtained through the combustion of the gas stream fed to the process, carried out with air in a reaction furnace.

The gases leaving this stage are cooled to remove the sulfide formed in this stage. It is then reheated and the catalytic reaction takes place, after which a condensation is carried out to obtain the additional sulphur. Several steps can be carried out to increase the conversion of the process. With two catalytic stages, conversions of up to 95% can be obtained.

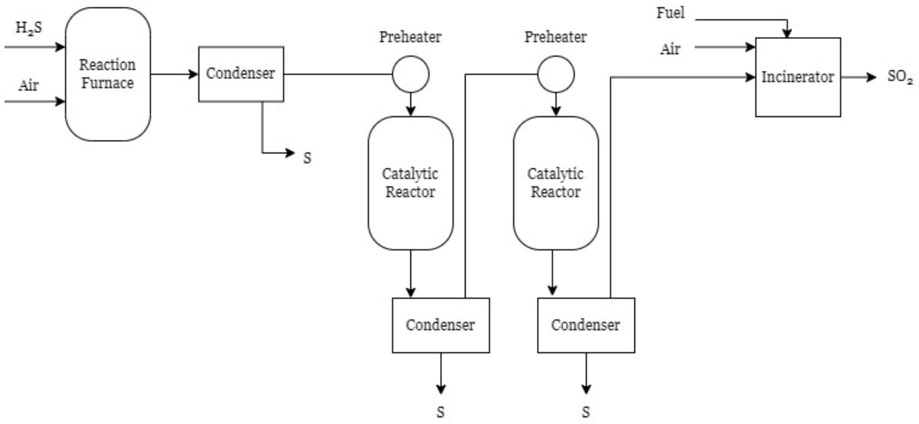


Figure 7.3 Diagram of a two stage Claus process.(Stewart & Arnold, 2011)

8. Conclusions

As a recapitulation to the initially defined objectives, this section summarizes the project and presents the conclusions reached after carrying it out.

The main objective of this project has been the preliminary design and optimization of the biogas upgrading stage as part of an LBM production process. An approach from the point of view of chemical engineering has been given to the process, carrying out the design of the basic and conceptual engineering, with the aim of obtaining as a result an efficient process and with adequate control of its operation and safety.

Regarding the design of the upgrade process, as presented in this report, there are several mature alternatives that are being used in the industry. The choice of one or another alternative is strongly conditioned mainly by the end use intended for biomethane, which defines the specifications of the final product. In this way, processes that are not capable of providing the required quality of the final product are discarded.

In this case, the production of LBM involves strict composition specifications, both to ensure good performance in its final use as a fuel and to ensure the integrity of the production process equipment. This restriction has made it possible to rule out several of the available alternatives. According to (Farghali et al., 2022) and the data presented in Table 3.2, the only two processes capable of providing the required quality of the final product, shown in Table 4.1, are chemical absorption and membrane separation.

From here, although not free of drawbacks, chemical absorption was chosen for the upgrading process, since, compared to separation with membranes, it presents considerably lower methane losses, lower energy consumption and its wide use in the industry makes it a reliable and easy-to-operate system. Therefore, it is concluded that due to the fact that there is no perfect solution to a design problem, the available options must be analyzed so that the final choice provides the desired results and presents the least possible disadvantages.

The implementation of the process in HYSYS consisted of different stages, with the aim of following a progression in the complexity of the simulation, facilitating the convergence of a highly non-linear model. As a step prior to the implementation in HYSYS, a bibliographic search of the operating conditions usually used in the industry was carried out, and the simplified method proposed by (Stewart & Arnold, 2011) was used to obtain initial estimates. This step proved to be useful in the efficiency of the model realization.

As in any process, the design possibilities are very extensive. In this case, the solvent can be of a different nature, as well as the ranges of the different operating variables associated with the solvent and the different unit operations. However, the search for an optimal process requires making the appropriate decisions regarding the operating parameters. For this reason, and as a prior step to optimizing the model, different sensitivity analyzes of some of the process variables were carried out to obtain their respective ranges of best performance regarding energy and product quality, and to be able to use this information. in performing the optimization.

Moving forward with the objectives, a preliminary optimization was carried out making use of the information obtained in the sensitivity analyses. As mentioned throughout this report, upgrading is a highly energy-demanding process, so it is interesting to find the operating conditions that meet the product specifications with the lowest energy consumption. Two objective functions referring to energy consumption in the compression of the biogas feed and the reboiler of the regeneration stage were defined, defining the different constraints of the problem (operation limits and final product specifications).

Based on bibliographic sources, the optimization was carried out using the Hyprotech SQP solver, which has shown to give good results in highly non-linear processes as the object of this project. (Rødstøl, 2015) However, a good knowledge of its operation It is necessary to obtain satisfactory results and to be able to make appropriate decisions based on these results.

The final results are shown in table 5.10. Regarding the biogas compression stage, a reduction in energy consumption of 7,66% was achieved. However, regarding the consumption of the reboiler, an increase in energy consumption of 11,59% was necessary to comply with the restrictions imposed.

Being two interconnected operations in a process, it is logical to think that the optimization of one OF will have effects on the other. For this reason, the results of both OFs were monitored at all times in search of possible interactions. In this case, the interaction of OF1 with OF2 was observed when the solvent flow rate was increased, since this implies both better absorption, and therefore less compression duty, as well as higher energy consumption in the reboiler process. Another source of interaction was the variation in the acid content of the regenerated solvent due to the optimization of the OF2 and the changing variables. The composition of the solvent has a direct effect on the absorption stage. However, with the working ranges of the optimization carried out, no dramatic interaction was observed, and the results remained almost unchanged.

It should be noted that the optimization of this stage alone can have interactions with the liquefaction stage of the LBM production process, but this is not the case with the liquefaction stage, since its optimization would not affect the upgrading due to the fact that it is a later stage. The consideration of this fact has not been within the scope of the project, but it is a factor to take into account in the results presented.

On the other hand, from an engineering point of view, it must be ensured that the plant satisfies the operating requirements, even in the presence of external influences. For this reason, a control solution has been successfully carried out, as well as its corresponding representation in a P&ID diagram.

Likewise, plant safety management is crucial in any industrial plant, and especially with the handling of toxic substances. For this reason, a study of the safety in the operation of the stripping column has been carried out using the HazOp methodology. The different sources of danger have been identified and actions or implementation of safeguards have been proposed to avoid and/or alleviate these situations.

Finally, regarding the objective of the treatment of residual streams, the purge stream of CO_2 and H_2S resulting from the regeneration of the solvent was identified. This stream cannot be released into the atmosphere without being treated to comply with the imposed regulations. On the other hand, an alternative solution is to give it an economic output by applying a treatment process. The proposed treatment process consists of 4 stages; dehydration, separation of CO_2 and H_2S, conversion of H_2S to S through the Claus process, and finally the liquefaction of CO_2. In this way, both S and CO_2 can be sold to different interested parties, usually to other chemical plants that can use these substances as raw materials to produce their products.

In summary, it has been possible to satisfactorily meet the objectives initially set, with the points made in this section.

8.1. Further Work

After carrying out the project, several relevant points have been left out of its scope. Below are proposals for future work on topics that could not be dealt with in this project.

- Consider situations in which the feeding conditions (mainly composition) vary, as for example with the presence of methanation in the process. Check how they affect the process, its variables and equipment design.
- The number of degrees of freedom considered in the optimization has been limited, some of the data have been fixed according to bibliographical recommendations. Considering more variables could mean an optimization with better results.
- Upgrading is part of a larger process. any change in its variables affects the subsequent liquefaction but not vice versa. For this reason, it is relevant to check how the optimization of the upgrade affects the liquefaction stage, and if the latter supposes a limitation to the optimization of the upgrade.
- Carry out an optimization model that gives priority to an objective function or part of it over the other in case of interactions. For example, give priority to minimizing the consumption of electricity over heat
- Carry out an economic evaluation of the process proposal to treat the residual stream of acids to verify its economic viability.

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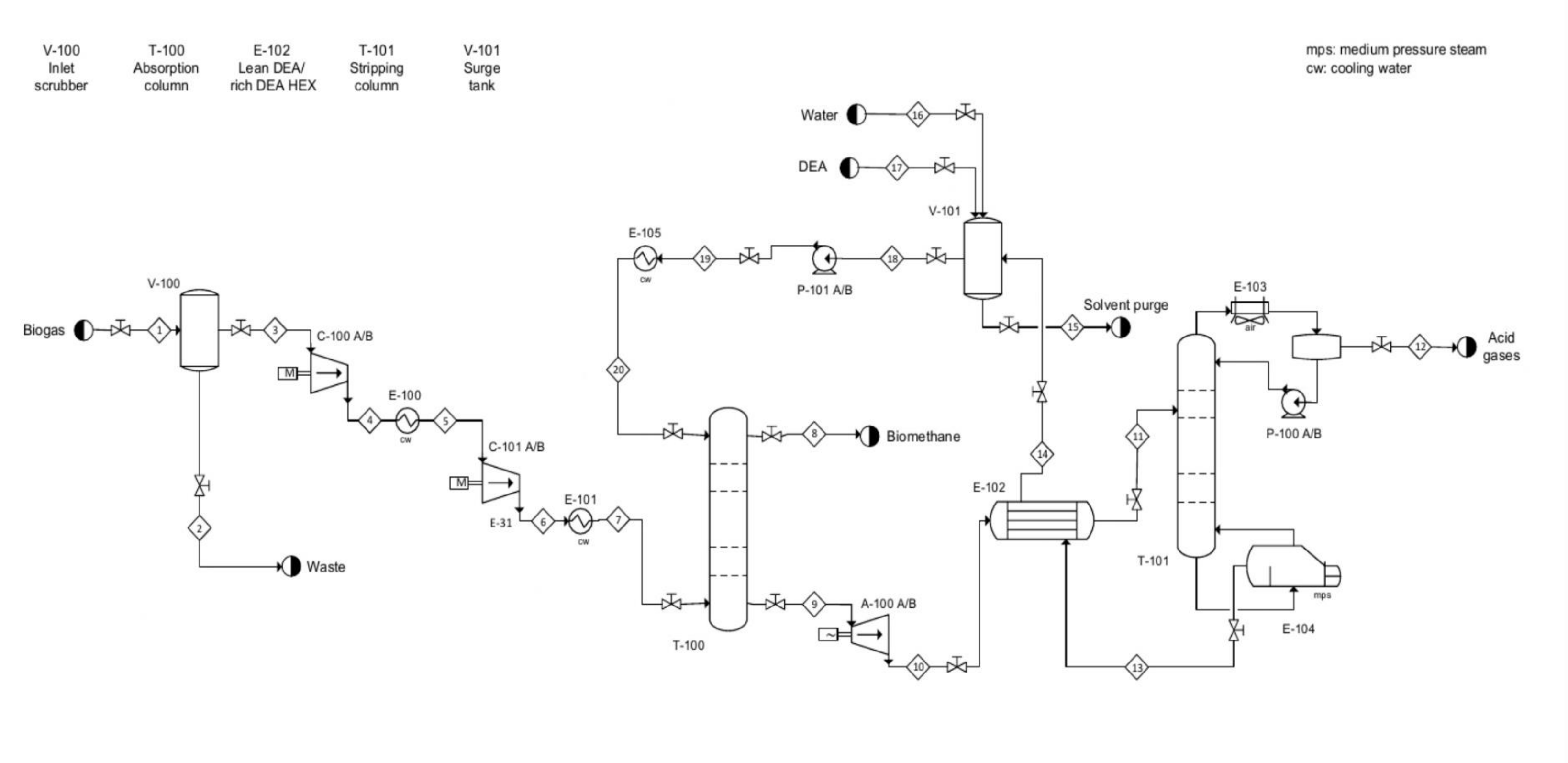
A. Process Flow Diagram



Line no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Stream component	Biogas feed	Dirt waste stream	Clean biogas	1st comp. biogas	1st cooled biogas	2nd comp. biogas	Comp. biogas to abs.	Biomethane	Rich DEA	Rich DEA to HEX	Stripp. feed	Acids waste stream	Lean DEA to HEX	Lean DEA to surge	Solvnt. purge	Water	Pure DEA	Lean DEA to pump	Lean DEA to cool	Lean DEA to abs
CH_4	0,600	-	0,600	0,600	0,600	0,600	0,600	0,993	-	-	-	0,006	-	-	-	-	-	-	-	-
CO_2	0,399	-	0,399	0,399	0,399	0,399	0,399	$5\cdot10^{-5}$	0,033	0,033	0,033	0,934	$5\cdot10^{-4}$	$5\cdot10^{-4}$	$5\cdot10^{-4}$	-	-	$5\cdot10^{-4}$	$5\cdot10^{-4}$	$5\cdot10^{-4}$
H_2S	0,001	-	0,001	0,001	0,001	0,001	0,001	-	$8\cdot10^{-5}$	$8\cdot10^{-5}$	$8\cdot10^{-5}$	0,002	-	-	-	-	-	-	-	-
DEA	-	-	-	-	-	-	-	-	0,082	0,082	0,082	-	0,085	0,085	0,085	-	1,000	0,085	0,085	0,085
Water	-	Traces	-	-	-	-	-	0,007	0,885	0,885	0,885	0,054	0,915	0,915	0,915	1,000	-	0,915	0,915	0,915
Total (kmol/h)	199,8		199,8	199,8	199,8	199,8	199,8	120,2	2442	2442	2442	85	2357	2357	2357	5,4	$1\cdot10^{-5}$	2363	2363	2363
Vap. Frac.	1	0	1	1	1	1	1	1	0	0	0	1	0	0	0	0	0	0	0	0
Press. (bar)	1,013	1,013	1,013	6,745	6,745	13,49	13,49	13,50	13,49	1,35	1,35	1,68	1,98	1,98	1,98	1,98	1,98	1,98	13,50	13,50
Temp. (ºC)	35	35	35	219	35	99	35	45	73	73	103	43	123	123	95	95	95	95	95	45

Process Flow Diagram

Biogas upgrading

Drawn: Chaymae El Hmidi
Reviewed: Chaymae El Hmidi

Date: 26/04/2023

B. Piping and Instrumentation Diagram